

WHAT'S AHEAD

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- 20.2 ► Balancing Redox Equations
- 20.3 ► Voltaic Cells
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20

ELECTROCHEMISTRY

20.1 | Oxidation States and Oxidation–Reduction Reactions



The electricity that powers much of modern society has many favorable characteristics, but it has a serious shortcoming: it cannot easily be stored. The electricity that flows into power lines is consumed as it is generated, but for many applications, stored electrical energy is needed. In such cases, electrical energy is converted into chemical energy, which can be stored and is portable, and then converted back to electricity when needed.

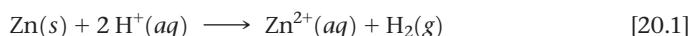
Oxidation–reduction (redox) reactions occur when electrons are transferred from an atom that is oxidized to an atom that is reduced. Redox reactions are involved not only in the operation of batteries but also in a wide variety of important natural processes,

including the rusting of iron, the browning of foods, and the respiration of animals. Electrochemistry is the study of the relationships between electricity and chemical reactions. It includes the study of both spontaneous and nonspontaneous processes.

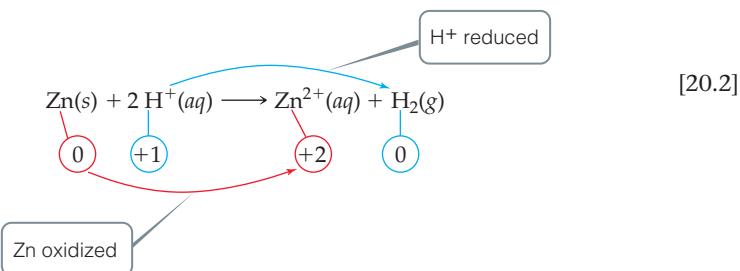
By the end of this section, you should be able to

- Identify the components of a redox reaction

We determine whether a given chemical reaction is an oxidation–reduction reaction by keeping track of the *oxidation numbers* (*oxidation states*) of the elements involved in the reaction. This procedure identifies whether the oxidation number changes for any elements involved in the reaction. For example, consider the net reaction that occurs spontaneously when zinc metal is added to a strong acid (Figure 20.1):



Assigning oxidation numbers to all species in the reaction, we have

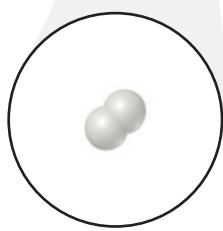
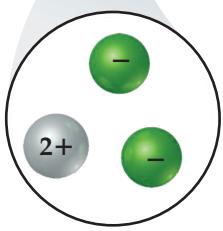
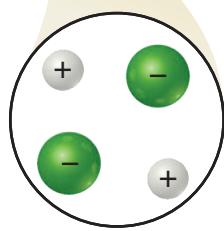


The oxidation numbers below the equation show that the oxidation number of Zn changes from 0 to +2, while that of H changes from +1 to 0. Thus, this is an oxidation–reduction



Go Figure

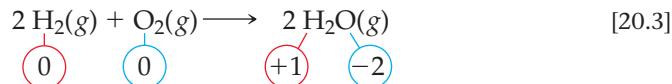
Is this reaction exothermic or endothermic?



▲ Figure 20.1 Oxidation of zinc by hydrochloric acid.

reaction. Electrons are transferred from zinc atoms to hydrogen ions; Zn is oxidized and H⁺ is reduced.

In a reaction such as Equation 20.2, a clear transfer of electrons occurs. In some reactions, however, the oxidation numbers change, but we cannot say that any substance literally gains or loses electrons. For example, in the combustion of hydrogen gas,



hydrogen is oxidized from the 0 to the +1 oxidation state and oxygen is reduced from the 0 to the -2 oxidation state, indicating that Equation 20.3 is an oxidation-reduction reaction. While keeping track of oxidation states offers a convenient form of “bookkeeping,” you should not generally equate the oxidation state of an atom with its actual charge in a chemical compound.

In any redox reaction, both oxidation and reduction must occur. If one substance is oxidized, another must be reduced. The substance that oxidizes another substance is called either the **oxidizing agent** or the **oxidant**. The oxidizing agent acquires electrons from the other substance and so is itself reduced. A **reducing agent**, or **reductant**, is a substance that gives up electrons, thereby causing another substance to be reduced. The reducing agent is therefore oxidized in the process. In Equation 20.2, H⁺(aq), the species that is reduced, is the oxidizing agent and Zn(s), the species that is oxidized, is the reducing agent.

Sample Exercise 20.1

Identifying Oxidizing and Reducing Agents

The nickel–cadmium (nicad) battery uses the following redox reaction to generate electricity:



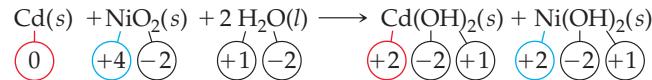
Identify the substances that are oxidized and reduced, and indicate which is the oxidizing agent and which is the reducing agent.

SOLUTION

Analyze We are given a redox equation and asked to identify the substance oxidized and the substance reduced and to label the oxidizing agent and the reducing agent.

Plan First, we use the rules outlined earlier to assign oxidation states, or numbers, to all the atoms and determine which elements change oxidation state. Second, we apply the definitions of oxidation and reduction.

Solve



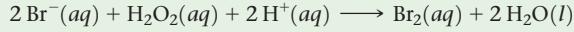
The oxidation state of Cd increases from 0 to +2, and that of Ni decreases from +4 to +2. Thus, the Cd atom is oxidized (loses

electrons) and is the reducing agent. The oxidation state of Ni decreases as NiO₂ is converted into Ni(OH)₂. Thus, NiO₂ is reduced (gains electrons) and is the oxidizing agent.

Comment A common mnemonic for remembering oxidation and reduction is “LEO the lion says GER”: *losing electrons is oxidation; gaining electrons is reduction*.

► Practice Exercise

What is the reducing agent in the following reaction?



- (a) Br⁻(aq) (b) H₂O₂(aq) (c) H⁺(aq) (d) Br₂(aq)

Self-Assessment Exercise

20.1 What are the oxidation number of chlorine in the perchlorate ion, ClO₄⁻?

- (a) -1
- (b) +3
- (c) +7

Exercises

- 20.2** (a) What is meant by the term *reduction*? (b) On which side of a reduction half-reaction do the electrons appear? (c) What is meant by the term *reductant*? (d) What is meant by the term *reducing agent*?

20.3 Indicate whether each of the following statements is true or false:

 - (a) If something is reduced, it is formally losing electrons.
 - (b) A reducing agent gets oxidized as it reacts.
 - (c) An oxidizing agent is needed to convert CO into CO₂.

20.4 For each of the following balanced oxidation-reduction reactions, (i) identify the oxidation numbers for all the elements in the reactants and products and (ii) state the total number of electrons transferred in each reaction.

- (a)** $\text{H}_2(g) + \text{F}_2(g) \longrightarrow 2 \text{HF}(g)$

(b) $2 \text{Fe}^{2+}(aq) + \text{H}_2\text{O}_2(aq) + 2 \text{H}^+(aq)$
 $\longrightarrow 2 \text{Fe}^{3+}(aq) + \text{H}_2\text{O}(l)$

(c) $\text{CH}_4(g) + 2 \text{O}_2(g) \longrightarrow \text{CO}_2(g) + 2 \text{H}_2\text{O}(l)$

20.5 Indicate whether the following balanced equations involve oxidation-reduction. If they do, identify the elements that undergo changes in oxidation number.

(a) $2 \text{AgNO}_3(aq) + \text{CoCl}_2(aq) \longrightarrow 2 \text{AgCl}(s) + \text{Co}(\text{NO}_3)_2(aq)$

(b) $2 \text{PbO}_2(s) \longrightarrow 2 \text{PbO}(s) + \text{O}_2(g)$

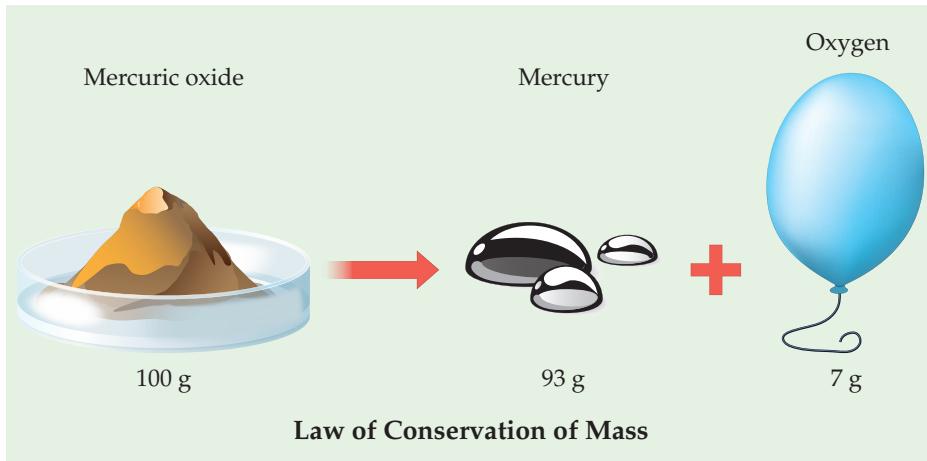
(c) $2 \text{H}_2\text{SO}_4(aq) + 2 \text{NaBr}(s) \longrightarrow \text{Br}_2(l) + \text{SO}_2(g) + \text{Na}_2\text{SO}_4(aq) + 2 \text{H}_2\text{O}(l)$

20.1 (c)

Answers to Self-Assessment Exercise



20.2 | Balancing Redox Equations



Whenever we balance a chemical equation, we must obey the law of conservation of mass: The amount of each element must be the same on both sides of the equation. (Atoms are neither created nor destroyed in any chemical reaction.) As we balance oxidation-reduction reactions, there is an additional requirement: The gains and losses of electrons must be balanced. If a substance loses a certain number of electrons during a reaction, another substance must gain that same number of electrons. (Electrons are neither created nor destroyed in any chemical reaction.)

In many simple chemical equations, such as Equation 20.2, balancing the electrons is handled “automatically”—that is, we balance the equation without explicitly accounting for the transfer of electrons. Many redox equations are more complex than Equation 20.2, however, and cannot be balanced easily without taking into account the number of electrons lost and gained. In this section, we examine the *method of half-reactions*, a systematic procedure for balancing redox equations.

By the end of this section, you should be able to

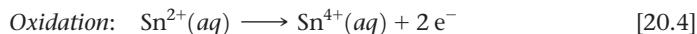
- Balance redox equations

Half-Reactions

Although oxidation and reduction must take place simultaneously, it is often convenient to consider them as separate processes. For example, the oxidation of Sn^{2+} by Fe^{3+} ,



can be considered as consisting of two processes: oxidation of Sn^{2+} and reduction of Fe^{3+} :



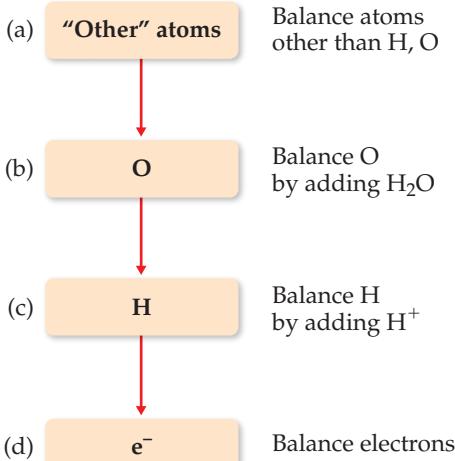
Notice that electrons are shown as products in the oxidation process and as reactants in the reduction process.

Equations that show either oxidation or reduction alone, such as Equations 20.4 and 20.5, are called **half-reactions**. In the overall redox reaction, the number of electrons lost in the oxidation half-reaction must equal the number of electrons gained in the reduction half-reaction. When this condition is met and each half-reaction is balanced, the electrons on the two sides cancel when the two half-reactions are added to give the balanced oxidation-reduction equation.

Balancing Equations by the Method of Half-Reactions

In the half-reaction method, we usually begin with a “skeleton” ionic equation showing only the substances undergoing oxidation and reduction. In such cases, we assign oxidation numbers only when we are unsure whether the reaction involves oxidation-reduction. We will find that H^+ (for acidic solutions), OH^- (for basic solutions), and H_2O are often involved as reactants or products in redox reactions. Unless H^+ , OH^- , or H_2O is being oxidized or reduced, these species do not appear in the skeleton equation. Their presence, however, can be deduced as we balance the equation.

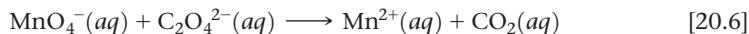
How to Balance Redox Reactions in Acidic Aqueous Solution



- Divide the equation into one oxidation half-reaction and one reduction half-reaction.
- Balance each half-reaction.
 - First, balance elements other than H and O.
 - Next, balance O atoms by adding H_2O as needed.
 - Then balance H atoms by adding H^+ as needed.
 - Finally, balance charge by adding e^- as needed.

This specific sequence (a)–(d) is important, and it is summarized in the diagram in the margin. At this point, you can check whether the number of electrons in each half-reaction corresponds to the changes in oxidation state.
- Multiply half-reactions by integers as needed to make the number of electrons lost in the oxidation half-reaction equal the number of electrons gained in the reduction half-reaction.
- Add half-reactions and, if possible, simplify by canceling species appearing on both sides of the combined equation.
- Check to make sure that atoms and charges are balanced.

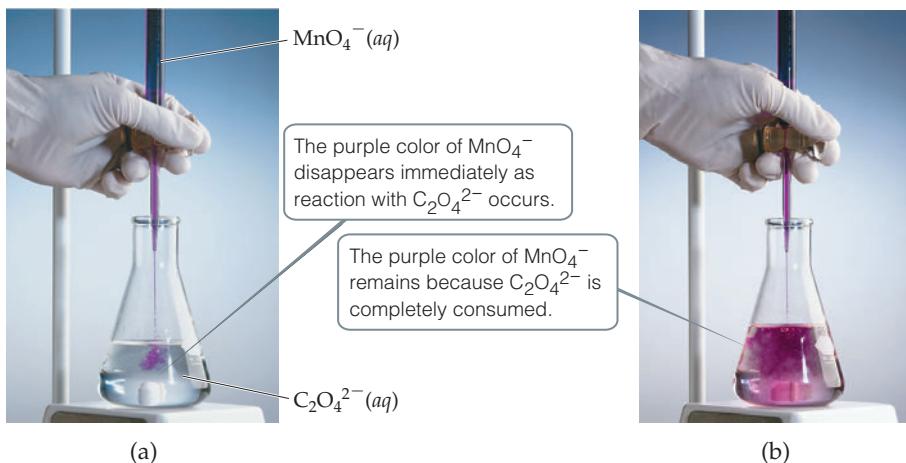
As an example, let's consider the reaction between permanganate ion (MnO_4^-) and oxalate ion ($\text{C}_2\text{O}_4^{2-}$) in acidic aqueous solution (Figure 20.2). When MnO_4^- is added to an acidified solution of $\text{C}_2\text{O}_4^{2-}$, the deep purple color of the MnO_4^- ion fades, bubbles of CO_2 form, and the solution takes on the pale pink color of Mn^{2+} . We can write the skeleton equation as



Experiments show that H^+ is consumed and H_2O is produced in the reaction. We will see that their involvement in the reaction is deduced in the course of balancing the equation.

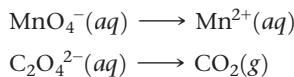

Go Figure

Which species is reduced in this reaction? Which species is the reducing agent?

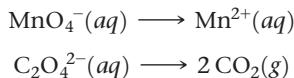


▲ Figure 20.2 Titration of an acidic solution of $\text{Na}_2\text{C}_2\text{O}_4$ with $\text{KMnO}_4(aq)$.

To complete and balance Equation 20.6, we first write the two half-reactions (Step 1). One half-reaction must have Mn on both sides of the arrow, and the other must have C on both sides of the arrow:



We next complete and balance each half-reaction. First, we balance all the atoms except H and O (Step 2a). In the permanganate half-reaction, we have one manganese atom on each side of the equation and so need to do nothing. In the oxalate half-reaction, we add a coefficient 2 on the right to balance the two carbons on the left:



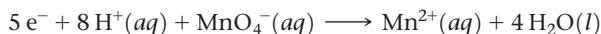
Next we balance O (Step 2b). The permanganate half-reaction has four oxygens on the left and none on the right; to balance these four oxygen atoms, we add four H_2O molecules on the right:



The eight hydrogen atoms now in the products must be balanced by adding 8 H^+ to the reactants (Step 2c):

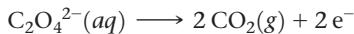


Now there are equal numbers of each type of atom on the two sides of the equation, but the charge still needs to be balanced. The charge of the reactants is $8(1+) + 1(1-) = 7+$, and that of the products is $1(2+) + 4(0) = 2+$. To balance the charge, we add five electrons to the reactant side (Step 2d):



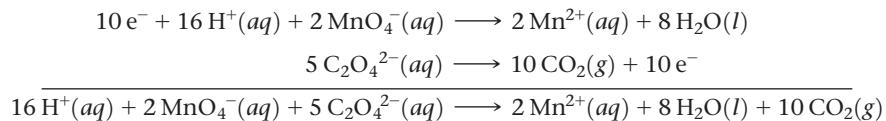
We can use oxidation states to check our result. In this half-reaction, Mn goes from the +7 oxidation state in MnO_4^- to the +2 oxidation state of Mn^{2+} . Therefore, each Mn atom gains five electrons, in agreement with our balanced half-reaction.

In the oxalate half-reaction, we have C and O balanced (Step 2a). We balance the charge (Step 2d) by adding two electrons to the products:



We can check this result using oxidation states. Carbon goes from the +3 oxidation state in $\text{C}_2\text{O}_4^{2-}$ to the +4 oxidation state in CO_2 . Thus, each C atom loses one electron; therefore, the two C atoms in $\text{C}_2\text{O}_4^{2-}$ lose two electrons, in agreement with our balanced half-reaction.

Now we multiply each half-reaction by an appropriate integer so that the number of electrons gained in one half-reaction equals the number of electrons lost in the other (Step 3). We multiply the MnO_4^- half-reaction by 2 and the $\text{C}_2\text{O}_4^{2-}$ half-reaction by 5:



The balanced equation is the sum of the balanced half-reactions (Step 4). Note that the electrons on the reactant and product sides of the equation cancel each other.

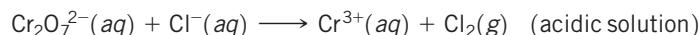
We check the balanced equation by counting atoms and charges (Step 5). There are 16 H, 2 Mn, 28 O, 10 C, and a net charge of +4 on each side of the equation, confirming that the equation is correctly balanced.

Sample Exercise 20.2

Balancing Redox Equations in Acidic Solution



Complete and balance this equation by the method of half-reactions:

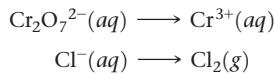


SOLUTION

Analyze We are given an incomplete, unbalanced (skeleton) equation for a redox reaction occurring in acidic solution and asked to complete and balance it.

Solve

Step 1: We divide the equation into two half-reactions:



Step 2: We balance each half-reaction. In the first half-reaction the presence of one $\text{Cr}_2\text{O}_7^{2-}$ among the reactants requires two Cr^{3+} among the products. The seven oxygen atoms in $\text{Cr}_2\text{O}_7^{2-}$ are balanced by adding seven H_2O to the products. The 14 hydrogen atoms in 7 H_2O are then balanced by adding 14 H^+ to the reactants:

We then balance the charge by adding electrons to the left side of the equation so that the total charge is the same on the two sides:

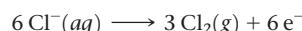
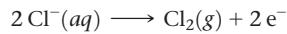
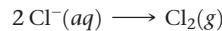
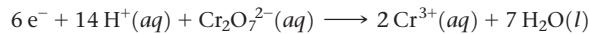
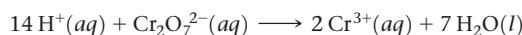
We can check this result by looking at the oxidation state changes. Each chromium atom goes from +6 to +3, gaining three electrons; therefore, the two Cr atoms in $\text{Cr}_2\text{O}_7^{2-}$ gain six electrons, in agreement with our half-reaction.

In the second half-reaction, two Cl^- are required to balance one Cl_2 :

We add two electrons to the right side to attain charge balance:

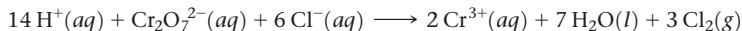
This result agrees with the oxidation state changes. Each chlorine atom goes from -1 to 0, losing one electron; therefore, the two chlorine atoms lose two electrons.

Step 3: We equalize the number of electrons transferred in the two half-reactions. To do so, we multiply the Cl half-reaction by 3 so that the number of electrons gained in the Cr half-reaction (6) equals the number lost in the Cl half-reaction, allowing the electrons to cancel when the half-reactions are added:



Plan We use the half-reaction procedure we just learned.

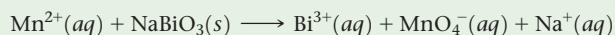
Step 4: The equations are added to give the balanced equation:



Step 5: There are equal numbers of atoms of each kind on the two sides of the equation (14 H, 2 Cr, 7 O, 6 Cl). In addition, the charge is the same on the two sides (6+). Thus, the equation is balanced.

► Practice Exercise

If you complete and balance the following equation in acidic solution



how many water molecules are there in the balanced equation (for the reaction balanced with the smallest whole-number coefficients)? (a) Four on the reactant side (b) Three on the product side (c) One on the reactant side (d) Seven on the product side (e) Two on the product side

Balancing Equations for Reactions Occurring in Basic Solution

If a redox reaction occurs in basic solution, the equation must be balanced by using OH^- and H_2O rather than H^+ and H_2O . Because the water molecule and the hydroxide ion both contain hydrogen, this approach can take more moving back and forth from one side of the equation to the other to arrive at the appropriate half-reaction. There is an alternate approach.

How to Balance Redox Reactions in Basic Aqueous Solution

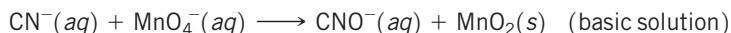
1. Balance the half-reactions as if they occurred in acidic solution.
2. Count the number of H^+ in each half-reaction, and then add the same number of OH^- to each side of the half-reaction.

Using this method, the reaction is mass-balanced because you are adding the same thing to both sides. In essence, what you are doing is “neutralizing” the protons to form water ($\text{H}^+ + \text{OH}^- \longrightarrow \text{H}_2\text{O}$) on the side containing H^+ , and the other side ends up with the OH^- . The resulting water molecules can be canceled as needed.

Sample Exercise 20.3

Balancing Redox Equations in Basic Solution

Complete and balance this equation for a redox reaction that takes place in basic solution:



SOLUTION

Analyze We are given an incomplete equation for a basic redox reaction and asked to balance it.

Plan We go through the first steps of our procedure as if the reaction were occurring in acidic solution. We then add the

appropriate number of OH^- to each side of the equation, combining H^+ and OH^- to form H_2O . We complete the process by simplifying the equation.

Solve

Step 1: We write the incomplete, unbalanced half-reactions:



Continued

Step 2: We balance each half-reaction as if it took place in acidic solution: Now we must take into account that the reaction occurs in basic solution, adding OH^- to both sides of both half-reactions to neutralize H^+ :

We “neutralize” H^+ and OH^- by forming H_2O when they are on the same side of either half-reaction:

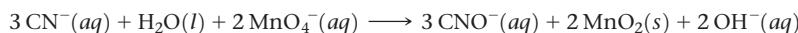
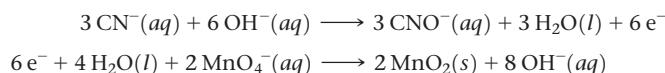
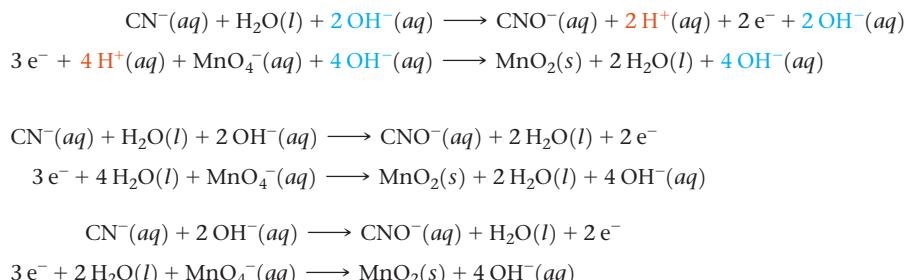
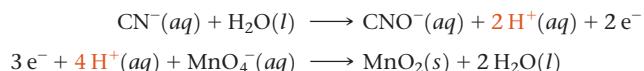
Next, we cancel water molecules that appear as both reactants and products: Both half-reactions are now balanced. You can check the atoms and the overall charge.

Step 3: We multiply the cyanide half-reaction by 3, which gives six electrons on the product side, and multiply the permanganate half-reaction by 2, which gives six electrons on the reactant side:

Step 4: We add the two half-reactions together and simplify by canceling species that appear as both reactants and products:

Step 5: Check that the atoms and charges are balanced.

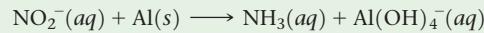
Comment It is important to remember that this procedure does not imply that H^+ ions are involved in the chemical reaction. Recall that in aqueous solutions at 25°C , $K_w = [\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14}$. Thus, $[\text{H}^+]$ is very small in this basic solution.



There are 3 C, 3 N, 2 H, 9 O, 2 Mn, and a charge of 5– on both sides of the equation.

► Practice Exercise

If you complete and balance the following oxidation-reduction reaction in basic solution

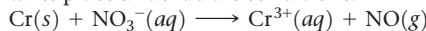


how many hydroxide ions are there in the balanced equation (for the reaction balanced with the smallest whole-number coefficients)?

- (a) One on the reactant side
- (b) One on the product side
- (c) Four on the reactant side
- (d) Seven on the product side
- (e) None

Self-Assessment Exercise

- 20.6** Complete and balance the following redox equation which takes place under acidic conditions:



Exercises

- 20.7** Hydrazine (N_2H_4) and dinitrogen tetroxide (N_2O_4) form a self-igniting mixture that has been used as a rocket propellant. The reaction products are N_2 and H_2O .
- (a) Write a balanced chemical equation for this reaction.
- (b) What is

being oxidized, and what is being reduced? (c) Which substance serves as the reducing agent and which as the oxidizing agent?

20.8 Complete and balance the following half-reactions. In each case indicate whether the half-reaction is an oxidation or a reduction.

- (a) $\text{Mo}^{3+}(aq) \longrightarrow \text{Mo}(s)$ (acidic solution)
- (b) $\text{H}_2\text{SO}_3(aq) \longrightarrow \text{SO}_4^{2-}(aq)$ (acidic solution)
- (c) $\text{NO}_3^-(aq) \longrightarrow \text{NO}(g)$ (acidic solution)
- (d) $\text{O}_2(g) \longrightarrow \text{H}_2\text{O}(l)$ (acidic solution)
- (e) $\text{O}_2(g) \longrightarrow \text{H}_2\text{O}(l)$ (basic solution)
- (f) $\text{Mn}^{2+}(aq) \longrightarrow \text{MnO}_2(s)$ (basic solution)
- (g) $\text{Cr(OH)}_3(s) \longrightarrow \text{CrO}_4^{2-}(aq)$ (basic solution)

20.9 Complete and balance the following equations, and identify the oxidizing and reducing agents. (Recall that the O atoms in hydrogen peroxide, H_2O_2 , have an atypical oxidation state.)

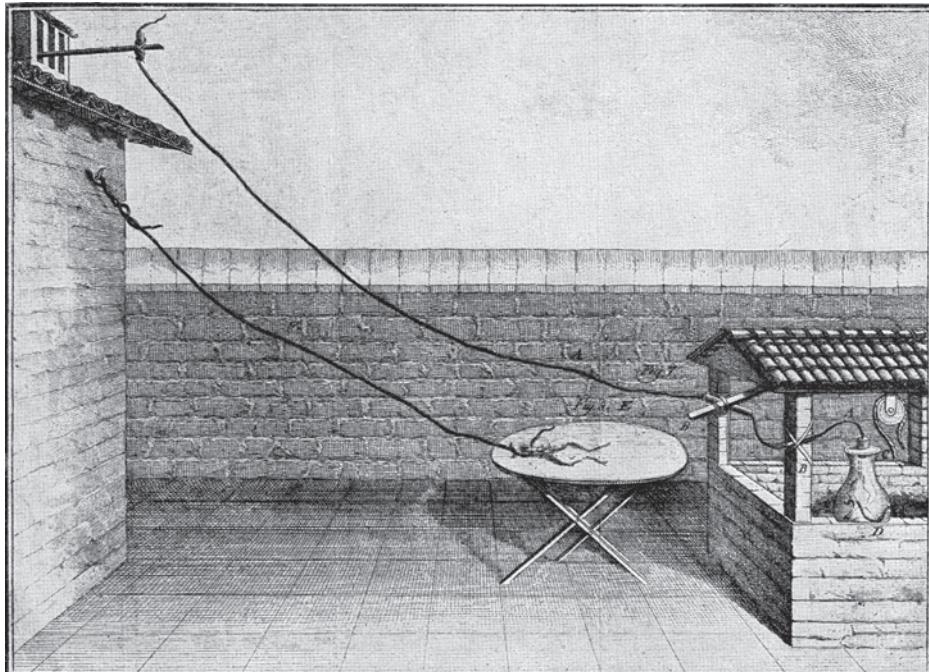
- (a) $\text{NO}_2^-(aq) + \text{Cr}_2\text{O}_7^{2-}(aq) \longrightarrow \text{Cr}^{3+}(aq) + \text{NO}_3^-(aq)$ (acidic solution)
- (b) $\text{S}(s) + \text{HNO}_3(aq) \longrightarrow \text{H}_2\text{SO}_3(aq) + \text{N}_2\text{O}(g)$ (acidic solution)
- (c) $\text{Cr}_2\text{O}_7^{2-}(aq) + \text{CH}_3\text{OH}(aq) \longrightarrow \text{HCOOH}(aq) + \text{Cr}^{3+}(aq)$ (acidic solution)
- (d) $\text{BrO}_3^-(aq) + \text{N}_2\text{H}_4(g) \longrightarrow \text{Br}^-(aq) + \text{N}_2(g)$ (acidic solution)
- (e) $\text{NO}_2^-(aq) + \text{Al}(s) \longrightarrow \text{NH}_4^+(aq) + \text{AlO}_2^-(aq)$ (basic solution)
- (f) $\text{H}_2\text{O}_2(aq) + \text{ClO}_2(aq) \longrightarrow \text{ClO}_2^-(aq) + \text{O}_2(g)$ (basic solution)

20.6 (c)

Answers to Self-Assessment Exercise



20.3 | Voltaic Cells



The story goes that Luigi Galvani and his wife were conducting experiments in static electricity generated by rubbing frog skin. A scalpel touched a nerve in the leg of the frog and they saw a spark and the leg twitched, ‘as if it were alive’. They coined the term animal electricity. Alessandro Volta checked these findings after they were published in 1790 and found that the frog was not necessary but instead an electrical current could be generated using two different metals separated by an electrolyte.

By the end of this section, you should be able to

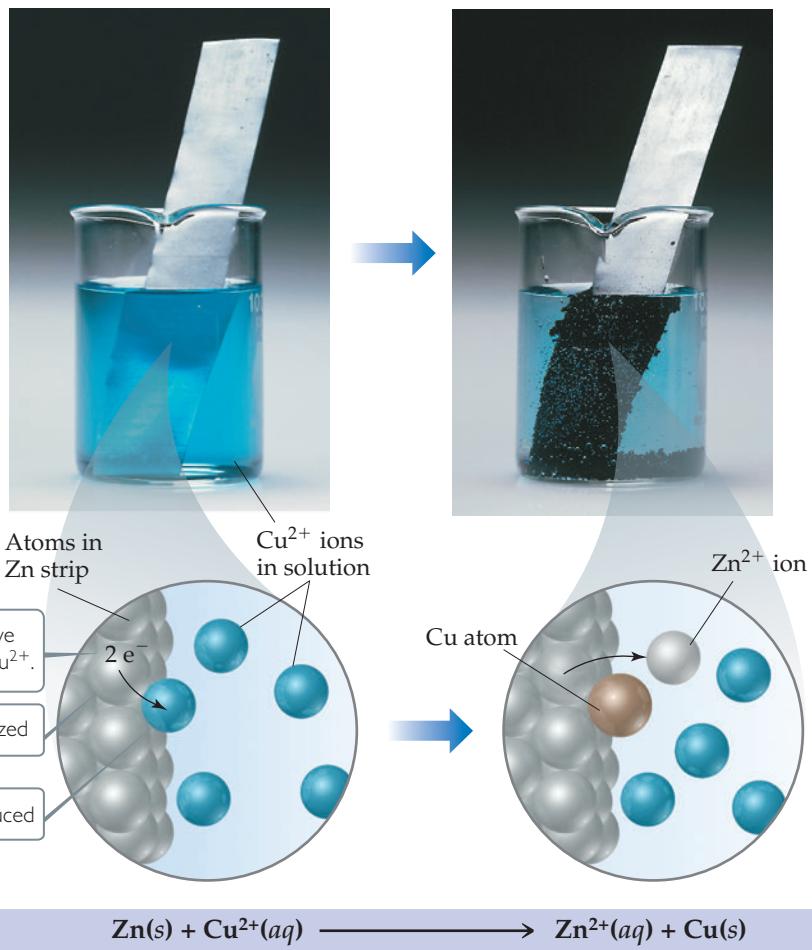
- Identify the component parts of a voltaic cell

The energy released in a spontaneous redox reaction can be used to perform electrical work. This task is accomplished through a **voltaic** (or **galvanic**) **cell**, a device in which the transfer of electrons takes place through an external pathway rather than directly between reactants present in the same reaction vessel.

One such spontaneous reaction occurs when a strip of zinc is placed in contact with a solution containing $\text{Cu}^{2+}(aq)$. As the reaction proceeds, the blue color of $\text{Cu}^{2+}(aq)$ ions fades and copper metal deposits on the zinc. At the same time, the zinc

**Go Figure**

Why does the intensity of the blue solution color lessen as the reaction proceeds?



▲ Figure 20.3 A spontaneous oxidation–reduction reaction involving zinc and copper.

**Go Figure**

Which metal, Cu or Zn, is oxidized in this voltaic cell?



▲ Figure 20.4 A Cu–Zn voltaic cell based on the reaction in Equation 20.7.

begins to dissolve. These transformations, shown in Figure 20.3, are summarized by the equation

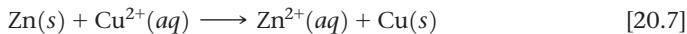


Figure 20.4 shows a voltaic cell that uses the redox reaction given in Equation 20.7. Although the setup in Figure 20.4 is more complex than that in Figure 20.3, the reaction is the same in both cases. The significant difference is that in the voltaic cell the Zn metal and $\text{Cu}^{2+}(aq)$ are not in direct contact with each other. Instead, Zn metal is in contact with $\text{Zn}^{2+}(aq)$ in one compartment, and Cu metal is in contact with $\text{Cu}^{2+}(aq)$ in the other compartment. Consequently, $\text{Cu}^{2+}(aq)$ reduction can occur only by the flow of electrons through an external circuit, namely, a wire connecting the Zn and Cu strips. Electrons flowing through a wire and ions moving in solution both constitute an *electrical current*. This flow of electrical charge can be used to accomplish electrical work.

The two solid metals connected by the external circuit are called *electrodes*. By definition, the electrode at which oxidation occurs is the **anode** and the electrode at which reduction occurs is the **cathode**.* The electrodes can be made of materials that

*To help remember these definitions, note that *anode* and *oxidation* both begin with a vowel, and *cathode* and *reduction* both begin with a consonant.

Another aid is ‘An Ox – Red Cat’ linking the Anode with Oxidation and Reduction with the Cathode.

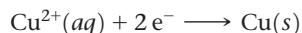
participate in the reaction, as in the present example. Over the course of the reaction, the Zn electrode gradually disappears and the copper electrode gains mass. More typically, the electrodes are made of a conducting material, such as platinum or graphite, that does not gain or lose mass during the reaction but serves as a surface at which electrons are transferred.

Each compartment of a voltaic cell is called a *half-cell*. One half-cell is the site of the oxidation half-reaction, and the other is the site of the reduction half-reaction. In our present example, Zn is oxidized and Cu²⁺ is reduced:

Anode (oxidation half-reaction)



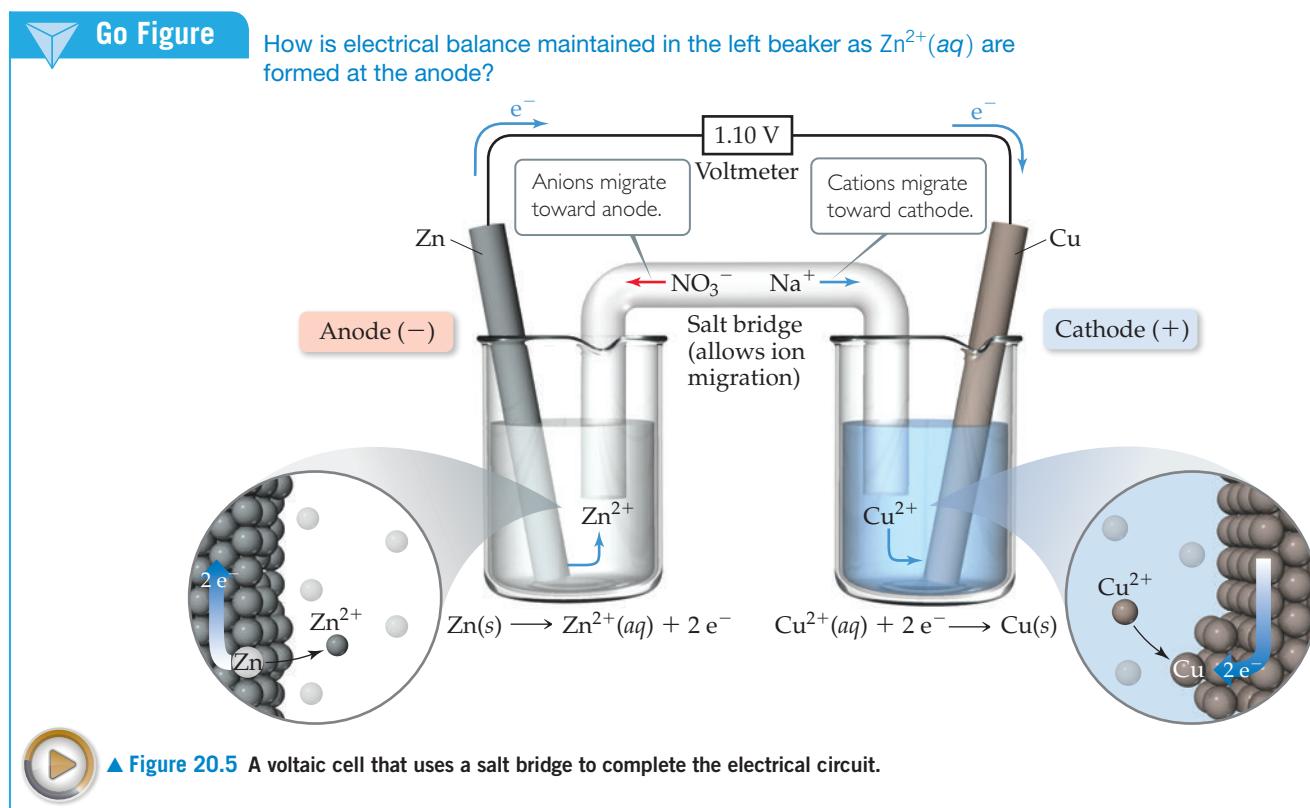
Cathode (reduction half-reaction)



Electrons become available as zinc metal is oxidized at the anode. They flow through the external circuit to the cathode, where they are consumed as Cu²⁺(aq) is reduced. Because Zn(s) is oxidized in the cell, the zinc electrode loses mass, and the concentration of the Zn²⁺(aq) solution increases as the cell operates. At the same time, the Cu electrode gains mass, and the Cu²⁺(aq) solution becomes less concentrated as Cu²⁺(aq) is reduced to Cu(s).

For a voltaic cell to work, the solutions in the two half-cells must remain electrically neutral. As Zn is oxidized in the anode half-cell, Zn²⁺(aq) ions enter the solution, upsetting the initial Zn²⁺/SO₄²⁻ charge balance. To keep the solution electrically neutral, there must be some means for Zn²⁺(aq) cations to migrate out of the anode half-cell and for anions to migrate in. Similarly, the reduction of Cu²⁺(aq) at the cathode removes these cations from the solution, leaving an excess of SO₄²⁻ anions in that half-cell. To maintain electrical neutrality, some of these anions must migrate out of the cathode half-cell, and positive ions must migrate in. In fact, no measurable electron flow occurs between electrodes unless a means is provided for ions to migrate through the solution from one half-cell to the other, thereby completing the circuit.

In Figure 20.4, a porous glass disc separating the two half-cells allows ions to migrate and maintain the electrical neutrality of the solutions. In **Figure 20.5**, a



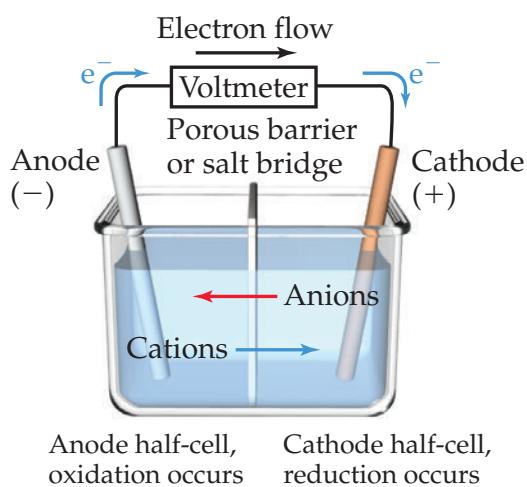


Figure 20.6 Summary of reactions occurring in a voltaic cell. The half-cells can be separated by either a porous glass disc (as in Figure 20.4) or by a salt bridge (as in Figure 20.5).

salt bridge serves this purpose. The salt bridge consists of a U-shaped tube containing an electrolyte solution, such as $\text{NaNO}_3(aq)$, whose ions will not react with other ions in the voltaic cell or with the electrodes. The electrolyte is often incorporated into a paste or gel so that the electrolyte solution does not pour out when the U-tube is inverted. As oxidation and reduction proceed at the electrodes, ions from the salt bridge migrate into the two half-cells—cations migrating to the cathode half-cell and anions migrating to the anode half-cell—to neutralize charge in the half-cell solutions. Whichever device is used to allow ions to migrate between half-cells, *anions always migrate toward the anode and cations toward the cathode*.

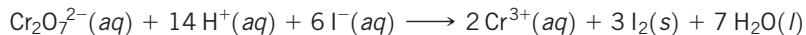
Figure 20.6 summarizes the various relationships in a voltaic cell. Notice in particular that *electrons flow from the anode through the external circuit to the cathode*. Because of this directional flow, the anode in a voltaic cell is labeled with a negative sign and the cathode is labeled with a positive sign. We can envision the electrons as being attracted to the positive cathode from the negative anode through the external circuit.



Sample Exercise 20.4

Describing a Voltaic Cell

The oxidation-reduction reaction



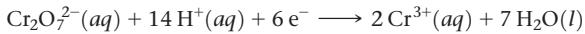
is spontaneous. A solution containing $\text{K}_2\text{Cr}_2\text{O}_7$ and H_2SO_4 is poured into one beaker, and a solution of KI is poured into another. A salt bridge is used to join the beakers. A metallic conductor that will not react with either solution (such as platinum foil) is suspended in each solution, and the two conductors are connected with wires through a voltmeter or some other device to detect an electric current. The resulting voltaic cell generates an electric current. Indicate the reaction occurring at the anode, the reaction at the cathode, the direction of electron migration, the direction of ion migration, and the signs of the electrodes.

SOLUTION

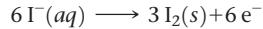
Analyze We are given the equation for a spontaneous reaction that takes place in a voltaic cell and a description of how the cell is constructed. We are asked to write the half-reactions occurring at the anode and at the cathode, as well as the directions of electron and ion movements and the signs assigned to the electrodes.

Plan Our first step is to divide the chemical equation into half-reactions so that we can identify the oxidation and the reduction processes. We then use the definitions of anode and cathode and the other terminologies summarized in Figure 20.6.

Solve In one half-reaction, $\text{Cr}_2\text{O}_7^{2-}(aq)$ is converted into $\text{Cr}^{3+}(aq)$. Starting with these ions and then completing and balancing the half-reaction, we have



In the other half-reaction, $\text{I}^-(aq)$ is converted to $\text{I}_2(s)$:



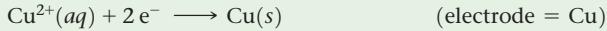
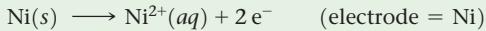
Now we can use the summary in Figure 20.6 to help us describe the voltaic cell. The first half-reaction is the reduction process (electrons on the reactant side of the equation). By definition, the reduction process occurs at the cathode. The second half-reaction is the oxidation process (electrons on the product side of the equation), which occurs at the anode.

The I^- ions are the source of electrons, and the $\text{Cr}_2\text{O}_7^{2-}$ ions accept the electrons. Hence, the electrons flow through the external

circuit from the electrode immersed in the KI solution (the anode) to the electrode immersed in the $\text{K}_2\text{Cr}_2\text{O}_7-\text{H}_2\text{SO}_4$ solution (the cathode). The electrodes themselves do not react in any way; they merely provide a means of transferring electrons from or to the solutions. The cations move through the solutions toward the cathode, and the anions move toward the anode. The anode (from which the electrons move) is the negative electrode, and the cathode (toward which the electrons move) is the positive electrode.

► Practice Exercise

The following two half-reactions occur in a voltaic cell:



Which one of the following descriptions most accurately describes what is occurring in the half-cell containing the Cu electrode and $\text{Cu}^{2+}(aq)$ solution?

- (a) The electrode is losing mass and cations from the salt bridge are flowing into the half-cell.
- (b) The electrode is gaining mass and cations from the salt bridge are flowing into the half-cell.
- (c) The electrode is losing mass and anions from the salt bridge are flowing into the half-cell.
- (d) The electrode is gaining mass and anions from the salt bridge are flowing into the half-cell.

Self-Assessment Exercise

20.10 Which statement about the working of a voltaic cell is true?

- (a) Electrons flow from the anode to the cathode
- (b) Oxidation occurs at the cathode

(c) Anions flow through the salt bridge to the cathode

(d) The cathode is negatively charged

Exercises

20.11 Indicate whether each statement is true or false: (a) The anode is the electrode at which oxidation takes place. (b) A voltaic cell always has a positive emf. (c) A salt bridge or permeable barrier is necessary to allow a voltaic cell to operate.

20.12 A voltaic cell similar to that shown in Figure 20.5 is constructed. One half-cell consists of an iron strip placed in a solution of FeSO_4 , and the other has an aluminum strip placed in a solution of $\text{Al}_2(\text{SO}_4)_3$. The overall cell reaction is



(a) What is being oxidized, and what is being reduced? (b) Write the half-reactions that occur in the two half-cells. (c) Which electrode is the anode, and which is the cathode? (d) Indicate the signs of the electrodes. (e) Do electrons flow from the aluminum electrode to the iron electrode or from the iron to the aluminum? (f) In which directions do the cations and anions migrate through the solution? Assume the Al is not coated with its oxide.

20.10 (a)

Answers to Self-Assessment Exercise

20.4 | Cell Potentials under Standard Conditions



There are many different combinations of materials that can make up a voltaic cell, and, in this section, we see how they may be quantified. By the end of this section, you should be able to

- Calculate the emf of a cell from standard reduction potentials

Why do electrons transfer spontaneously from a Zn atom to a Cu²⁺ ion, either directly as in Figure 20.3 or through an external circuit as in Figure 20.4? In a simple sense, we can compare the electron flow to the flow of water in a waterfall (**Figure 20.7**). Water flows spontaneously over a waterfall because of a difference in potential energy between the top of the falls and the bottom. In a similar fashion, electrons flow spontaneously through an external circuit from the anode of a voltaic cell to the cathode because of a difference in potential energy. The potential energy of electrons is higher in the anode than in the cathode. Thus, electrons flow spontaneously toward the electrode with the more positive electrical potential.

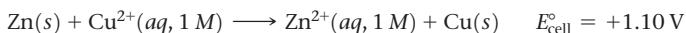
The difference in potential energy per electrical charge (the *potential difference*) between two electrodes is measured in *volts*. One volt (V) is the potential difference required to impart 1 joule (J) of energy to a charge of 1 coulomb (C):

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

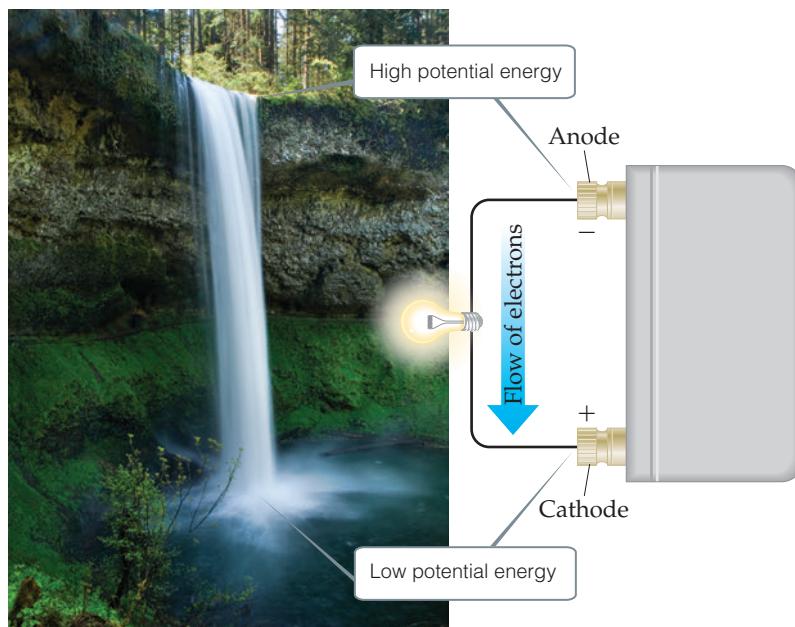
Recall that one electron has a charge of $1.60 \times 10^{-19} \text{ C}$.

The potential difference between the two electrodes of a voltaic cell is called the **cell potential**, denoted E_{cell} . Because the potential difference provides the driving force that pushes electrons through the external circuit, we also call it the **electromotive force**, or **emf**. Because E_{cell} is measured in volts, it is also commonly called the *voltage* of the cell.

The cell potential of any voltaic cell is positive. The magnitude of the cell potential depends on the reactions that occur at the cathode and anode, the concentrations of reactants and products, and the temperature, which we will assume to be 25 °C unless otherwise noted. In this section, we focus on cells that are operated at 25 °C under *standard conditions*. Recall from Table 19.2 that standard conditions include 1 M concentration for reactants and products in solution and 100.0 kPa pressure for gaseous reactants and products. The cell potential under standard conditions is called either the **standard cell potential** or **standard emf** and is denoted E_{cell}° . For the Zn–Cu voltaic cell in Figure 20.5, for example, the standard cell potential at 25 °C is +1.10 V:



Recall that the superscript \circ indicates standard-state conditions.



▲ Figure 20.7 Water analogy for electron flow. Just as water spontaneously flows downhill, electrons flow spontaneously from the anode to the cathode in a voltaic cell.

Standard Reduction Potentials

The standard cell potential of a voltaic cell, E_{cell}° , depends on the particular cathode and anode half-cells. We could, in principle, tabulate the standard cell potentials for all possible cathode–anode combinations. However, it is not necessary to undertake this arduous task. Rather, we can assign a standard potential to each half-cell and then use these half-cell potentials to determine E_{cell}° . The cell potential is the difference between two half-cell potentials. By convention, the potential associated with each electrode is chosen to be the potential for *reduction* at that electrode. Thus, standard half-cell potentials are tabulated for reduction reactions, which means they are **standard reduction potentials**, denoted E_{red}° . The standard cell potential, E_{cell}° , is the standard reduction potential of the cathode reaction, E_{red}° (cathode), *minus* the standard reduction potential of the anode reaction, E_{red}° (anode):

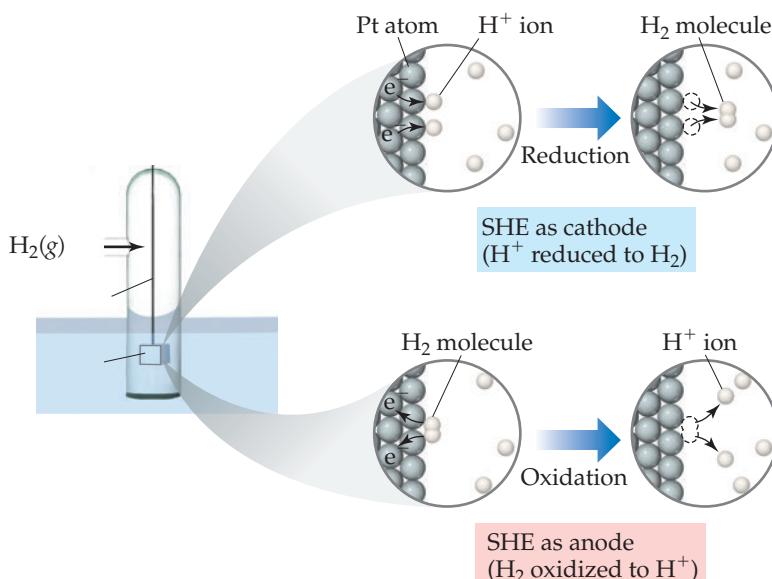
$$E_{\text{cell}}^{\circ} = E_{\text{red}}^{\circ} (\text{cathode}) - E_{\text{red}}^{\circ} (\text{anode}) \quad [20.8]$$

It is not possible to measure the standard reduction potential of a half-reaction directly. If we assign a standard reduction potential to a certain reference half-reaction, however, we can then determine the standard reduction potentials of other half-reactions relative to that reference value. The reference half-reaction is the reduction of $\text{H}^+(aq)$ to $\text{H}_2(g)$ under standard conditions, which is assigned a standard reduction potential of exactly 0 V:

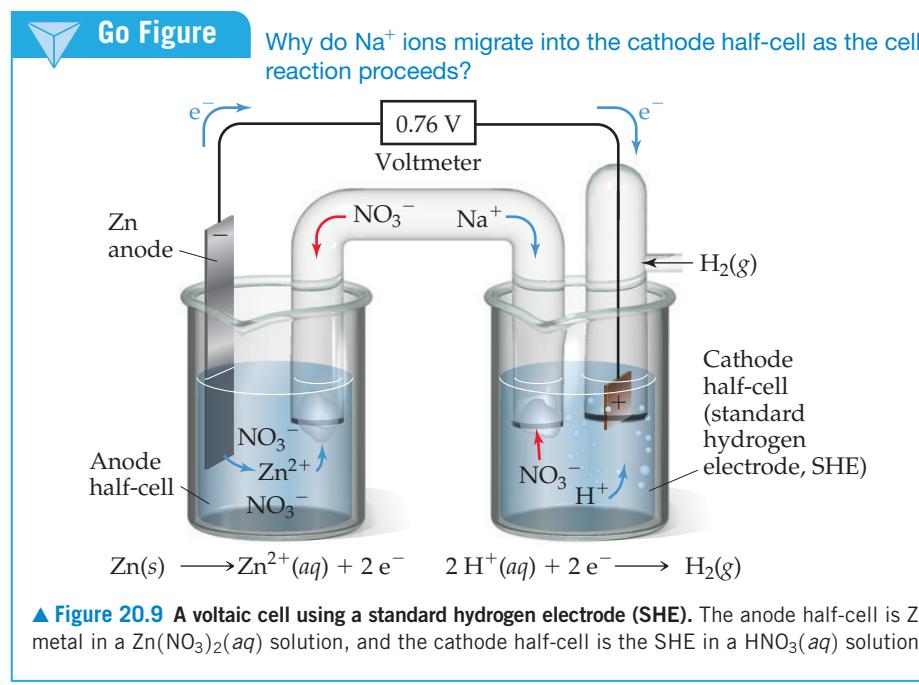


An electrode designed to produce this half-reaction is called a **standard hydrogen electrode** (SHE). A SHE consists of a platinum wire connected to a piece of platinum foil covered with finely divided platinum that serves as an inert surface for the reaction (**Figure 20.8**). The SHE allows the platinum to be in contact with both 1 M $\text{H}^+(aq)$ and a stream of hydrogen gas at 100 kPa. The SHE can operate as either the anode or cathode of a cell, depending on the nature of the other electrode.

Figure 20.9 shows a voltaic cell using a SHE. The spontaneous reaction is the one shown in Figure 20.1, namely, oxidation of Zn and reduction of H^+ :



▲ **Figure 20.8** The standard hydrogen electrode (SHE) is used as a reference electrode.



When the cell is operated under standard conditions, the cell potential is +0.76 V. By using the standard cell potential ($E_{\text{cell}}^\circ = 0.76 \text{ V}$), the defined standard reduction potential of H^+ ($E_{\text{red}}^\circ = 0 \text{ V}$) and Equation 20.8, we can determine the standard reduction potential for the Zn^{2+}/Zn half-reaction:

$$\begin{aligned} E_{\text{cell}}^\circ &= E_{\text{red}}^\circ (\text{cathode}) - E_{\text{red}}^\circ (\text{anode}) \\ +0.76 \text{ V} &= 0 \text{ V} - E_{\text{red}}^\circ (\text{anode}) \\ E_{\text{red}}^\circ (\text{anode}) &= -0.76 \text{ V} \end{aligned}$$

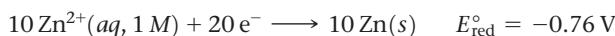
Thus, a standard reduction potential of -0.76 V can be assigned to the reduction of Zn^{2+} to Zn :



We write the reaction as a reduction even though the Zn reaction in Figure 20.9 is an oxidation. *Whenever we assign an electrical potential to a half-reaction, we write the reaction as a reduction.* Half-reactions, however, are reversible, being able to operate as either reductions or oxidations. Consequently, half-reactions are sometimes written using two arrows (\rightleftharpoons) between reactants and products, as in equilibrium reactions.

The standard reduction potentials for other half-reactions can be determined in a fashion analogous to that used for the Zn^{2+}/Zn half-reaction. **Table 20.1** lists some standard reduction potentials; a more complete list is found in Appendix E. These standard reduction potentials, often called *half-cell potentials*, can be combined to calculate E_{cell}° values for a large variety of voltaic cells.

Because electrical potential measures potential energy per electrical charge, standard reduction potentials are intensive properties. In other words, if we increase the amount of substances in a redox reaction, we increase both the energy and the charges involved, but the ratio of energy (joules) to electrical charge (coulombs) remains constant ($V = \text{J/C}$). Thus, *changing the stoichiometric coefficient in a half-reaction does not affect the value of the standard reduction potential.* For example, E_{red}° for the reduction of 10 mol Zn^{2+} is the same as that for the reduction of 1 mol Zn^{2+} :



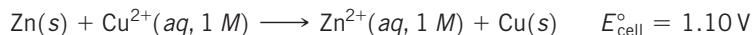
For each half-cell in a voltaic cell, the standard reduction potential provides a measure of the tendency for reduction to occur: *The more positive the value of E_{red}° , the*

TABLE 20.1 Standard Reduction Potentials in Water at 25°C

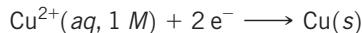
$E^\circ_{\text{red}}(\text{V})$	Reduction Half-Reaction
+2.87	$\text{F}_2(g) + 2 \text{e}^- \longrightarrow 2 \text{F}^-(aq)$
+1.51	$\text{MnO}_4^-(aq) + 8 \text{H}^+(aq) + 5 \text{e}^- \longrightarrow \text{Mn}^{2+}(aq) + 4 \text{H}_2\text{O}(l)$
+1.36	$\text{Cl}_2(g) + 2 \text{e}^- \longrightarrow 2 \text{Cl}^-(aq)$
+1.33	$\text{Cr}_2\text{O}_7^{2-}(aq) + 14 \text{H}^+(aq) + 6 \text{e}^- \longrightarrow 2 \text{Cr}^{3+}(aq) + 7 \text{H}_2\text{O}(l)$
+1.23	$\text{O}_2(g) + 4 \text{H}^+(aq) + 4 \text{e}^- \longrightarrow 2 \text{H}_2\text{O}(l)$
+1.06	$\text{Br}_2(l) + 2 \text{e}^- \longrightarrow 2 \text{Br}^-(aq)$
+0.96	$\text{NO}_3^-(aq) + 4 \text{H}^+(aq) + 3 \text{e}^- \longrightarrow \text{NO}(g) + 2 \text{H}_2\text{O}(l)$
+0.80	$\text{Ag}^+(aq) + \text{e}^- \longrightarrow \text{Ag}(s)$
+0.77	$\text{Fe}^{3+}(aq) + \text{e}^- \longrightarrow \text{Fe}^{2+}(aq)$
+0.68	$\text{O}_2(g) + 2 \text{H}^+(aq) + 2 \text{e}^- \longrightarrow \text{H}_2\text{O}_2(aq)$
+0.59	$\text{MnO}_4^-(aq) + 2 \text{H}_2\text{O}(l) + 3 \text{e}^- \longrightarrow \text{MnO}_2(s) + 4 \text{OH}^-(aq)$
+0.54	$\text{I}_2(s) + 2 \text{e}^- \longrightarrow 2 \text{I}^-(aq)$
+0.40	$\text{O}_2(g) + 2 \text{H}_2\text{O}(l) + 4 \text{e}^- \longrightarrow 4 \text{OH}^-(aq)$
+0.34	$\text{Cu}^{2+}(aq) + 2 \text{e}^- \longrightarrow \text{Cu}(s)$
0 [defined]	$2 \text{H}^+(aq) + 2 \text{e}^- \longrightarrow \text{H}_2(g)$
-0.28	$\text{Ni}^{2+}(aq) + 2 \text{e}^- \longrightarrow \text{Ni}(s)$
-0.44	$\text{Fe}^{2+}(aq) + 2 \text{e}^- \longrightarrow \text{Fe}(s)$
-0.76	$\text{Zn}^{2+}(aq) + 2 \text{e}^- \longrightarrow \text{Zn}(s)$
-0.83	$2 \text{H}_2\text{O}(l) + 2 \text{e}^- \longrightarrow \text{H}_2(g) + 2 \text{OH}^-(aq)$
-1.66	$\text{Al}^{3+}(aq) + 3 \text{e}^- \longrightarrow \text{Al}(s)$
-2.71	$\text{Na}^+(aq) + \text{e}^- \longrightarrow \text{Na}(s)$
-3.05	$\text{Li}^+(aq) + \text{e}^- \longrightarrow \text{Li}(s)$

Sample Exercise 20.5Calculating E°_{red} from E°_{cell}

For the Zn–Cu voltaic cell shown in Figure 20.5, we have



Given that the standard reduction potential of Zn^{2+} to $\text{Zn}(s)$ is -0.76 V , calculate the E°_{red} for the reduction of Cu^{2+} to Cu :

**SOLUTION**

Analyze We are given E°_{cell} and E°_{red} for Zn^{2+} and asked to calculate E°_{red} for Cu^{2+} .

Plan In the voltaic cell, Zn is oxidized and is therefore the anode. Thus, the given E°_{red} for Zn^{2+} is E°_{red} (anode). Because Cu^{2+} is reduced, it is in the cathode half-cell. Thus, the unknown reduction potential for Cu^{2+} is E°_{red} (cathode). Knowing E°_{cell} and E°_{red} (anode), we can use Equation 20.8 to solve for E°_{red} (cathode).

Solve

$$E^\circ_{\text{cell}} = E^\circ_{\text{red}}(\text{cathode}) - E^\circ_{\text{red}}(\text{anode})$$

$$1.10 \text{ V} = E^\circ_{\text{red}}(\text{cathode}) - (-0.76 \text{ V})$$

$$E^\circ_{\text{red}}(\text{cathode}) = 1.10 \text{ V} - 0.76 \text{ V} = 0.34 \text{ V}$$

Check This standard reduction potential agrees with the one listed in Table 20.1.

Comment The standard reduction potential for Cu^{2+} can be represented as $E^\circ_{\text{Cu}^{2+}} = 0.34 \text{ V}$ and that for Zn^{2+} as $E^\circ_{\text{Zn}^{2+}} = -0.76 \text{ V}$. The subscript identifies the ion that is reduced in the reduction half-reaction.

► Practice Exercise

A voltaic cell based on the reaction

$2 \text{Eu}^{2+}(aq) + \text{Ni}^{2+}(aq) \longrightarrow 2 \text{Eu}^{3+}(aq) + \text{Ni}(s)$ generates $E^\circ_{\text{cell}} = 0.07 \text{ V}$. Given the standard reduction potential of Ni^{2+} given in Table 20.1, what is the standard reduction potential for the reaction $\text{Eu}^{3+}(aq) + \text{e}^- \longrightarrow \text{Eu}^{2+}(aq)$?

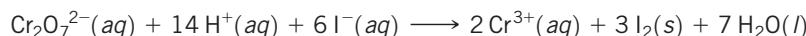
- (a) -0.35 V (b) 0.35 V (c) -0.21 V (d) 0.21 V (e) 0.07 V



Sample Exercise 20.6

Calculating E_{cell}° from E_{red}°

Use Table 20.1 to calculate E_{cell}° for the voltaic cell described in Sample Exercise 20.4, which is based on the reaction



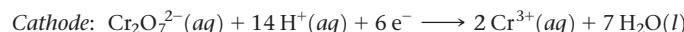
SOLUTION

Analyze We are given the equation for a redox reaction and asked to use data in Table 20.1 to calculate the standard cell potential for the associated voltaic cell.

Plan Our first step is to identify the half-reactions that occur at the cathode and anode, which we did in Sample Exercise 20.4. Then we use Table 20.1 and Equation 20.8 to calculate the standard cell potential.

Solve

The half-reactions are:



According to Table 20.1, the standard reduction potential for the reduction of $\text{Cr}_2\text{O}_7^{2-}$ to Cr^{3+} is +1.33 V and the standard reduction potential for the reduction of I_2 to I^- (the reverse of the oxidation half-reaction) is +0.54 V. We use these values in Equation 20.8:

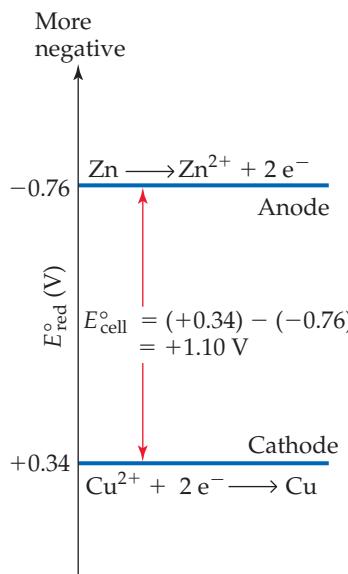
$$E_{\text{cell}}^{\circ} = E_{\text{red}}^{\circ}(\text{cathode}) - E_{\text{red}}^{\circ}(\text{anode}) = 1.33 \text{ V} - 0.54 \text{ V} = 0.79 \text{ V}$$

Although we must multiply the iodide half-reaction by 3 to obtain a balanced equation, we do *not* multiply the E_{red}° value by 3. As we have noted, the standard reduction potential is an intensive property and so is independent of the stoichiometric coefficients.

Check The cell potential, 0.79 V, is a positive number. As noted earlier, a voltaic cell must have a positive potential.

► Practice Exercise

Using the data in Table 20.1, what value would you calculate for the standard emf (E_{cell}°) for a voltaic cell that employs the overall cell reaction $2 \text{Ag}^+(\text{aq}) + \text{Ni}(\text{s}) \longrightarrow 2 \text{Ag}(\text{s}) + \text{Ni}^{2+}(\text{aq})$?
(a) +0.52 V **(b)** −0.52 V **(c)** +1.08 V **(d)** −1.08 V **(e)** +0.80 V



▲ **Figure 20.10** Half-cell potentials and standard cell potential for the Zn–Cu voltaic cell.

greater the tendency for reduction under standard conditions. In any voltaic cell operating under standard conditions, the E_{red}° value for the reaction at the cathode is more positive than the E_{red}° value for the reaction at the anode. Thus, electrons flow spontaneously through the external circuit from the electrode with the more negative value of E_{red}° to the electrode with the more positive value of E_{red}° . **Figure 20.10** graphically illustrates the relationship between the standard reduction potentials for the two half-reactions in the Zn–Cu voltaic cell of Figure 20.5.

Strengths of Oxidizing and Reducing Agents

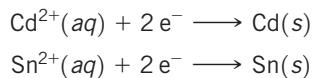
Table 20.1 lists half-reactions in the order of decreasing tendency to undergo reduction. For example, F_2 is located at the top of the table, having the most positive value for E_{red}° . Thus, F_2 is the most easily reduced species in Table 20.1 and therefore the strongest oxidizing agent listed.



Sample Exercise 20.7

Determining Half-Reactions at Electrodes and Calculating Cell Potentials

A voltaic cell is based on the two standard half-reactions



Use data in Appendix E to determine (a) which half-reaction occurs at the cathode and which occurs at the anode and (b) the standard cell potential.

SOLUTION

Analyze We have to look up E_{red}° for two half-reactions. We then use these values first to determine the cathode and the anode and then to calculate the standard cell potential, E_{cell}° .

Plan The cathode will have the reduction with the more positive E_{red}° value, and the anode will have the less positive E_{red}° . To write the half-reaction at the anode, we reverse the half-reaction written for the reduction, so that the half-reaction is written as an oxidation.

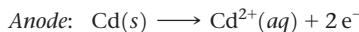
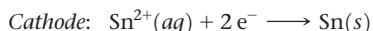
Solve

- (a) According to Appendix E, $E_{\text{red}}^{\circ}(\text{Cd}^{2+}/\text{Cd}) = -0.40 \text{ V}$ and $E_{\text{red}}^{\circ}(\text{Sn}^{2+}/\text{Sn}) = -0.14 \text{ V}$. The standard reduction potential for Sn^{2+} is more positive (less negative) than that for Cd^{2+} . Hence, the reduction of Sn^{2+} is the reaction that occurs at the cathode:

The anode reaction, therefore, is the loss of electrons by Cd:

- (b) The cell potential is given by the difference in the standard reduction potentials at the cathode and anode (Equation 20.8):

Notice that it is unimportant that the E_{red}° values of both half-reactions are negative; the negative values merely indicate how these reductions compare to the reference reaction, the reduction of $\text{H}^+(aq)$.



$$\begin{aligned} E_{\text{cell}}^{\circ} &= E_{\text{red}}^{\circ}(\text{cathode}) - E_{\text{red}}^{\circ}(\text{anode}) \\ &= (-0.14 \text{ V}) - (-0.40 \text{ V}) = 0.26 \text{ V} \end{aligned}$$

Check The cell potential is positive, as it must be for a voltaic cell.

► Practice Exercise

Consider three voltaic cells, each similar to the one shown in Figure 20.5. In each voltaic cell, one half-cell contains a 1.0 M $\text{Fe}(\text{NO}_3)_2(aq)$ solution with an Fe electrode. The contents of the other half-cells are as follows:

Cell 1: a 1.0 M $\text{CuCl}_2(aq)$ solution with a Cu electrode

Cell 2: a 1.0 M $\text{NiCl}_2(aq)$ solution with a Ni electrode

Cell 3: a 1.0 M $\text{ZnCl}_2(aq)$ solution with a Zn electrode

In which voltaic cell(s) does iron act as the anode?

- (a) Cell 1
- (b) Cell 2
- (c) Cell 3
- (d) Cells 1 and 2
- (e) All three cells

Among the most frequently used oxidizing agents are the halogens, O_2 , and oxyanions such as MnO_4^- , $\text{Cr}_2\text{O}_7^{2-}$, and NO_3^- , whose central atoms have high positive oxidation states. As seen in Table 20.1, all these species have large positive values of E_{red}° and therefore easily undergo reduction.

The lower the tendency for a half-reaction to occur in one direction, the greater the tendency for it to occur in the opposite direction. Thus, *the half-reaction with the most negative reduction potential in Table 20.1 is the one most easily reversed and run as an oxidation*. Being at the bottom of Table 20.1, $\text{Li}^+(aq)$ is the most difficult species in the list to reduce and is therefore the poorest oxidizing agent listed. Although $\text{Li}^+(aq)$ has little tendency to gain electrons, the reverse reaction, oxidation of $\text{Li}(s)$ to $\text{Li}^+(aq)$, is highly favorable. Thus, Li is the strongest reducing agent among the substances listed in Table 20.1. (Note that, because Table 20.1 lists half-reactions as reductions, only the substances on the

reactant side of these equations can serve as oxidizing agents; only those on the product side can serve as reducing agents.)

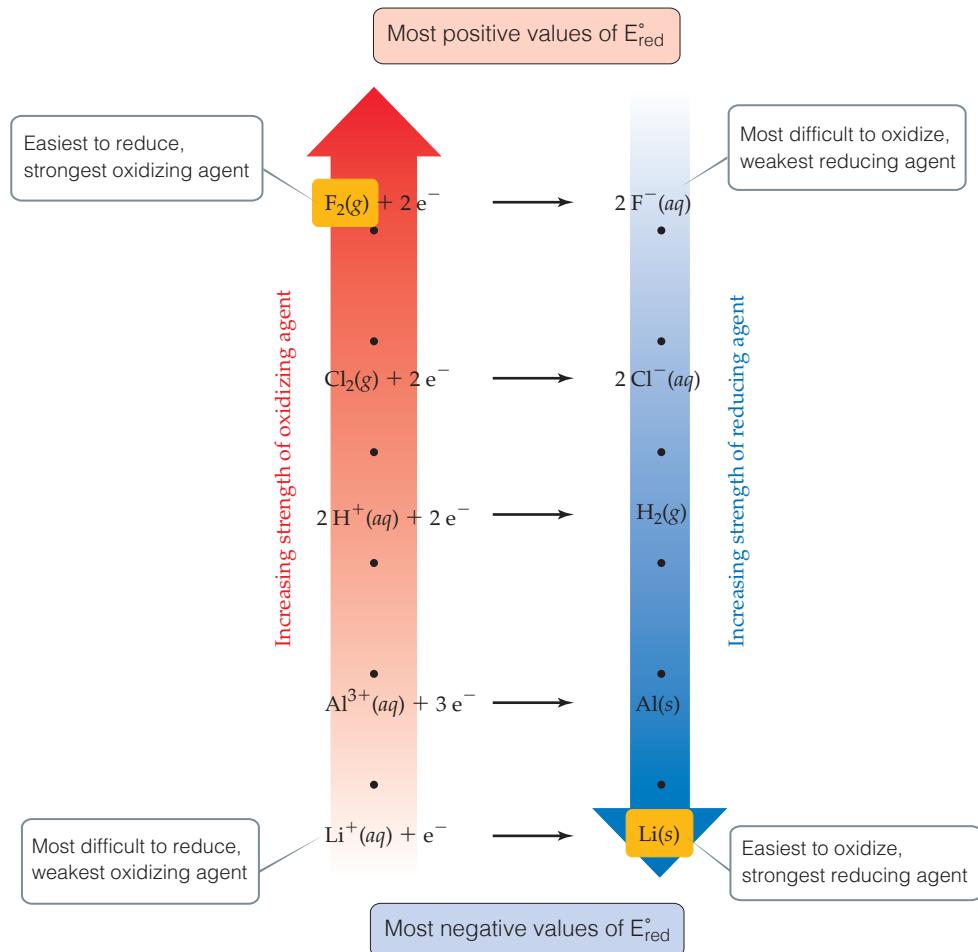
Commonly used reducing agents include H₂ and the active metals, such as the alkali metals and the alkaline earth metals. Other metals whose cations have negative E_{red}° values—Zn and Fe, for example—are also used as reducing agents. Solutions of reducing agents are difficult to store for extended periods because of the ubiquitous presence of O₂, a good oxidizing agent.

The information contained in Table 20.1 is summarized graphically in Figure 20.11. For the half-reactions at the top of Table 20.1 the substances on the reactant side of the equation are the most readily reduced species in the table and are therefore the strongest oxidizing agents. Substances on the product side of these reactions are the most difficult to oxidize and so are the weakest reducing agents in the table. Thus, Figure 20.11 shows F₂(g) as the strongest oxidizing agent and F[−](aq) as the weakest reducing agent. Conversely, the reactants in half-reactions at the bottom of Table 20.1, such as Li⁺(aq) are the most difficult to reduce and so are the weakest oxidizing agents, while the products of these reactions, such as Li(s), are the most readily oxidized species in the table and so are the strongest reducing agents.

This inverse relationship between oxidizing and reducing strength is similar to the inverse relationship between the strengths of conjugate acids and bases.

Go Figure

Can an acidic solution oxidize a piece of aluminum?



▲ Figure 20.11 Relative strengths of oxidizing and reducing agents.



Sample Exercise 20.8

Determining Relative Strengths of Oxidizing Agents

Using Table 20.1, rank the following ions in the order of increasing strength as oxidizing agents: $\text{NO}_3^-(aq)$, $\text{Ag}^+(aq)$, $\text{Cr}_2\text{O}_7^{2-}(aq)$.

SOLUTION

Analyze We are asked to rank the abilities of several ions to act as oxidizing agents.

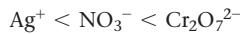
Plan The more readily an ion is reduced (the more positive its E_{red}° value), the stronger it is as an oxidizing agent.

Solve

From Table 20.1, we have:



Because the standard reduction potential of $\text{Cr}_2\text{O}_7^{2-}$ is the most positive, $\text{Cr}_2\text{O}_7^{2-}$ is the strongest oxidizing agent of the three. The rank order is:



► Practice Exercise

Based on the data in Table 20.1, which of the following species would you expect to be the strongest oxidizing agent?

- (a) $\text{Cl}^-(aq)$ (b) $\text{Cl}_2(g)$ (c) $\text{O}_2(g)$ (d) $\text{H}^+(aq)$ (e) $\text{Na}^+(aq)$

Self-Assessment Exercise

20.13 The standard reduction potential of $\text{Ni}^{2+}(aq)$ is $E_{\text{red}}^\circ = -0.28 \text{ V}$, and that of $\text{Fe}^{2+}(aq)$ is $E_{\text{red}}^\circ = -0.44 \text{ V}$. In a Ni-Fe voltaic cell, which electrode is the cathode, Ni or Fe?

- (a) Fe
(b) Ni

Exercises

20.14 (a) Which electrode of a voltaic cell, the cathode or the anode, corresponds to the higher potential energy for the electrons? (b) What are the units for electrical potential? How does this unit relate to energy expressed in joules?

20.15 A voltaic cell that uses the reaction

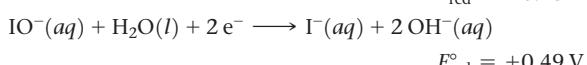
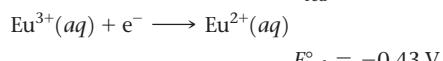
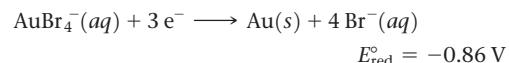


has a measured standard cell potential of $+1.03 \text{ V}$. (a) Write the two half-cell reactions. (b) By using data from Appendix E, determine E_{red}° for the reaction involving Pd. (c) Sketch the voltaic cell, label the anode and cathode, and indicate the direction of electron flow.

20.16 Using data in Appendix E, calculate the standard emf for each of the following reactions:

- (a) $\text{H}_2(g) + \text{F}_2(g) \longrightarrow 2 \text{H}^+(aq) + 2 \text{F}^-(aq)$
 (b) $\text{Cu}^{2+}(aq) + \text{Ca}(s) \longrightarrow \text{Cu}(s) + \text{Ca}^{2+}(aq)$
 (c) $3 \text{Fe}^{2+}(aq) \longrightarrow \text{Fe}(s) + 2 \text{Fe}^{3+}(aq)$
 (d) $2 \text{ClO}_3^-(aq) + 10 \text{Br}^-(aq) + 12 \text{H}^+(aq) \longrightarrow \text{Cl}_2(g) + 5 \text{Br}_2(l) + 6 \text{H}_2\text{O}(l)$

20.17 Given the following half-reactions and associated standard reduction potentials:



(a) Write the equation for the combination of these half-cell reactions that leads to the largest positive emf and calculate the value. (b) Write the equation for the combination of half-cell reactions that leads to the smallest positive emf and calculate that value.

20.18 A voltaic cell consists of a strip of cadmium metal in a solution of $\text{Cd}(\text{NO}_3)_2$ in one beaker, and in the other beaker a platinum electrode is immersed in a NaCl solution, with Cl_2 gas bubbled around the electrode. A salt bridge connects the two beakers. (a) Which electrode serves as the anode, and which as the cathode? (b) Does the Cd

electrode gain or lose mass as the cell reaction proceeds? (c) Write the equation for the overall cell reaction. (d) What is the emf generated by the cell under standard conditions?

- 20.19** From each of the following pairs of substances, use data in Appendix E to choose the one that is the stronger oxidizing agent:

- (a) $\text{Cl}_2(g)$ or $\text{Br}_2(l)$
- (b) $\text{Zn}^{2+}(aq)$ or $\text{Cd}^{2+}(aq)$
- (c) $\text{Cl}^-(aq)$ or $\text{ClO}_3^-(aq)$
- (d) $\text{H}_2\text{O}_2(aq)$ or $\text{O}_3(g)$

- 20.20** Is each of the following substances likely to serve as an oxidant or a reductant: (a) $\text{Ce}^{3+}(aq)$, (b) $\text{Ca}(s)$, (c) $\text{ClO}_3^-(aq)$, (d) $\text{N}_2\text{O}_5(g)$?

- 20.21** The standard reduction potential for the reduction of $\text{RuO}_4^-(aq)$ to $\text{RuO}_4^{2-}(aq)$ is +0.59 V. By using Appendix E, which of the following substances can oxidize $\text{RuO}_4^{2-}(aq)$ to $\text{RuO}_4^-(aq)$ under standard conditions: $\text{Br}_2(l)$, $\text{BrO}_3^-(aq)$, $\text{Mn}^{2+}(aq)$, $\text{O}_2(g)$, $\text{Sn}^{2+}(aq)$?

20.13 (b)

Answers to Self-Assessment Exercise



20.5 | Free Energy and Redox Reactions



Surprisingly, electric cars have been around since the end of the nineteenth century, however with a limited range and high battery cost they could not compete with the internal combustion engine. Recently, the development of new lithium ion battery technology and the falling cost of lithium has meant that electric vehicles are now edging into the domestic car market. The cost of the batteries remains a significant factor but in the decade since 2010 this has dropped by 600%. Electric vehicles have engine efficiencies of around 70%, significantly higher than either petrol or diesel engines which use only around 15-20% of the fuel energy content to move the vehicle. You can read more on electric vehicles in the Chemistry Put to Work box on page 987.

In this section, we examine the relationship between redox potentials and ΔG° , and by the end you should be able to

- Relate E° to ΔG° and K .

We have observed that voltaic cells use spontaneous redox reactions to produce a positive cell potential. Given half-cell potentials, we can determine whether a given redox reaction is spontaneous. In this endeavor, we can use a form of Equation 20.8 that describes redox reactions in general, not just reactions in voltaic cells:

$$E^\circ = E_{\text{red}}^\circ \text{ (reduction process)} - E_{\text{red}}^\circ \text{ (oxidation process)}$$

[20.10]

In writing the equation this way, we have dropped the subscript “cell” to indicate that the calculated emf does not necessarily refer to a voltaic cell. Also, we have generalized the standard reduction potentials by using the general terms *reduction* and *oxidation* rather than the terms specific to voltaic cells, *cathode* and *anode*. We can now make a general statement about the spontaneity of a reaction and its associated emf, E : *A positive value of E indicates a spontaneous process; a negative value of E indicates a nonspontaneous process.* We use E to represent the emf under nonstandard conditions and E° to indicate the standard emf.

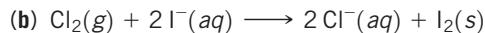
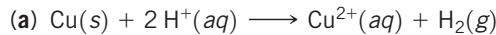
We can use standard reduction potentials to understand the activity series of metals. Recall that any metal in the activity series (Table 4.5) is oxidized by the ions of any metal below it. We can now recognize the origin of this rule based on standard reduction potentials. The activity series is based on the oxidation reactions of the metals, ordered from strongest reducing agent at the top to weakest reducing agent at the bottom. (Thus, the ordering is inverted relative to that in Table 20.1.) For example, nickel lies above silver in the activity series, making nickel the stronger reducing agent. Because a reducing agent is oxidized in any redox reaction, nickel is more easily oxidized than



Sample Exercise 20.9

Determining Spontaneity

Use Table 20.1 to determine whether the following reactions are spontaneous under standard conditions.



SOLUTION

Analyze We are given two reactions and must determine whether each is spontaneous.

Plan To determine whether a redox reaction is spontaneous under standard conditions, we first need to write its reduction and

oxidation half-reactions. We can then use the standard reduction potentials and Equation 20.10 to calculate the standard emf, E° , for the reaction. If a reaction is spontaneous, its standard emf must be a positive number.

Solve

- (a) We first must identify the oxidation and reduction half-reactions that when combined give the overall reaction.

We look up standard reduction potentials for both half-reactions and use them to calculate E° using Equation 20.10:

Because E° is negative, the reaction is not spontaneous in the direction written. Copper metal does not react with acids as written in Equation (a). The reverse reaction, however, is spontaneous and has a positive E° value:

Thus, Cu^{2+} can be reduced by H_2 .

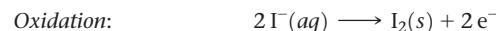
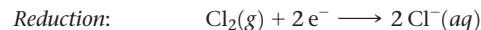
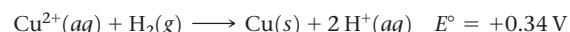
- (b) We follow a procedure analogous to that in (a):

In this case:

Because the value of E° is positive, this reaction is spontaneous and could be used to build a voltaic cell.



$$E^\circ = E_{\text{red}}^\circ (\text{reduction process}) - E_{\text{red}}^\circ (\text{oxidation process}) \\ = (0 \text{ V}) - (0.34 \text{ V}) = -0.34 \text{ V}$$



$$E^\circ = (1.36 \text{ V}) - (0.54 \text{ V}) = +0.82 \text{ V}$$

► Practice Exercise

Which of the following elements is capable of oxidizing $\text{Fe}^{2+}(aq)$ ions to $\text{Fe}^{3+}(aq)$ ions: chlorine, bromine, iodine?

- (a) I₂ (b) Cl₂ (c) Cl₂ and I₂ (d) Cl₂ and Br₂ (e) all three elements

silver. In a mixture of nickel metal and silver cations, therefore, we expect a displacement reaction in which the silver ions are displaced in the solution by nickel ions:



In this reaction, Ni is oxidized and Ag^+ is reduced. Therefore, the standard emf for the reaction is

$$\begin{aligned} E^\circ &= E_{\text{red}}^\circ(\text{Ag}^+/\text{Ag}) - E_{\text{red}}^\circ(\text{Ni}^{2+}/\text{Ni}) \\ &= (+0.80 \text{ V}) - (-0.28 \text{ V}) = +1.08 \text{ V} \end{aligned}$$

The positive value of E° indicates that the displacement of silver by nickel resulting from oxidation of Ni metal and reduction of Ag^+ is a spontaneous process. Remember that although we multiply the silver half-reaction by 2, the reduction potential is not multiplied.

Emf, Free Energy, and the Equilibrium Constant

The change in the Gibbs free energy, ΔG , is a measure of the spontaneity of a process that occurs at constant temperature and pressure. The emf, E , of a redox reaction also indicates whether the reaction is spontaneous. The relationship between emf and the free-energy change is

$$\Delta G = -nFE \quad [20.11]$$

In this equation, n is a positive number without units that represents the number of moles of electrons transferred according to the balanced equation for the reaction, and F is the **Faraday constant**, named after Michael Faraday (Figure 20.12):

$$F = 96,485 \text{ C/mol} = 96,485 \text{ J/V mol}$$

The Faraday constant is the quantity of electrical charge on 1 mol of electrons.

The units of ΔG calculated with Equation 20.11 are J/mol. As in Equation 19.19, we use “per mole” to mean per mole of reaction as indicated by the coefficients in the balanced equation.

Because both n and F are positive numbers, a positive value of E in Equation 20.11 leads to a negative value of ΔG . Remember: *A positive value of E and a negative value of ΔG both indicate a spontaneous reaction.* When the reactants and products are all in their standard states, Equation 20.11 can be modified to relate ΔG° and E° .

$$\Delta G^\circ = -nFE^\circ \quad [20.12]$$

Because ΔG° is related to the equilibrium constant, K , for a reaction by the expression $\Delta G^\circ = -RT \ln K$ (Equation 19.20), we can relate E° to K by solving Equation 20.12 for E° and then substituting the Equation 19.20 expression for ΔG° .

$$E^\circ = \frac{\Delta G^\circ}{-nF} = \frac{-RT \ln K}{-nF} = \frac{RT}{nF} \ln K \quad [20.13]$$

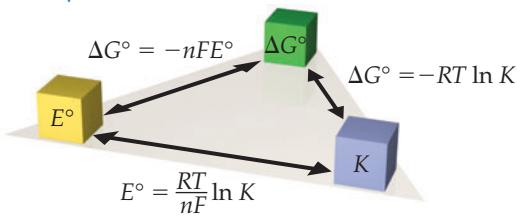
Figure 20.13 summarizes the relationships among E° , ΔG° , and K .



▲ Figure 20.12 Michael Faraday. Faraday (1791–1867) was born in England, a child of a poor blacksmith. At the age of 14 he was apprenticed to a bookbinder who gave him time to read and to attend lectures. In 1812 he became an assistant in Humphry Davy's laboratory at the Royal Institution. He succeeded Davy as the most famous and influential scientist in England, making an amazing number of important discoveries, including his formulation of the quantitative relationships between electrical current and the extent of chemical reaction in electrochemical cells.

Go Figure

What does the variable n represent in the ΔG° and E° equations?



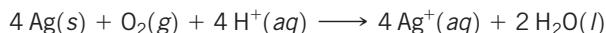
▲ Figure 20.13 Relationships of E° , ΔG° , and K . Any one of these important parameters can be used to calculate the other two. The signs of E° and ΔG° determine the direction in which the reaction proceeds under standard conditions. The magnitude of K determines the relative amounts of reactants and products in an equilibrium mixture.



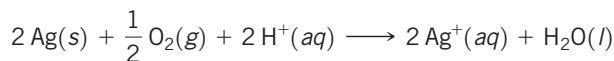
Sample Exercise 20.10

Using Standard Reduction Potentials to Calculate ΔG° and K

- (a) Use the standard reduction potentials in Table 20.1 to calculate the standard free energy change, ΔG° , and the equilibrium constant, K , at 298 K for the reaction



- (b) Suppose the reaction in part (a) is written



What are the values of E° , ΔG° , and K when the reaction is written this way?

SOLUTION

Analyze We are asked to determine ΔG° and K for a redox reaction, using standard reduction potentials.

Plan We use the data in Table 20.1 and Equation 20.10 to determine E° for the reaction and then use E° in Equation 20.12 to calculate ΔG° . We can then use either Equation 19.20 or Equation 20.13 to calculate K .

Solve

- (a) We first calculate E° by breaking the equation into two half-reactions and obtaining E_{red}° values from Table 20.1 (or Appendix E):



Even though the second half-reaction has 4 Ag, we use the E_{red}° value directly from Table 20.1 because emf is an intensive property.

Using Equation 20.10, we have:

$$E^\circ = (1.23 \text{ V}) - (0.80 \text{ V}) = 0.43 \text{ V}$$

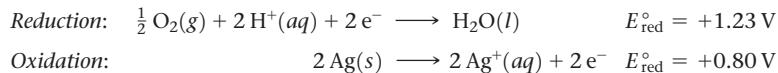
The half-reactions show the transfer of four electrons. Thus, for this reaction $n = 4$. We now use Equation 20.12 to calculate ΔG° :

$$\begin{aligned} \Delta G^\circ &= -nFE^\circ \\ &= -(4)(96,485 \text{ J/V mol})(+0.43 \text{ V}) \\ &= -1.7 \times 10^5 \text{ J/mol} = -170 \text{ kJ/mol} \end{aligned}$$

Now we need to calculate the equilibrium constant, K , using $\Delta G^\circ = RT \ln K$. Because ΔG° is a large negative number, which means the reaction is thermodynamically very favorable, we expect K to be large.

$$\begin{aligned} \Delta G^\circ &= -RT \ln K \\ -1.7 \times 10^5 \text{ J/mol} &= -(8.314 \text{ J/K mol})(298 \text{ K}) \ln K \\ \ln K &= \frac{-1.7 \times 10^5 \text{ J/mol}}{-(8.314 \text{ J/K mol})(298 \text{ K})} \\ \ln K &= 69 \\ K &= 9 \times 10^{29} \end{aligned}$$

- (b) The overall equation is the same as that in part (a), multiplied by $\frac{1}{2}$. The half-reactions are:



The values of E_{red}° are the same as they were in part (a); they are not changed by multiplying the half-reactions by $\frac{1}{2}$. Thus, E° has the same value as in part (a): $E^\circ = +0.43 \text{ V}$. Notice, though, that the value of n has changed to $n = 2$, which is one-half the value in part (a). Thus, ΔG° is half as large as in part (a):

The value of ΔG° is half that in part (a) because the coefficients in the chemical equation are half those in (a).

$$\Delta G^\circ = -(2)(96,485 \text{ J/V mol})(+0.43 \text{ V}) = -83 \text{ kJ/mol}$$

Now we can calculate K as before:

$$-8.3 \times 10^4 \text{ J/mol} = -(8.314 \text{ J/K mol})(298 \text{ K}) \ln K$$

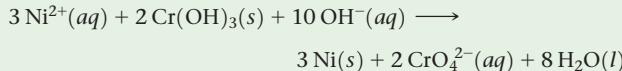
$$K = 4 \times 10^{14}$$

Continued

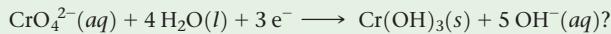
Comment E° is an *intensive* quantity, so multiplying a chemical equation by a certain factor will not affect the value of E° . Multiplying an equation will change the value of n , however, and hence the value of ΔG° . The change in free energy, in units of J/mol of reaction as written, is an *extensive* quantity. The equilibrium constant is also an extensive quantity.

► Practice Exercise

For the reaction



$\Delta G^\circ = +87 \text{ kJ/mol}$. Given the standard reduction potential of $\text{Ni}^{2+}(aq)$ in Table 20.1, what value do you calculate for the standard reduction potential of the half-reaction



- (a) -0.43 V (b) -0.28 V (c) 0.02 V (d) -0.13 V (e) -0.15 V

A CLOSER LOOK Electrical Work

For any spontaneous process, ΔG is a measure of the maximum useful work, w_{\max} , that can be extracted from the process: $\Delta G = w_{\max}$. Because $\Delta G = -nFE$, the maximum useful electrical work obtainable from a voltaic cell is

$$w_{\max} = -nFE_{\text{cell}} \quad [20.14]$$

Because cell emf, E_{cell} , is always positive for a voltaic cell, w_{\max} is negative, indicating that work is done *by* a system *on* its surroundings, as we expect for a voltaic cell.

As Equation 20.14 shows, the more charge a voltaic cell moves through a circuit (that is, the larger nF is) and the larger the emf pushing the electrons through the circuit (that is, the larger E_{cell} is), the more work the cell can accomplish. In Sample Exercise 20.10, we calculated $\Delta G^\circ = -170 \text{ kJ/mol}$ for the reaction $4 \text{Ag}(s) + \text{O}_2(g) + 4 \text{H}^+(aq) \longrightarrow 4 \text{Ag}^+(aq) + 2 \text{H}_2\text{O}(l)$. Thus, a voltaic cell utilizing this reaction could perform a maximum of 170 kJ of work in consuming 4 mol Ag, 1 mol O₂, and 4 mol H⁺.

If a reaction is not spontaneous, ΔG is positive and E is negative. To force a nonspontaneous reaction to occur in an electrochemical cell, we need to apply an external potential, E_{ext} , that exceeds $|E_{\text{cell}}|$. For example, if a nonspontaneous process has $E = -0.9 \text{ V}$, then the external potential E_{ext} must be greater than +0.9 V in order for the process to occur. We will examine such nonspontaneous processes in Section 20.9.

Electrical work can be expressed in energy units of watts times time. The *watt* (W) is a unit of electrical power (that is, rate of energy expenditure):

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

Thus, a watt-second is a joule. The unit employed by electric utilities is the kilowatt-hour (kWh), which equals $3.6 \times 10^6 \text{ J}$:

$$1 \text{ kWh} = (1000 \text{ W})(1 \text{ h}) \left(\frac{3600 \text{ s}}{1 \text{ h}} \right) \left(\frac{1 \text{ J/s}}{1 \text{ W}} \right) = 3.6 \times 10^6 \text{ J}$$

Related Exercises: 20.27, 20.87

Self-Assessment Exercise

20.22 For a cell in which $E^\circ > 0 \text{ V}$, which statement is true?

- (a) $\Delta G^\circ > 0$ and $K > 1$
 (b) $\Delta G^\circ < 0$ and $K > 1$

(c) $\Delta G^\circ > 0$ and $0 < K < 1$

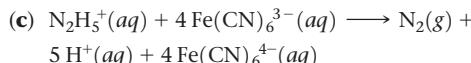
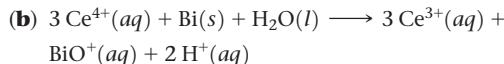
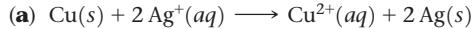
(d) $\Delta G^\circ < 0$ and $0 < K < 1$

Exercises

20.23 For each of the following reactions, write a balanced equation, calculate the standard emf, calculate ΔG° at 298 K, and calculate the equilibrium constant K at 298 K.
 (a) Aqueous iodide ion is oxidized to I₂(s) by Hg₂²⁺(aq).
 (b) In acidic solution, copper(I) ion is oxidized to copper(II) ion by nitrate ion. (c) In basic solution, Cr(OH)₃(s) is oxidized to CrO₄²⁻(aq) by ClO⁻(aq).

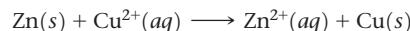
20.24 If the equilibrium constant for a two-electron redox reaction at 298 K is 2.2×10^5 , calculate the corresponding ΔG° and E° .

20.25 Using the standard reduction potentials listed in Appendix E, calculate the equilibrium constant for each of the following reactions at 298 K:



20.26 At 298 K a cell reaction has a standard cell potential of +0.63 V. The equilibrium constant for the reaction is 3.8×10^{10} . What is the value of n for the reaction?

20.27 Consider the voltaic cell illustrated in Figure 20.5, which is based on the cell reaction



Under standard conditions, what is the maximum electrical work, in joules, that the cell can accomplish if 50.0 g of copper is formed?

20.22 (b)



20.6 | Cell Potentials under Nonstandard Conditions



Many metabolic processes involve redox reactions, which not only store energy but allow its release in a controlled and efficient manner. One such example is photosynthesis, in which absorption of a photon by chlorophyll triggers release of an electron in photosystem I. This electron cascades down an electron transport chain, ultimately reducing nicotinamide adenine dinucleotide phosphate (NADP) to NADPH, used by all cells as a reducing agent. The electron lost by photosystem I is replaced by photosystem II on oxidation of water to oxygen and hydrogen ions. Of course, the process is much more complex than suggested here, but is based on redox reactions and concentration gradients, which we can understand.

By the end of this section, you should be able to

- Calculate emf under nonstandard conditions.

We have seen how to calculate the emf of a cell when the reactants and products are under standard conditions. As a voltaic cell is discharged, however, reactants are consumed and products are generated, so concentrations change. The emf progressively drops until $E = 0$, at which point we say the cell is “dead.” In this section, we examine how the emf generated under nonstandard conditions can be calculated by using an equation first derived by Walther Nernst (1864–1941), a German chemist who established many of the theoretical foundations of electrochemistry.

The Nernst Equation

The effect of concentration on cell emf can be obtained from the effect of concentration on free-energy change. Recall that the free-energy change for any chemical reaction, ΔG , is related to the standard free-energy change for the reaction, ΔG° :

$$\Delta G = \Delta G^\circ + RT \ln Q \quad [20.15]$$

The quantity Q is the reaction quotient, which has the form of the equilibrium expression except that the concentrations are those that exist in the reaction mixture at a given moment.

Substituting $\Delta G = -nFE$ (Equation 20.11) into Equation 20.15 gives

$$-nFE = -nFE^\circ + RT \ln Q$$

Solving this equation for E gives the **Nernst equation**:

$$E = E^\circ - \frac{RT}{nF} \ln Q \quad [20.16]$$

This equation is customarily expressed in terms of the base-10 logarithm:

$$E = E^\circ - \frac{2.303 RT}{nF} \log Q \quad [20.17]$$

At $T = 298$ K, the quantity $2.303 RT/F$ equals 0.0592, with units of volts, and so the Nernst equation simplifies to

$$E = E^\circ - \frac{0.0592 V}{n} \log Q \quad (T = 298 \text{ K}) \quad [20.18]$$

We can use this equation to find the emf E produced by a cell under nonstandard conditions or to determine the concentration of a reactant or product by measuring E for the cell. For example, consider the following reaction:



In this case $n = 2$ (two electrons are transferred from Zn to Cu^{2+}), and the standard emf is +1.10 V. Thus, at 298 K the Nernst equation gives

$$E = 1.10 \text{ V} - \frac{0.0592 \text{ V}}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \quad [20.19]$$

Recall that pure solids are excluded from the expression for Q . According to Equation 20.19, the emf increases as $[\text{Cu}^{2+}]$ increases and as $[\text{Zn}^{2+}]$ decreases. For example, when $[\text{Cu}^{2+}]$ is 5.0 M and $[\text{Zn}^{2+}]$ is 0.050 M, we have

$$\begin{aligned} E &= 1.10 \text{ V} - \frac{0.0592 \text{ V}}{2} \log \left(\frac{0.050}{5.0} \right) \\ &= 1.10 \text{ V} - \frac{0.0592 \text{ V}}{2} (-2.00) = 1.16 \text{ V} \end{aligned}$$

Thus, increasing the concentration of reactant Cu^{2+} and decreasing the concentration of product Zn^{2+} relative to standard conditions increases the emf of the cell relative to standard conditions ($E^\circ = +1.10$ V).

The Nernst equation helps us understand why the emf of a voltaic cell drops as the cell discharges. As reactants are converted to products, the value of Q increases, so the value of E decreases, eventually reaching $E = 0$. Because $\Delta G = -nFE$ (Equation 20.11), it follows that $\Delta G = 0$ when $E = 0$. Recall that a system is at equilibrium when $\Delta G = 0$. Thus, when $E = 0$, the cell reaction has reached equilibrium, and no net reaction occurs.

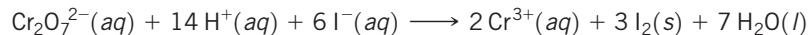
In general, increasing the concentration of reactants or decreasing the concentration of products increases the driving force for the reaction, resulting in a higher emf. Conversely, decreasing the concentration of reactants or increasing the concentration of products causes the emf to decrease from its value under standard conditions.



Sample Exercise 20.11

Cell Potential under Nonstandard Conditions

Calculate the emf at 298 K generated by a voltaic cell in which the reaction is



when

$$[\text{Cr}_2\text{O}_7^{2-}] = 2.0 \text{ M}, [\text{H}^+] = 1.0 \text{ M}, [\text{I}^-] = 1.0 \text{ M}, \text{ and } [\text{Cr}^{3+}] = 1.0 \times 10^{-5} \text{ M}$$

SOLUTION

Analyze We are given a chemical equation for a voltaic cell and the concentrations of reactants and products under which it operates. We are asked to calculate the emf of the cell under these nonstandard conditions.

Plan To calculate the emf of a cell under nonstandard conditions, we use the Nernst equation in the form of Equation 20.18.

Solve

We calculate E° for the cell from standard reduction potentials (Table 20.1 or Appendix E). The standard emf for this reaction was calculated in Sample Exercise 20.6: $E^\circ = 0.79$ V. As that exercise shows, six electrons are transferred from reducing agent to oxidizing agent, so $n = 6$. The reaction quotient, Q , is:

$$Q = \frac{[\text{Cr}^{3+}]^2}{[\text{Cr}_2\text{O}_7^{2-}][\text{H}^+]^{14}[\text{I}^-]^6}$$

$$= \frac{(1.0 \times 10^{-5})^2}{(2.0)(1.0)^{14}(1.0)^6} = 5.0 \times 10^{-11}$$

Using Equation 20.18, we have:

$$E = 0.79 \text{ V} - \left(\frac{0.0592 \text{ V}}{6}\right) \log(5.0 \times 10^{-11})$$

$$= 0.79 \text{ V} - \left(\frac{0.0592 \text{ V}}{6}\right)(-10.30)$$

$$= 0.79 \text{ V} + 0.10 \text{ V} = 0.89 \text{ V}$$

Check This result is qualitatively what we expect: Because the concentration of $\text{Cr}_2\text{O}_7^{2-}$ (a reactant) is greater than 1 M and the concentration of Cr^{3+} (a product) is less than 1 M, the emf is greater than E° . Because Q is about 10^{-10} , $\log Q$ is about -10 . Thus, the correction to E° is about $0.06 \times 10/6$, which is 0.1, in agreement with the more detailed calculation.

► Practice Exercise

Consider a voltaic cell whose overall reaction is $\text{Pb}^{2+}(aq) + \text{Zn}(s) \longrightarrow \text{Pb}(s) + \text{Zn}^{2+}(aq)$. What is the emf generated by this voltaic cell when the ion concentrations are $[\text{Pb}^{2+}] = 1.5 \times 10^{-3}$ M and $[\text{Zn}^{2+}] = 0.55$ M?
(a) 0.71 V **(b)** 0.56 V **(c)** 0.49 V **(d)** 0.79 V **(e)** 0.64 V

Sample Exercise 20.12

Calculating Concentrations in a Voltaic Cell

If the potential of a Zn–H₂ cell (like that in Figure 20.9) is 0.45 V at 25 °C when $[\text{Zn}^{2+}] = 1.0$ M and $P_{\text{H}_2} = 100.0$ kPa, what is the pH of the cathode solution?

SOLUTION

Analyze We are given a description of a voltaic cell, its emf, the concentration of Zn^{2+} , and the partial pressure of H_2 (both products in the cell reaction). We are asked to calculate the pH of the cathode solution, which we can calculate from the concentration of H^+ , a reactant.

Plan We write the equation for the cell reaction and use standard reduction potentials to calculate E° for the reaction. After determining the value of n from our reaction equation, we solve the Nernst equation, Equation 20.18, for Q . We use the equation for the cell reaction to write an expression for Q that contains $[\text{H}^+]$ to determine $[\text{H}^+]$. Finally, we use $[\text{H}^+]$ to calculate pH.

Solve

The cell reaction is:



The standard emf is:

$$E^\circ = E_{\text{red}}^\circ(\text{reduction}) - E_{\text{red}}^\circ(\text{oxidation})$$

$$= 0 \text{ V} - (-0.76 \text{ V}) = +0.76 \text{ V}$$

Because each Zn atom loses two electrons,

$$n = 2$$

Using Equation 20.18, we can solve for Q :

$$0.45 \text{ V} = 0.76 \text{ V} - \frac{0.0592 \text{ V}}{2} \log Q$$

$$Q = 10^{10.5} = 3 \times 10^{10}$$

Q has the form of the equilibrium constant for the reaction:

$$Q = \frac{[\text{Zn}^{2+}]P_{\text{H}_2}}{[\text{H}^+]^2} = \frac{(1.0)100.0}{[\text{H}^+]^2} = 3 \times 10^{10}$$

Solving for $[\text{H}^+]$, we have:

$$[\text{H}^+]^2 = \frac{101.3}{3 \times 10^{10}} = 3.4 \times 10^{-9}$$

$$[\text{H}^+] = \sqrt{3.4 \times 10^{-9}} = 6 \times 10^{-5} \text{ M}$$

Finally, we use $[\text{H}^+]$ to calculate the pH of the cathode solution.

$$\text{pH} = \log [\text{H}^+] = -\log(6 \times 10^{-5}) = 4.2$$

Comment A voltaic cell whose cell reaction involves H^+ can be used to measure $[H^+]$ or pH. A pH meter is a specially designed voltaic cell with a voltmeter calibrated to read pH directly.

► Practice Exercise

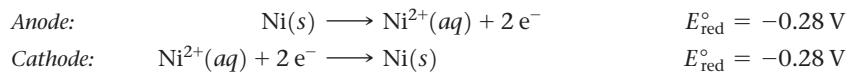
Consider a voltaic cell where the anode half-reaction is $Zn(s) \longrightarrow Zn^{2+}(aq) + 2 e^-$ and the cathode half-reaction

is $Sn^{2+}(aq) + 2 e^- \longrightarrow Sn(s)$. What is the concentration of Sn^{2+} if Zn^{2+} is $2.5 \times 10^{-3} M$ and the cell emf is $0.660 V$? Use the reduction potentials in Appendix E that are reported to three significant figures. (a) $3.3 \times 10^{-2} M$ (b) $1.9 \times 10^{-4} M$ (c) $9.0 \times 10^{-3} M$ (d) $6.9 \times 10^{-4} M$ (e) $7.6 \times 10^{-3} M$

Concentration Cells

In the voltaic cells we have looked at thus far, the reactive species at the anode has been different from the reactive species at the cathode. Cell emf depends on concentration, however, so a voltaic cell can be constructed using the *same* species in both half-cells as long as the concentrations are different. A cell based solely on the emf generated because of a difference in a concentration is called a **concentration cell**.

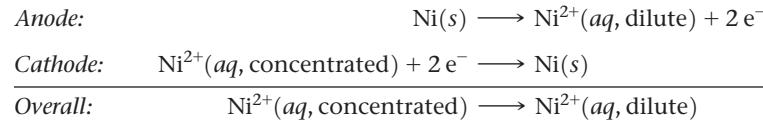
An example of a concentration cell is diagrammed in **Figure 20.14(a)**. One half-cell consists of a strip of nickel metal immersed in a $1.00 \times 10^{-3} M$ solution of $Ni^{2+}(aq)$. The other half-cell also has an $Ni(s)$ electrode, but it is immersed in a $1.00 M$ solution of $Ni^{2+}(aq)$. The two half-cells are connected by a salt bridge and by an external wire running through a voltmeter. The half-cell reactions are the reverse of each other:



Although the *standard* emf for this cell is zero,

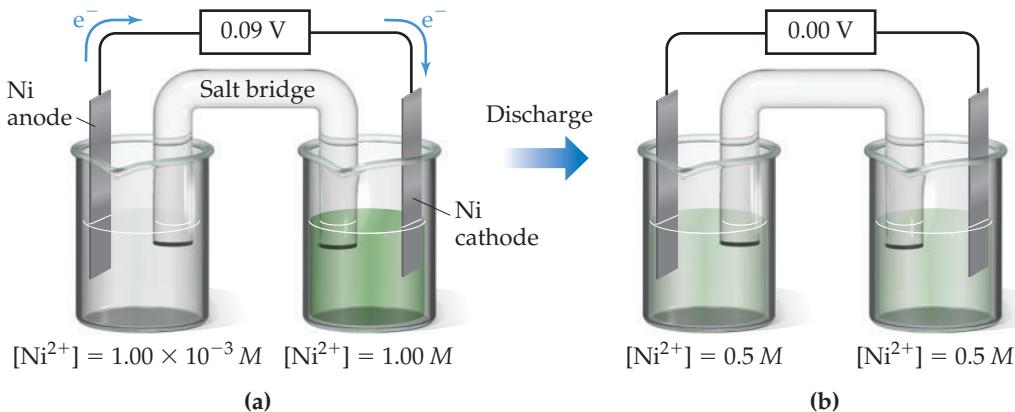
$$E_{\text{cell}}^\circ = E_{\text{red}}^\circ(\text{cathode}) - E_{\text{red}}^\circ(\text{anode}) = (-0.28 V) - (-0.28 V) = 0 V$$

the cell operates under *nonstandard* conditions because the concentration of $Ni^{2+}(aq)$ is not $1 M$ in both half-cells. In fact, the cell operates until $[Ni^{2+}]_{\text{anode}} = [Ni^{2+}]_{\text{cathode}}$. Oxidation of $Ni(s)$ occurs in the half-cell containing the more dilute solution, which means this is the anode of the cell. Reduction of $Ni^{2+}(aq)$ occurs in the half-cell containing the more concentrated solution, making it the cathode. The *overall* cell reaction is therefore



Go Figure

Which electrode, if any, gains mass as the reaction proceeds?



▲ **Figure 20.14** Concentration cell based on $Ni^{2+}-Ni$ cell reaction. (a) Concentrations of $Ni^{2+}(aq)$ in the two half-cells are unequal, and the cell generates an electrical current and a voltage. (b) The cell operates until $[Ni^{2+}]$ is the same in the two half-cells, at which point the cell has reached equilibrium and the emf goes to zero.



◀ **Figure 20.15 An electric eel.** Differences in ion concentrations, mainly Na^+ and K^+ , in special cells called electrocytes produce an emf on the order of 0.1 V. By connecting thousands of these cells in series, these South American fish are able to generate short electric pulses as high as 500 V.

We can calculate the emf of a concentration cell by using the Nernst equation. For this particular cell, we see that $n = 2$. The expression for the reaction quotient for the overall reaction is $Q = [\text{Ni}^{2+}]_{\text{dilute}} / [\text{Ni}^{2+}]_{\text{concentrated}}$. Thus, the emf at 298 K is

$$\begin{aligned} E &= E^\circ - \frac{0.0592 \text{ V}}{n} \log Q \\ &= 0 - \frac{0.0592 \text{ V}}{2} \log \frac{[\text{Ni}^{2+}]_{\text{dilute}}}{[\text{Ni}^{2+}]_{\text{concentrated}}} = -\frac{0.0592 \text{ V}}{2} \log \frac{1.00 \times 10^{-3} \text{ M}}{1.00 \text{ M}} \\ &= +0.089 \text{ V} \end{aligned}$$

This concentration cell generates an emf of nearly 0.09 V, even though $E^\circ = 0$. The difference in concentration provides the driving force for the cell. When the concentrations in the two half-cells become the same, $Q = 1$ and $E = 0$.

The idea of generating a potential by a concentration difference is the basis for the operation of pH meters. It is also a critical aspect in biology. For example, nerve cells in the brain generate a potential across the cell membrane by having different concentrations of ions on the two sides of the membrane. Electric eels use cells called electrocytes that are based on a similar principle to generate short, but intense, pulses of electricity to stun prey and dissuade predators (Figure 20.15). The regulation of the heartbeat in mammals, as discussed in the following Chemistry and Life box, is another example of the importance of electrochemistry to living organisms.

CHEMISTRY AND LIFE Heartbeats and Electrocardiography

The human heart is a marvel of efficiency and dependability. In a typical day, an adult's heart pumps more than 7000 L of blood through the circulatory system, usually with no maintenance required beyond a sensible diet and lifestyle. We generally think of the heart as a mechanical device, a muscle that circulates blood via regularly spaced muscular contractions. However, more than two centuries ago, two pioneers in electricity, Luigi Galvani (1729–1787) and Alessandro Volta (1745–1827), discovered that the contractions of the heart are controlled by electrical phenomena, as are nerve impulses throughout the body. The pulses of electricity that cause the heart to beat result from a remarkable combination of electrochemistry and the properties of semipermeable membranes.

Cell walls are membranes with variable permeability with respect to a number of physiologically important ions (especially

Na^+ , K^+ , and Ca^{2+}). The concentrations of these ions are different for the fluids inside the cells (the *intracellular fluid*, or ICF) and outside the cells (the *extracellular fluid*, or ECF). In cardiac muscle cells, for example, the concentrations of K^+ in the ICF and ECF are typically about 135 millimolar (mM) and 4 mM, respectively. For Na^+ , however, the concentration difference between the ICF and ECF is opposite to that for K^+ ; typically, $[\text{Na}^+]_{\text{ICF}} = 10 \text{ mM}$ and $[\text{Na}^+]_{\text{ECF}} = 145 \text{ mM}$.

The cell membrane is initially permeable to K^+ ions but is much less so to Na^+ and Ca^{2+} . The difference in concentration of K^+ ions between the ICF and ECF generates a concentration cell. Even though the same ions are present on both sides of the membrane, there is a potential difference between the two fluids that we can calculate using the Nernst equation with $E^\circ = 0$. At physiological temperature (37°C) the potential in millivolts for moving K^+ from the ECF to the ICF is

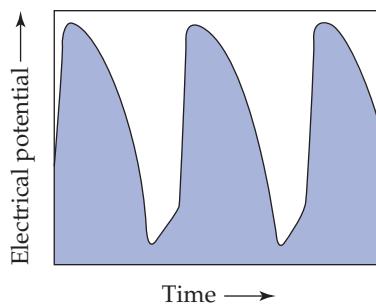
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$$E = E^\circ - \frac{2.30RT}{nF} \log \frac{[K^+]_{\text{ICF}}}{[K^+]_{\text{ECF}}}$$

$$= 0 - (61.5 \text{ mV}) \log \left(\frac{135 \text{ mM}}{4 \text{ mM}} \right) = -94 \text{ mV}$$

In essence, the interior of the cell and the ECF together serve as a voltaic cell. The negative sign for the potential indicates that work is required to move K⁺ into the ICF.

Changes in the relative concentrations of the ions in the ECF and ICF lead to changes in the emf of the voltaic cell. The cells of the heart that govern the rate of heart contraction are called the *pacemaker cells*. The membranes of the cells regulate the concentrations of ions in the ICF, allowing them to change in a systematic way. The concentration changes cause the emf to change in a cyclic fashion, as shown in Figure 20.16. The emf cycle determines the

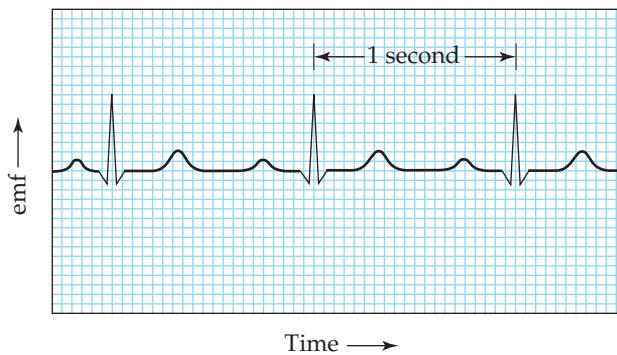


▲ Figure 20.16 Changes in electrical potential in the human heart.

Variation of the electrical potential caused by changes of ion concentrations in the pacemaker cells of the heart.

rate at which the heart beats. If the pacemaker cells malfunction because of disease or injury, an artificial pacemaker can be surgically implanted. The artificial pacemaker contains a small battery that generates the electrical pulses needed to trigger the contractions of the heart.

During the late 1800s, scientists discovered that the electrical impulses that cause the contraction of the heart muscle are strong enough to be detected at the surface of the body. This observation formed the basis for *electrocardiography*, noninvasive monitoring of the heart by using a complex array of electrodes on the skin to measure voltage changes during heartbeats. A typical electrocardiogram is shown in Figure 20.17. It is quite striking that, although the heart's major function is the *mechanical* pumping of blood, it is most easily monitored by using the *electrical* impulses generated by tiny voltaic cells.



▲ Figure 20.17 A typical electrocardiogram. The printout records the electrical events monitored by electrodes attached to the body surface.

Sample Exercise 20.13

Determining pH Using a Concentration Cell

A voltaic cell is constructed with two hydrogen electrodes. Electrode 1 has $P_{\text{H}_2} = 100.0 \text{ kPa}$ and an unknown concentration of H⁺(aq). Electrode 2 is a standard hydrogen electrode ($P_{\text{H}_2} = 100.0 \text{ kPa}$, $[\text{H}^+] = 1.00 \text{ M}$). At 298 K the measured cell potential is 0.211 V, and the electrical current is observed to flow from electrode 1 through the external circuit to electrode 2. What is the pH of the solution at electrode 1?

SOLUTION

Analyze We are given the potential of a concentration cell and the direction in which the current flows. We also have the concentrations or partial pressures of all reactants and products except for [H⁺] in half-cell 1, which is our unknown.

Plan We can use the Nernst equation to determine Q and then use Q to calculate the unknown concentration. Because this is a concentration cell, $E_{\text{cell}}^\circ = 0 \text{ V}$.

Solve

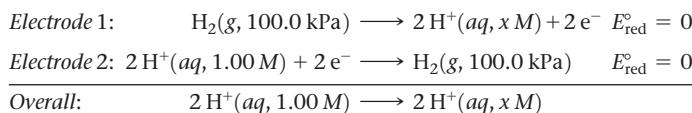
Using the Nernst equation, we have:

$$0.211 \text{ V} = 0 - \frac{0.0592 \text{ V}}{2} \log Q$$

$$\log Q = -(0.211 \text{ V}) \left(\frac{2}{0.0592 \text{ V}} \right) = -7.13$$

$$Q = 10^{-7.13} = 7.4 \times 10^{-8}$$

Because electrons flow from electrode 1 to electrode 2, electrode 1 is the anode of the cell and electrode 2 is the cathode. The electrode reactions are therefore as follows, with the concentration of H⁺(aq) in electrode 1 represented with the unknown x:



Thus,

$$\begin{aligned} Q &= \frac{[\text{H}^+(\text{aq}, x\text{M})]^2}{[\text{H}^+(\text{aq}, 1.00\text{M})]^2} \\ &= \frac{x^2}{(1.00)^2} = x^2 = 7.4 \times 10^{-8} \\ x &= [\text{H}^+] = \sqrt{7.4 \times 10^{-8}} = 2.7 \times 10^{-4} \end{aligned}$$

At electrode 1, therefore, the pH of the solution is:

$$\text{pH} = -\log[\text{H}^+] = -\log(2.7 \times 10^{-4}) = 3.57$$

Comment The concentration of H^+ at electrode 1 is lower than that in electrode 2, which is why electrode 1 is the anode of the cell: The oxidation of H_2 to $\text{H}^+(\text{aq})$ increases $[\text{H}^+]$ at electrode 1.

► Practice Exercise

A concentration cell is constructed with two $\text{Zn}(s)-\text{Zn}^{2+}(\text{aq})$ half-cells. In one half-cell $[\text{Zn}^{2+}] = 1.35\text{ M}$, and in the other $[\text{Zn}^{2+}] = 3.75 \times 10^{-4}\text{ M}$. (a) Which half-cell is the anode? (b) What is the emf of the cell?

Self-Assessment Exercise

- 20.28** A voltaic cell consisting of a Ni/Ni^{2+} half-cell and Sn/Sn^{2+} half-cell is constructed with the following initial concentrations: $[\text{Ni}^{2+}] = 1.0\text{ M}$; $[\text{Sn}^{2+}] = 1.0\text{ M}$. What is the concentration of ions in each half cell when the potential = 0.12 V?

(a) $[\text{Ni}^{2+}] = 1.7\text{ M}$ and $[\text{Sn}^{2+}] = 0.27\text{ M}$

(b) $[\text{Ni}^{2+}] = 1.4\text{ M}$ and $[\text{Sn}^{2+}] = 0.57\text{ M}$

Exercises

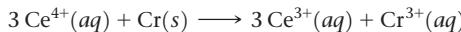
- 20.29** A voltaic cell is constructed with all reactants and products in their standard states. Will the concentration of the reactants increase, decrease, or remain the same as the cell operates?

- 20.30** A voltaic cell utilizes the following reaction:



What is the effect on the cell emf of each of the following changes? (a) Water is added to the anode half-cell, diluting the solution. (b) The size of the aluminum electrode is increased. (c) A solution of AgNO_3 is added to the cathode half-cell, increasing the quantity of Ag^+ but not changing its concentration. (d) HCl is added to the AgNO_3 solution, precipitating some of the Ag^+ as AgCl .

- 20.31** A voltaic cell utilizes the following reaction and operates at 298 K:



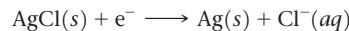
(a) What is the emf of this cell under standard conditions? (b) What is the emf of this cell when $[\text{Ce}^{4+}] = 3.0\text{ M}$, $[\text{Ce}^{3+}] = 0.10\text{ M}$, and $[\text{Cr}^{3+}] = 0.010\text{ M}$? (c) What is the emf of the cell when $[\text{Ce}^{4+}] = 0.010\text{ M}$, $[\text{Ce}^{3+}] = 2.0\text{ M}$, and $[\text{Cr}^{3+}] = 1.5\text{ M}$?

- 20.32** A voltaic cell utilizes the following reaction:



- (a) What is the emf of this cell under standard conditions? (b) What is the emf for this cell when $[\text{Fe}^{3+}] = 3.50\text{ M}$, $P_{\text{H}_2} = 96.3\text{ kPa}$, $[\text{Fe}^{2+}] = 0.0010\text{ M}$, and the pH in both half-cells is 4.00?

- 20.33** A voltaic cell is constructed with two silver-silver chloride electrodes, each of which is based on the following half-reaction:



The two half-cells have $[\text{Cl}^-] = 0.0150\text{ M}$ and $[\text{Cl}^-] = 2.55\text{ M}$, respectively. (a) Which electrode is the cathode of the cell? (b) What is the standard emf of the cell? (c) What is the cell emf for the concentrations given? (d) For each electrode, predict whether $[\text{Cl}^-]$ will increase, decrease, or stay the same as the cell operates.

- 20.34** A voltaic cell is constructed that is based on the following reaction:



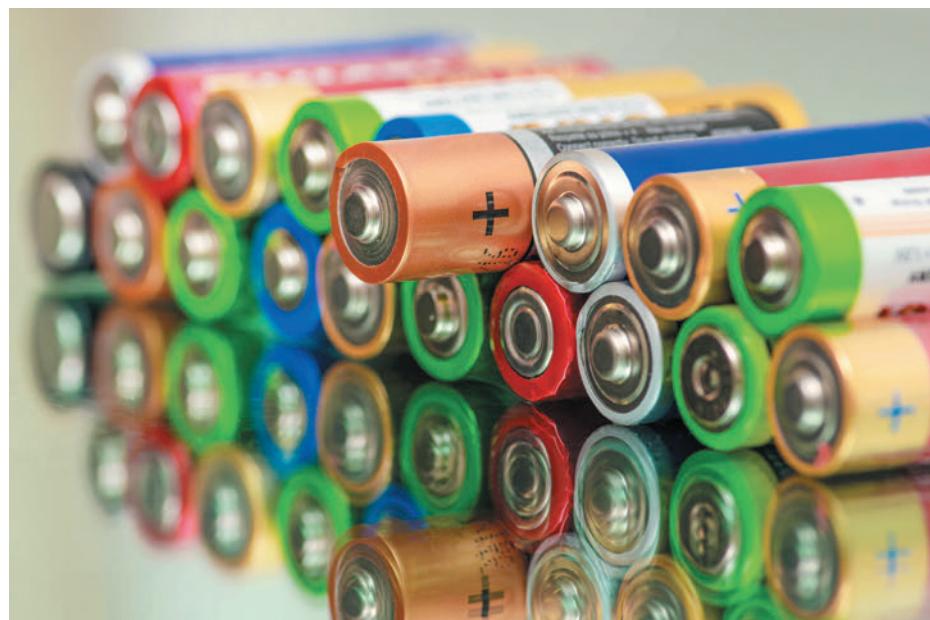
(a) If the concentration of Sn^{2+} in the cathode half-cell is 1.00 M and the cell generates an emf of +0.22 V, what is the concentration of Pb^{2+} in the anode half-cell? (b) If the anode half-cell contains $[\text{SO}_4^{2-}] = 1.00\text{ M}$ in equilibrium with $\text{PbSO}_4(s)$, what is the K_{sp} of PbSO_4 ?

20.28 (a)

Answers to Self-Assessment Exercises



20.7 | Batteries and Fuel Cells



Batteries are the most familiar devices for converting between electrical and chemical energies. Objects like laptop computers, cell phones, pacemakers, and countless other devices rely on batteries to provide the electricity needed for operation.

A considerable amount of effort is currently focused on research and development of new batteries, particularly for powering electric vehicles, for storage of solar energy and power tools. New batteries are needed that are lighter, can charge faster, deliver more power, and have longer lifetimes. At the heart of such developments are the oxidation-reduction reactions that power batteries.

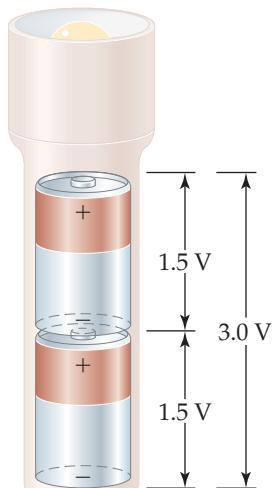
By the end of this section, you should be able to

- Identify the components of common batteries

A battery is a portable, self-contained electrochemical power source that consists of one or more voltaic cells. For example, the 1.5 V batteries used to power torches and many consumer electronic devices are single voltaic cells. Greater voltages can be achieved by using multiple cells, as in 12 V vehicle batteries. When cells are connected in series (which means the cathode of one attached to the anode of another), the battery produces a voltage that is the sum of the voltages of the individual cells. (**Figure 20.18**). Battery electrodes are marked following the convention of Figure 20.6—plus for cathode and minus for anode.

Although any spontaneous redox reaction can serve as the basis for a voltaic cell, making a commercial battery that has specific performance characteristics requires considerable ingenuity. The substances oxidized at the anode and reduced by the cathode determine the voltage, and the usable life of the battery depends on the quantities of these substances packaged in the battery. Usually, a barrier analogous to the porous barrier of Figure 20.6 separates the anode and cathode half-cells.

Different applications require batteries with different properties. The battery required to start a car, for example, must be capable of delivering a large electrical current for a short time period, whereas the battery that powers a heart pacemaker must be very small and capable of delivering a small but steady current over an extended time period. Some batteries are **primary cells**, meaning they cannot be recharged and must be either discarded or recycled after the voltage drops to zero. A **secondary cell** can be recharged from an external power source after its voltage has dropped.



▲ **Figure 20.18** Combining batteries. When batteries are connected in series, as in most flashlights, the total voltage is the sum of the individual voltages.

As we consider some common batteries, notice how the principles we have discussed so far help us understand these important sources of portable electrical energy.

Lead-Acid Battery

A 12 V lead-acid automotive battery consists of six voltaic cells in series, each producing 2 V. The cathode of each cell is lead dioxide (PbO_2) packed on a lead grid (Figure 20.19). The anode of each cell is lead. Both electrodes are immersed in sulfuric acid.

The reactions that occur during discharge are

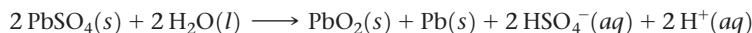


The standard cell potential can be obtained from the standard reduction potentials in Appendix E:

$$E_{\text{cell}}^{\circ} = E_{\text{red}}^{\circ}(\text{cathode}) - E_{\text{red}}^{\circ}(\text{anode}) = (+1.69 \text{ V}) - (-0.36 \text{ V}) = +2.05 \text{ V}$$

The reactants Pb and PbO_2 are the electrodes. Because these reactants are solids, there is no need to separate the cell into half-cells; the Pb and PbO_2 cannot come into contact with each other unless one electrode touches another. To keep the electrodes from touching, wood or glass-fiber spacers are placed between them (Figure 20.19). Using a reaction whose reactants and products are solids has another benefit. Because solids are excluded from the reaction quotient Q , the relative amounts of $\text{Pb}(s)$, $\text{PbO}_2(s)$, and $\text{PbSO}_4(s)$ have no effect on the voltage of the lead storage battery, helping the battery maintain a relatively constant voltage during discharge. The voltage does vary somewhat with use because the concentration of H_2SO_4 varies with the extent of discharge. As Equation 20.20 indicates, H_2SO_4 is consumed during the discharge.

A major advantage of the lead-acid battery is that it can be recharged. During recharging, an external source of energy is used to reverse the direction of the cell reaction, regenerating $\text{Pb}(s)$ and $\text{PbO}_2(s)$:

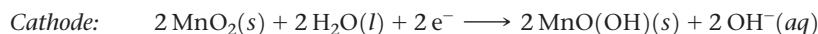


In a vehicle, the alternator provides the energy necessary for recharging the battery. Recharging is possible because PbSO_4 formed during discharge adheres to the electrodes. As the external source forces electrons from one electrode to the other, the PbSO_4 is converted to Pb at one electrode and to PbO_2 at the other.

Alkaline Battery

The most common primary (nonrechargeable) battery is the alkaline battery (Figure 20.20). The anode is powdered zinc metal immobilized in a gel in contact with a concentrated solution of KOH (hence, the name *alkaline* battery). The cathode is a mixture of $\text{MnO}_2(s)$ and graphite, separated from the anode by a porous fabric. The battery is sealed in a steel can to reduce the risk of any of the concentrated KOH escaping.

The cell reactions are complex but can be approximately represented as follows:

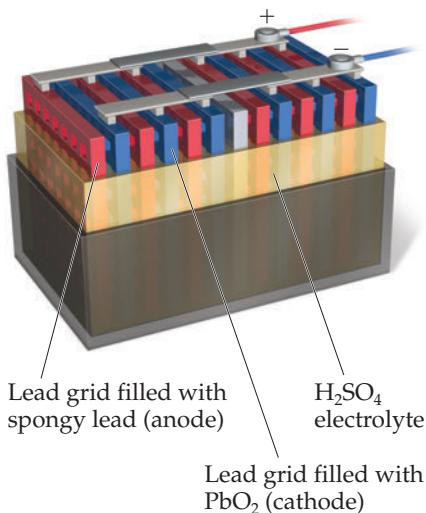


Nickel-Cadmium and Nickel-Metal Hydride Batteries

The tremendous growth in high-power-demand portable electronic devices in the last decade has increased the demand for lightweight, readily rechargeable batteries.

Go Figure

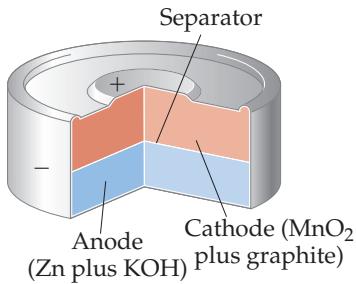
What is the oxidation state of lead in the cathode of this battery?



▲ Figure 20.19 A 12 V automotive lead-acid battery. Each anode/cathode pair in this schematic cutaway produces a voltage of about 2 V. Six pairs of electrodes are connected in series, producing 12 V.

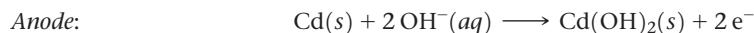
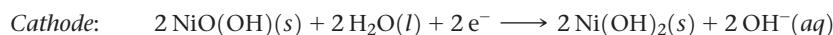
Go Figure

What substance is oxidized as the battery discharges?



▲ Figure 20.20 Cutaway view of a miniature alkaline battery.

One relatively common rechargeable battery is the nickel–cadmium (nicad) battery. During discharge, cadmium metal is oxidized at the anode while nickel oxyhydroxide $[NiO(OH)(s)]$ is reduced at the cathode:



As in the lead–acid battery, the solid reaction products adhere to the electrodes, which permits the electrode reactions to be reversed during charging. A single nicad voltaic cell has a voltage of 1.30 V. Nicad battery packs typically contain three or more cells in series to produce the higher voltages needed by most electronic devices.

Although nickel–cadmium batteries have a number of attractive characteristics, the use of cadmium as the anode introduces significant limitations. Because cadmium is toxic, these batteries must be recycled. The toxicity of cadmium has led to a decline in their popularity from a peak annual production level of approximately 1.5 billion batteries in the early 2000s. Cadmium also has a relatively high density, which increases battery weight, an undesirable characteristic for use in portable devices and electric vehicles. These shortcomings have fueled the development of the nickel–metal hydride (NiMH) battery. The cathode reaction is the same as that for nickel–cadmium batteries, but the anode reaction is very different. The anode consists of a metal alloy, typically with AM_5 stoichiometry, where A is lanthanum (La) or a mixture of metals from the lanthanide series, and M is mostly nickel alloyed with smaller amounts of other transition metals. On charging, water is reduced at the anode to form hydroxide ions and hydrogen atoms that are absorbed into the AM_5 alloy. When the battery is operating (discharging), the hydrogen atoms are oxidized and the resulting H^+ ions react with OH^- ions to form H_2O .

Lithium-Ion Batteries

Currently, most portable electronic devices, including cell phones and laptop computers, are powered by rechargeable lithium-ion (Li-ion) batteries. Because lithium is a very light element, Li-ion batteries achieve a greater *specific energy density*—the amount of energy stored per unit mass—than nickel-based batteries. Because Li^+ has a very large negative standard reduction potential (Table 20.1), Li-ion batteries produce a higher voltage per cell than other batteries. A Li-ion battery based on (LiCoO_2) cathode produces a maximum voltage of 3.7 V per cell, nearly three times higher than the 1.3 V per cell that nickel–cadmium and nickel–metal hydride batteries generate. As a result, a Li-ion battery can deliver more power than other batteries of comparable size, which leads to a higher *volumetric energy density*—the amount of energy stored per unit volume.

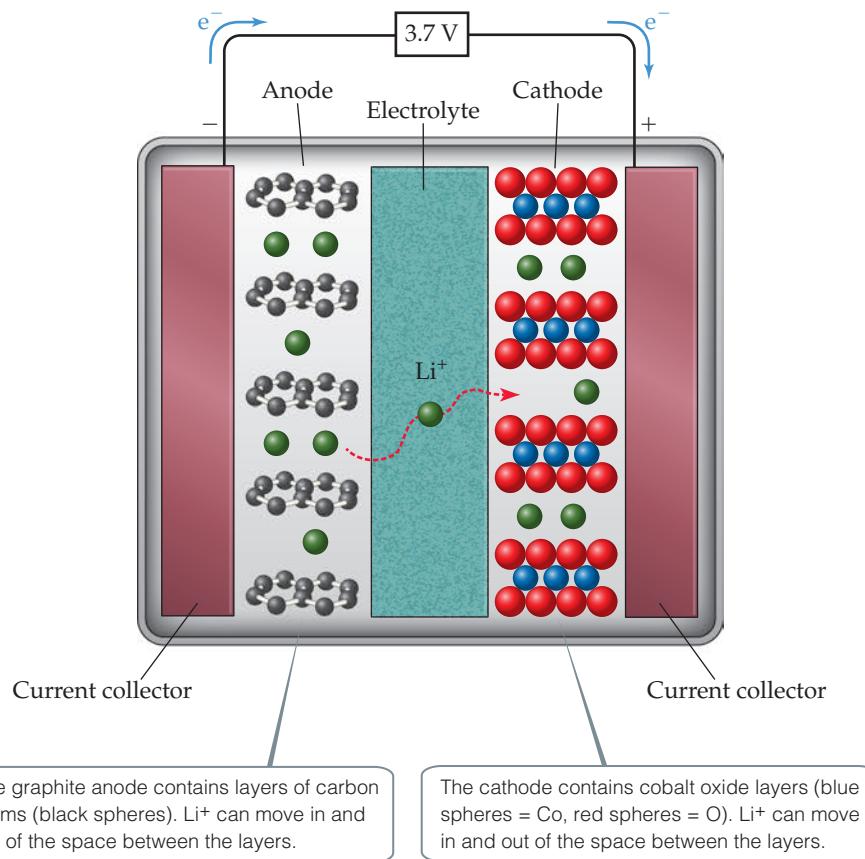
The technology of Li-ion batteries is based on the ability of Li^+ ions to be inserted into and removed from certain layered solids. In most commercial cells, the anode is made of graphite, which contains layers of sp^2 bonded carbon atoms [Figure 12.29(b)]. The cathode is made of a transition metal oxide that also has a layered structure, typically lithium cobalt oxide (LiCoO_2). The two electrodes are separated by an electrolyte, which functions like a salt bridge by allowing Li^+ ions to pass through it. When the cell is being charged, cobalt ions are oxidized and Li^+ ions migrate out of LiCoO_2 and into the graphite. During discharge, when the battery is producing electricity for use, the Li^+ ions spontaneously migrate from the graphite anode through the electrolyte to the cathode, enabling electrons to flow through the external circuit (Figure 20.21).

Hydrogen Fuel Cells

The thermal energy released by burning fuels can be converted to electrical energy. The thermal energy may convert water to steam, for instance, which drives a turbine that in turn drives an electrical generator. Typically, a maximum of only 40% of the energy from combustion is converted to electricity in this manner; the remainder is lost as heat. The direct production of electricity from fuels by a voltaic cell could, in principle, yield

 Go Figure

When a Li-ion battery is fully discharged, the cathode has an empirical formula of LiCoO_2 . What is the oxidation number of cobalt in this state? Does the oxidation number of the cobalt increase or decrease as the battery charges?



▲ Figure 20.21 Schematic of a Li-ion battery. When the battery is discharging (operating), Li^+ ions move out of the anode and migrate through the electrolyte where they enter the spaces between the cobalt oxide layers, reducing the cobalt ions. To recharge the battery, electrical energy is used to drive the Li^+ back to the anode, oxidizing the cobalt ions in the cathode.

CHEMISTRY PUT TO WORK | Batteries for Hybrid and Electric Vehicles

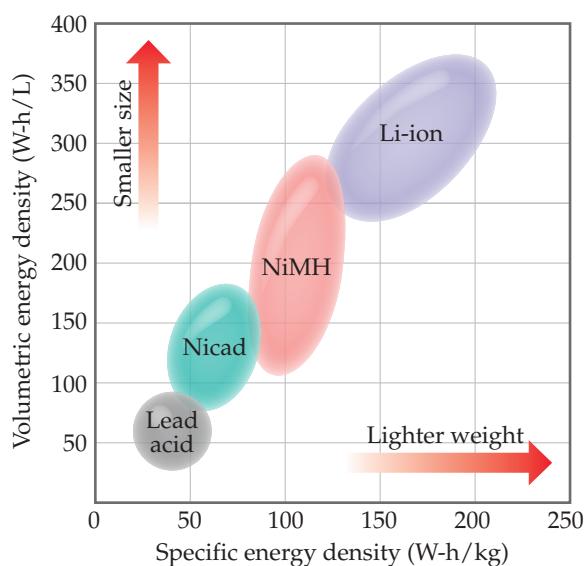
There has been a tremendous growth over the last two decades in the development of electric vehicles. This growth has been driven by a desire to reduce the use of fossil fuels and lower emissions. Today both hybrid electric vehicles and fully electric vehicles are commercially available. Hybrid electric vehicles can be powered either by electricity from batteries or by a conventional combustion engine, while fully electric vehicles are powered exclusively by the batteries (**Figure 20.22**). Hybrid electric vehicles can be further divided into plug-in hybrids, which require the owner to charge the battery by plugging it into a conventional outlet, or regular hybrids, which use regenerative braking and power from the combustion engine to charge the batteries.

Among the many technological advances needed to make electric vehicles practical, none is more important than advances in battery technology. Batteries for electric vehicles must have a high specific energy density, to reduce the weight of the car, as well as a high volumetric energy density, to minimize the space needed for the battery pack. A plot of energy densities for various types of rechargeable batteries is shown in **Figure 20.23**. The lead-acid batteries used in petrol- and diesel-powered automobiles are reliable and inexpensive, but their energy densities are far too low for



▲ Figure 20.22 Electric car. This Tesla electric automobile can go about 320 kilometers after 30 minutes of charging at this station.

Continued



▲ **Figure 20.23** Energy densities of various types of batteries.

The higher the volumetric energy density, the smaller the amount of space needed for the batteries. The higher the specific energy density, the smaller the mass of the batteries. A Watt-hour (W·h) is equivalent to 3.6×10^3 Joules.

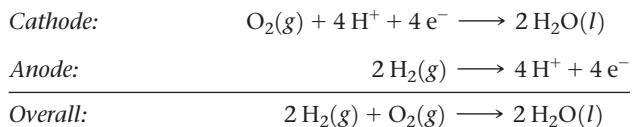
practical use in an electric vehicle. Nickel–metal hydride batteries offer roughly three times higher energy density and until recently were the batteries of choice for commercial hybrid vehicles, such as the Toyota Prius.

Fully electric vehicles and plug-in hybrids use Li-ion batteries because they offer the highest energy density of all commercially available batteries. As Li-ion battery technology has advanced, these batteries have started to displace the nickel–metal hydride batteries used in hybrid electric cars. Concern over safety is one factor that has delayed implementation of Li-ion batteries in commercial automobiles. In rare cases overheating and/or overcharging can cause Li-ion batteries to combust. Most electric vehicles now use Li-ion batteries where the LiCoO_2 cathode has been replaced by a cathode made from lithium manganese spinel (LiMn_2O_4). Batteries made with LiMn_2O_4 cathodes have several advantages. They are not prone to thermal runaway events that can lead to combustion, they tend to have longer lifetimes, and manganese is less expensive and more environmentally friendly than cobalt. However, they do have one important shortcoming—the capacity of batteries made from LiMn_2O_4 is only about two-thirds that of batteries with LiCoO_2 cathodes. Scientists and engineers are intensively looking for new materials that will lead to further improvements in the energy density, cost, lifetime, and safety of batteries.

Related Exercises: 20.39, 20.59, 20.97

a higher rate of conversion of chemical energy to electrical energy. Voltaic cells that perform this conversion using conventional fuels, such as H_2 and CH_4 , are called **fuel cells**. Fuel cells are *not* batteries because they are not self-contained systems—the fuel must be continuously supplied to generate electricity.

The most common fuel cell systems involve the reaction of $\text{H}_2(g)$ and $\text{O}_2(g)$ to form $\text{H}_2\text{O}(l)$. These cells can generate electricity twice as efficiently as the best internal combustion engine. Under acidic conditions, the reactions are



These cells employ hydrogen gas as the fuel and oxygen gas from air as the oxidant and generate about 1 V.

Fuel cells are often named for either the fuel or the electrolyte used. In the hydrogen-PEM fuel cell (the acronym PEM stands for either proton-exchange membrane or polymer-electrolyte membrane), the anode and cathode are separated by a membrane that is permeable to protons but not to electrons (Figure 20.24). The membrane therefore acts as the salt bridge. The electrodes are typically made from graphite.

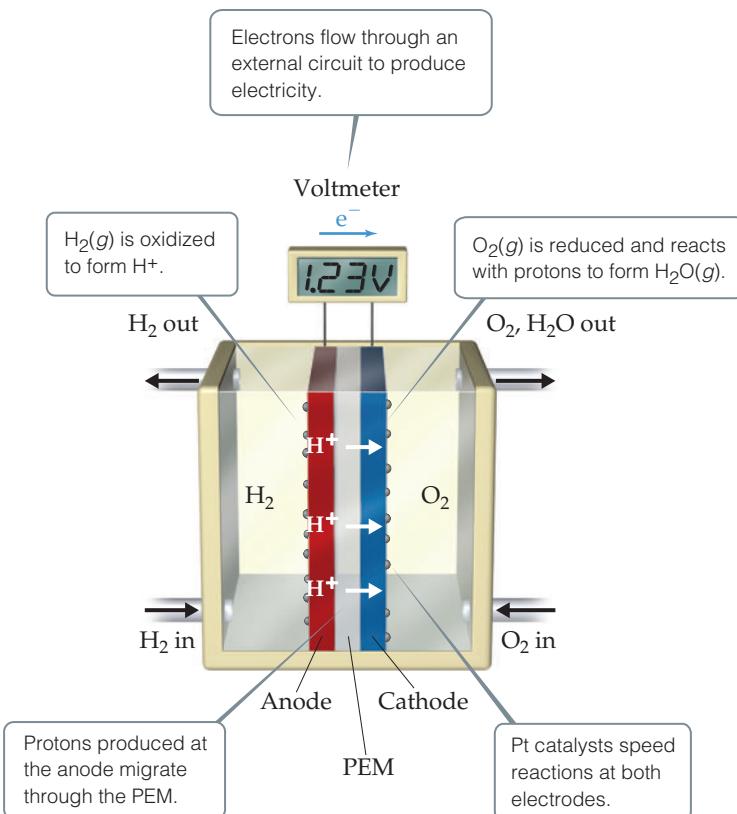
The hydrogen-PEM cell operates at around 80 °C. At this temperature, the electrochemical reactions would normally occur very slowly, and so small islands of platinum are deposited on each electrode to catalyze the reactions. The high cost and relative scarcity of platinum are two factors that limit wider use of hydrogen-PEM fuel cells.

In order to power a vehicle, multiple cells must be assembled into a fuel cell *stack*. The amount of power generated by a stack depends on the number and size of the fuel cells in the stack and on the surface area of the PEM.

Much fuel cell research today is directed toward improving electrolytes and catalysts and developing cells that use fuels such as hydrocarbons and alcohols, which are less difficult to handle and distribute than hydrogen gas.

Go Figure

What half-reaction occurs at the cathode?



▲ Figure 20.24 A hydrogen-PEM fuel cell. The proton-exchange membrane (PEM) allows H^+ ions generated by H_2 oxidation at the anode to migrate to the cathode, where H_2O is formed.

Self-Assessment Exercise

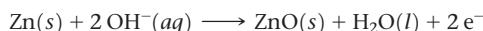
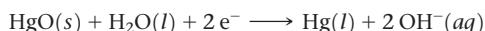
20.35 Which statement is true?

- (a) Primary batteries can be recharged.
- (b) The terminal of a battery marked with a plus is where the oxidation reaction occurs.
- (c) Batteries containing solid reactants have a constant voltage during discharge.

Exercises

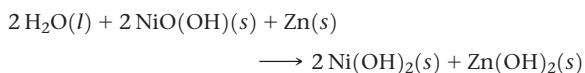
20.36 During the discharge of an alkaline battery, 4.50 g of Zn is consumed at the anode of the battery. (a) What mass of MnO_2 is reduced at the cathode during this discharge? (b) How many coulombs of electrical charge are transferred from Zn to MnO_2 ?

20.37 Mercuric oxide dry-cell batteries are often used where a flat discharge voltage and long life are required, such as in watches and cameras. The two half-cell reactions that occur in the battery are



(a) Write the overall cell reaction. (b) The value of E_{red}° for the cathode reaction is +0.098 V. The overall cell potential is +1.35 V. Assuming that both half-cells operate under standard conditions, what is the standard reduction potential for the anode reaction? (c) Why is the potential of the anode reaction different than would be expected if the reaction occurred in an acidic medium?

20.38 In some applications nickel-cadmium batteries have been replaced by nickel-zinc batteries. The overall cell reaction for this relatively new battery is:



(a) What is the cathode half-reaction? (b) What is the anode half-reaction? (c) A single nickel–cadmium cell has a voltage of 1.30 V. Based on the difference in the standard reduction potentials of Cd^{2+} and Zn^{2+} , what voltage would you estimate a nickel–zinc battery will produce? (d) Would you expect the specific energy density of a nickel–zinc battery to be higher or lower than that of a nickel–cadmium battery?

- 20.39** Li-ion batteries used in automobiles typically use a LiMn_2O_4 cathode in place of the LiCoO_2 cathode found in most Li-ion batteries. (a) Calculate the mass percent

lithium in each electrode material. (b) Which material has a higher percentage of lithium? Does this help to explain why batteries made with LiMn_2O_4 cathodes deliver less power on discharging? (c) In a battery that uses a LiCoO_2 cathode, approximately 50% of the lithium migrates from the cathode to the anode on charging. In a battery that uses a LiMn_2O_4 cathode, what fraction of the lithium in LiMn_2O_4 would need to migrate out of the cathode to deliver the same amount of lithium to the graphite anode?

- 20.40** (a) What is the difference between a battery and a fuel cell?
(b) Can the “fuel” of a fuel cell be a solid?

20.35 (c)

ANSWERS TO SELF-ASSESSMENT EXERCISE



20.8 | Corrosion



The rusting of iron is a familiar corrosion process that carries a significant economic impact. Rust has a higher volume than iron, and this can destroy the structural integrity of iron-reinforced constructions if appropriate corrosion protection is not in place. One estimate suggests that up to 20% of the iron produced annually in the United States is used to replace iron objects that have been discarded because of rust damage. This can be particularly problematic in iron boats, where sea water acts as a good electrolyte and the site of corrosion is often hidden from view by the water. One method of protecting the iron is to attach a more active metal, usually zinc, to the hull, which will corrode preferentially, and may be easier to inspect for electrochemical corrosion than the entire hull of a ship.

In this section, we examine the undesirable redox reactions that lead to **corrosion** of metals. Corrosion reactions are spontaneous redox reactions in which a metal is attacked by some substance in its environment and converted to an unwanted compound.

By the end of this section, you should be able to

- Appreciate the factors affecting corrosion and how to prevent corrosion

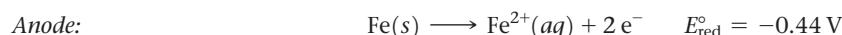
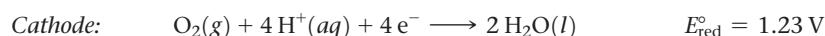
For nearly all metals, oxidation is thermodynamically favorable in air at room temperature. When oxidation of a metal object is not inhibited, it can destroy the object. Oxidation can form an insulating protective oxide layer, however, that prevents further

reaction of the underlying metal. Based on the standard reduction potential for Al^{3+} , for example, we expect aluminum metal to be readily oxidized. The many aluminum soft-drink and beer cans that litter the environment are ample evidence, however, that aluminum undergoes only very slow chemical corrosion. The exceptional stability of this active metal in air is due to the formation of a thin protective coat of oxide—a hydrated form of Al_2O_3 —on the metal surface. The oxide coat is impermeable to O_2 or H_2O and so protects the underlying metal from further corrosion.

Magnesium metal is similarly protected, and some metal alloys, such as stainless steel, likewise form protective impervious oxide coats.

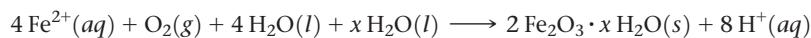
Corrosion of Iron (Rusting)

Rusting of iron requires both oxygen and water, and the process can be accelerated by other factors such as pH, presence of salts, contact with metals more difficult to oxidize than iron, and stress on the iron. The corrosion process involves oxidation and reduction, and the metal conducts electricity. Thus, electrons can move through the metal from a region where oxidation occurs to a region where reduction occurs, as in voltaic cells. Because the standard reduction potential for reduction of $\text{Fe}^{2+}(aq)$ is less positive than that for reduction of O_2 , $\text{Fe}(s)$ can be oxidized by $\text{O}_2(g)$:



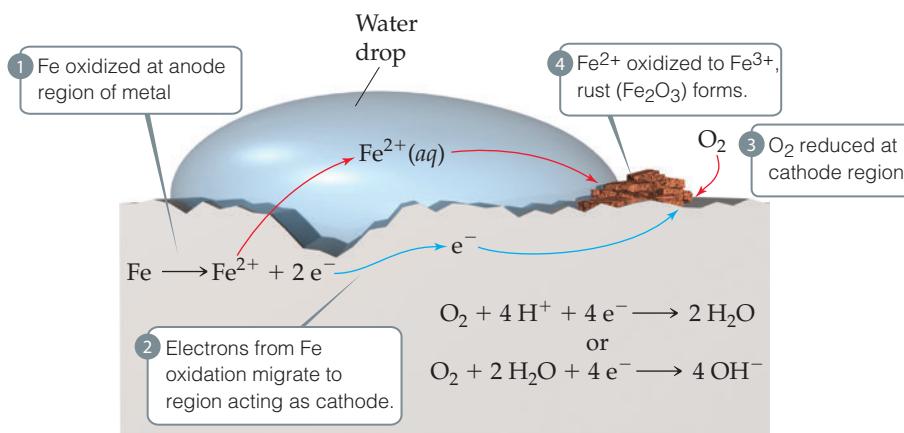
A portion of the iron, often associated with a dent or region of strain, can serve as an anode at which Fe is oxidized to Fe^{2+} (Figure 20.25). The electrons produced in the oxidation migrate through the metal from this anodic region to another portion of the surface, which serves as the cathode where O_2 is reduced. The reduction of O_2 requires H^+ , so lowering the concentration of H^+ (increasing the pH) makes O_2 reduction less favorable. Iron in contact with a solution whose pH is greater than 9 does not corrode.

The Fe^{2+} formed at the anode is eventually oxidized to Fe^{3+} , which forms the hydrated iron(III) oxide known as rust:^{*}



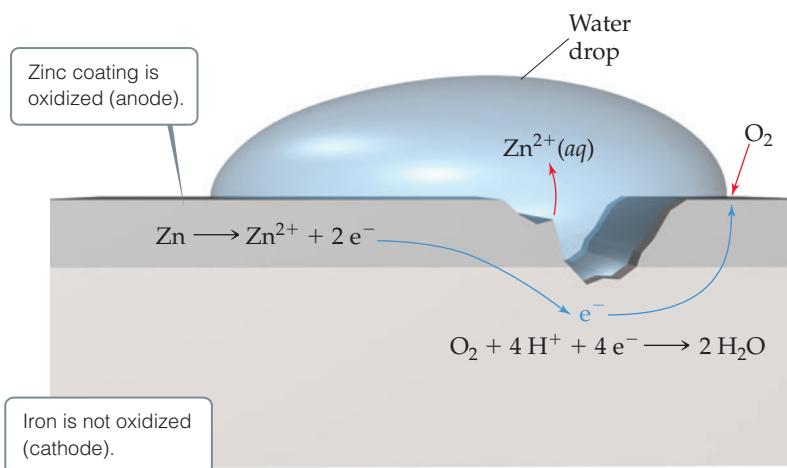
Go Figure

What is the oxidizing agent in this corrosion reaction?



▲ Figure 20.25 Corrosion of iron in contact with water. One region of the iron acts as the cathode, and another region acts as the anode.

*Frequently, metal compounds obtained from aqueous solution have water associated with them. For example, copper(II) sulfate crystallizes from water with 5 mol of water per mole of CuSO_4 . We represent this substance by the formula $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. Such compounds are called hydrates. Rust is a hydrate of iron(III) oxide with a variable amount of water of hydration. We represent this variable water content by writing the formula $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$.



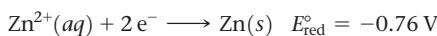
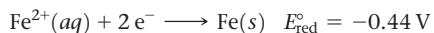
▲ **Figure 20.26** Cathodic protection of iron in contact with zinc. The standard reduction potentials are $E_{\text{red}, Fe^{2+}}^\circ = -0.44 \text{ V}$, $E_{\text{red}, Zn^{2+}}^\circ = -0.76 \text{ V}$, making the zinc more readily oxidized.

Because the cathode is generally the area having the largest supply of O_2 , rust often deposits there. If you look closely at a shovel after it has stood outside in the moist air with wet dirt adhered to its blade, you may notice that pitting has occurred under the dirt but that rust has formed elsewhere, where O_2 is more readily available. The enhanced corrosion caused by the presence of salts is usually evident on cars in areas where roads are heavily salted during winter. Like a salt bridge in a voltaic cell, the ions of the salt provide the electrolyte necessary to complete the electrical circuit.

Preventing Corrosion of Iron

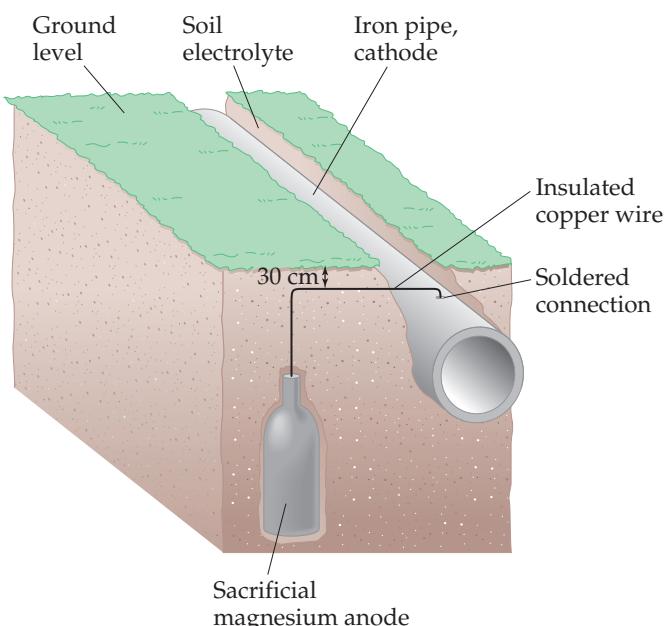
Objects made of iron are often covered with a coat of paint or another metal to protect against corrosion. Covering the surface with paint prevents oxygen and water from reaching the iron surface. If the coating is broken, however, and the iron is exposed to oxygen and water, corrosion begins as the iron is oxidized.

With *galvanized iron*, which is iron coated with a thin layer of zinc, the iron is protected from corrosion even after the surface coat is broken. The standard reduction potentials are



Because E_{red}° for Fe^{2+} is less negative (more positive) than E_{red}° for Zn^{2+} , $Zn(s)$ is more readily oxidized than $Fe(s)$. Thus, even if the zinc coating is broken and the galvanized iron is exposed to oxygen and water, as in **Figure 20.26**, the zinc serves as the anode and is corroded (oxidized) instead of the iron. The iron serves as the cathode at which O_2 is reduced.

Protecting a metal from corrosion by making it the cathode in an electrochemical cell is known as **cathodic protection**. The metal that is oxidized while protecting the cathode is called the *sacrificial anode*. Underground pipelines and storage tanks made of iron are often protected against corrosion by making the iron the cathode of a voltaic cell. For example, pieces of a metal that is more easily oxidized than iron, such as magnesium ($E_{\text{red}}^\circ = -2.37 \text{ V}$), are buried near the pipe or storage tank and connected to it by wire (**Figure 20.27**). In moist soil, where corrosion can occur, the sacrificial metal serves as the anode, and the pipe or tank experiences cathodic protection.



▲ **Figure 20.27** Cathodic protection of an iron pipe. A mixture of gypsum, sodium sulfate, and clay surrounds the sacrificial magnesium anode to promote conductivity of ions.

Self-Assessment Exercise

20.41 Based on the values in Table 20.1, which of these metals could provide cathodic protection to iron: Ag, Zn, Cu, Ni?

- (a) Ag
(b) Zn

- (c) Cu
(d) Ni

Exercises

20.42 (a) Write the anode and cathode reactions that cause the corrosion of iron metal to aqueous iron(II). (b) Write the balanced half-reactions involved in the air oxidation of $\text{Fe}^{2+}(aq)$ to $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}(s)$.

20.43 An iron object is plated with a coating of tin (Sn) to protect against corrosion. Does the tin protect iron by cathodic protection?

20.44 Copper corrodes to cuprous oxide, Cu_2O , or cupric oxide, CuO , depending on environmental conditions. (a) What is

the oxidation state of copper in cuprous oxide? (b) What is the oxidation state of copper in cupric oxide? (c) Copper peroxide is another oxidation product of elemental copper. Suggest a formula for copper peroxide based on its name. (d) Copper(III) oxide is another unusual oxidation product of elemental copper. Suggest a chemical formula for copper(III) oxide.

20.41 (d)

Answers to Self-Assessment Exercise

20.9 | Electrolysis

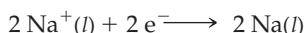
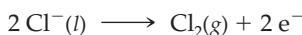
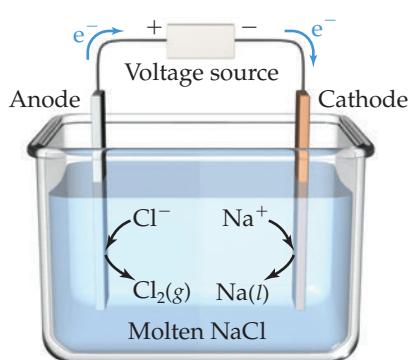


There are many materials around us that combine the structural or economic properties of one material with the decorative or corrosion-resistive properties of another. For example, a chrome plating on iron to give a highly resistant, shiny surface or the plating of gold onto copper for connectors used in the electronics industry and the silver plating onto a copper-nickel-zinc alloy for decorative purposes. These examples use an electrical current to drive a nonspontaneous process. The same principle is used for the extraction of some metals from their ore.

By the end of this section, you should be able to

- Describe, quantitatively, the reactions occurring in an electrolytic cell

Voltaic cells are based on spontaneous redox reactions. It is also possible for *non-spontaneous* redox reactions to occur, however, by using electrical energy to drive them.

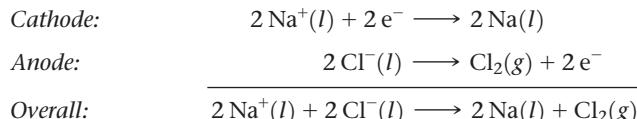


▲ Figure 20.28 **Electrolysis of molten sodium chloride.** Pure NaCl melts at 801 °C.

For example, electricity can be used to decompose molten sodium chloride into its component elements Na and Cl₂. Such processes driven by an outside source of electrical energy are called **electrolysis reactions** and take place in **electrolytic cells**.

An electrolytic cell consists of two electrodes immersed either in a molten salt or in a solution. A battery or some other source of electrical energy acts as an electron pump, pushing electrons into one electrode and pulling them from the other. Just as in voltaic cells, the electrode at which reduction occurs is called the cathode, and the electrode at which oxidation occurs is called the anode.

In the electrolysis of molten NaCl, Na⁺ ions gain electrons and are reduced to Na at the cathode, **Figure 20.28**. As Na⁺ ions near the cathode are depleted, additional Na⁺ ions migrate in. Similarly, there is net movement of Cl⁻ ions to the anode where they are oxidized. The electrode reactions for the electrolysis are

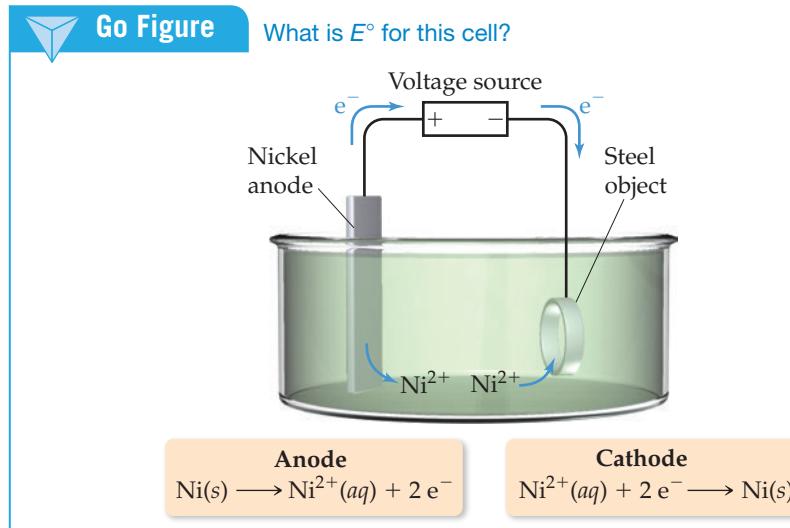


Notice how the energy source is connected to the electrodes in Figure 20.28. The positive terminal is connected to the anode and the negative terminal is connected to the cathode, which forces electrons to move from the anode to the cathode.

Because of the high melting points of ionic substances, the electrolysis of molten salts requires very high temperatures. Do we obtain the same products if we electrolyze the aqueous solution of a salt instead of the molten salt? Frequently, the answer is no because water itself might be oxidized to form O₂ or reduced to form H₂ rather than the ions of the salt.

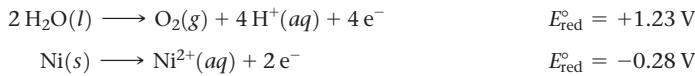
In our examples of the electrolysis of NaCl, the electrodes are *inert*; they do not react but merely serve as the surface where oxidation and reduction occur. Several practical applications of electrochemistry, however, are based on *active* electrodes—electrodes that participate in the electrolysis process. *Electroplating*, for example, uses electrolysis to deposit a thin layer of one metal on another metal to improve beauty or resistance to corrosion. Examples include electroplating nickel or chromium onto steel and electroplating a precious metal like silver onto a less expensive one.

Figure 20.29 illustrates an electrolytic cell for electroplating nickel onto a piece of steel. The anode is a strip of nickel metal, and the cathode is the steel. The electrodes are immersed in a solution of NiSO₄(aq). When an external voltage is applied, reduction occurs at the cathode. The standard reduction potential of Ni²⁺ ($E_{\text{red}}^\circ = -0.28 \text{ V}$) is less negative than that of H₂O ($E_{\text{red}}^\circ = -0.83 \text{ V}$), so Ni²⁺ is preferentially reduced, depositing a layer of nickel metal on the steel cathode.



▲ Figure 20.29 **Electrolytic cell with an active metal electrode.** Nickel dissolves from the anode to form Ni²⁺(aq). At the cathode, Ni²⁺(aq) is reduced and forms a nickel “plate” on the steel cathode.

At the anode, the nickel metal is oxidized. To explain this behavior, we need to compare the substances in contact with the anode, H_2O and $\text{NiSO}_4(aq)$, with the anode material, Ni. For the $\text{NiSO}_4(aq)$ solution, neither Ni^{2+} nor SO_4^{2-} can be oxidized (because both already have their elements in their highest common oxidation state). Both the H_2O solvent and the Ni atoms in the anode, however, can undergo oxidation:



We saw in Section 20.4 that the half-reaction with the more negative E_{red}° undergoes oxidation more readily. (Remember Figure 20.11: The strongest reducing agents, which are the substances oxidized most readily, have the most negative E_{red}° values.) Thus, it is the $\text{Ni}(s)$, with its $E_{\text{red}}^\circ = -0.28 \text{ V}$, that is oxidized at the anode rather than the H_2O . If we look at the overall reaction, it appears as if nothing has been accomplished. However, this is not true because Ni atoms are transferred from the Ni anode to the steel cathode, plating the steel with a thin layer of nickel atoms.

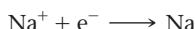
The standard emf for the overall reaction is

$$E_{\text{cell}}^\circ = E_{\text{red}}^\circ(\text{cathode}) - E_{\text{red}}^\circ(\text{anode}) = (-0.28 \text{ V}) - (-0.28 \text{ V}) = 0$$

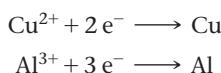
Because the standard emf is zero, only a small emf is needed to cause the transfer of nickel atoms from one electrode to the other.

Quantitative Aspects of Electrolysis

The stoichiometry of a half-reaction shows how many electrons are needed to achieve an electrolytic process. For example, the reduction of Na^+ to Na is a one-electron process:



Thus, 1 mol of electrons plates out 1 mol of Na metal, 2 mol of electrons plate out 2 mol of Na metal, and so forth. Similarly, 2 mol of electrons are required to produce 1 mol of Cu from Cu^{2+} , and 3 mol of electrons are required to produce 1 mol of Al from Al^{3+} :



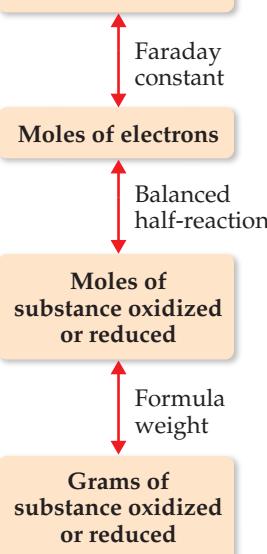
For any half-reaction, the amount of substance reduced or oxidized in an electrolytic cell is directly proportional to the number of electrons passed into the cell.

The quantity of charge passing through an electrical circuit, such as that in an electrolytic cell, is generally measured in *coulombs*. As noted in Section 20.5, the charge on 1 mol of electrons is 96,485 C. A coulomb is the quantity of charge passing a point in a circuit in 1 s when the current is 1 ampere (A). Therefore, the number of coulombs passing through a cell can be obtained by multiplying the current in amperes by the elapsed time in seconds.

$$\text{coulombs} = \text{amperes} \times \text{seconds} \quad [20.21]$$

Figure 20.30 shows how the quantities of substances produced or consumed in electrolysis are related to the quantity of electrical charge used. The same relationships can also be applied to voltaic cells. In other words, electrons can be thought of as “reagents” in electrolysis reactions.

Quantity of charge
(coulombs) =
current (amperes)
× time (seconds)



▲ **Figure 20.30** Relationship between charge and amount of reactant and product in electrolysis reactions.

Sample Exercise 20.14

Relating Electrical Charge and Quantity of Electrolysis

Calculate the number of grams of aluminum produced in 1.00 h by the electrolysis of molten AlCl_3 if the electrical current is 10.0 A.

SOLUTION

Analyze We are told that AlCl_3 is electrolyzed to form Al and asked to calculate the number of grams of Al produced in 1.00 h with 10.0 A.

Plan Figure 20.30 provides a roadmap for this problem. Using the current, time, a balanced half-reaction, and the atomic weight of aluminum we can calculate the mass of Al produced.

Continued

Solve

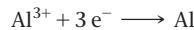
First, we calculate the coulombs of electrical charge passed into the electrolytic cell (note that $10.0 \text{ A} = 10.0 \text{ C/s}$):

$$\text{Coulombs} = \text{amperes} \times \text{seconds} = (10.0 \text{ C/s})(1.00 \text{ h})\left(\frac{3600 \text{ s}}{\text{h}}\right) = 3.60 \times 10^4 \text{ C}$$

Second, we calculate the number of moles of electrons that pass into the cell:

$$\text{Moles e}^- = (3.60 \times 10^4 \text{ C})\left(\frac{1 \text{ mol e}^-}{96,485 \text{ C}}\right) = 0.373 \text{ mol e}^-$$

Third, we relate number of moles of electrons to number of moles of aluminum formed, using the half-reaction for the reduction of Al^{3+} :



Thus, 3 mol of electrons are required to form 1 mol of Al:

$$\text{Moles Al} = (0.373 \text{ mol e}^-)\left(\frac{1 \text{ mol Al}}{3 \text{ mol e}^-}\right) = 0.124 \text{ mol Al}$$

Finally, we convert moles to grams:

$$\text{Grams Al} = (0.124 \text{ mol Al})\left(\frac{27.0 \text{ g Al}}{1 \text{ mol Al}}\right) = 3.36 \text{ g Al}$$

Or, we could have combined all of the above steps:

$$\text{Grams Al} = (3.60 \times 10^4 \text{ C})\left(\frac{1 \text{ mol e}^-}{96,485 \text{ C}}\right)\left(\frac{1 \text{ mol Al}}{3 \text{ mol e}^-}\right)\left(\frac{27.0 \text{ g Al}}{1 \text{ mol Al}}\right) = 3.36 \text{ g Al}$$

► Practice Exercise

How much time is needed to deposit 1.0 g of chromium metal from an aqueous solution of CrCl_3 using a current of 1.5 A ?

- (a) $3.8 \times 10^{-2} \text{ s}$ (b) 21 min (c) 62 min (d) 139 min
(e) $3.2 \times 10^3 \text{ min}$

CHEMISTRY PUT TO WORK Electrometallurgy of Aluminum

Many processes used to produce or refine metals are based on electrolysis. Collectively, these processes are referred to as *electrometallurgy*. Electrometallurgical procedures can be broadly differentiated according to whether they involve electrolysis of a molten salt or of an aqueous solution.

Electrolytic methods using molten salts are important for obtaining the more active metals, such as sodium, magnesium, and aluminum. These metals cannot be obtained from aqueous solution because water is more easily reduced than the metal ions. The standard reduction potentials of water under both acidic ($E_{\text{red}}^\circ = 0.00 \text{ V}$) and basic ($E_{\text{red}}^\circ = -0.83 \text{ V}$) conditions are more positive than those of Na^+ ($E_{\text{red}}^\circ = -2.71 \text{ V}$), Mg^{2+} ($E_{\text{red}}^\circ = -2.37 \text{ V}$), and Al^{3+} ($E_{\text{red}}^\circ = -1.66 \text{ V}$).

Historically, obtaining aluminum metal has been a challenge. It is obtained from bauxite ore, which is chemically treated to concentrate aluminum oxide (Al_2O_3). The melting point of aluminum oxide is above 2000°C , which is too high to permit its use as a molten medium for electrolysis.

The electrolytic process used commercially to produce aluminum is the *Hall-Héroult process*, named after its inventors, Charles M. Hall and Paul Héroult. Hall (1863–1914) (Figure 20.31) began working on the problem of reducing aluminum in about 1885 after he had learned from a professor of the difficulty of reducing ores of very active metals. Before the development of an electrolytic process, aluminum was obtained by a chemical reduction using sodium or potassium as the reducing agent, a costly procedure that made aluminum metal expensive. As late as 1852, the cost of aluminum was \$545 per pound, far greater than the cost of gold. During the Paris



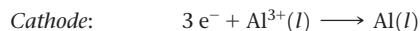
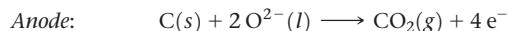
▲ Figure 20.31 Charles M. Hall as a young man.

Exposition in 1855, aluminum was exhibited as a rare metal, even though it is the third most abundant element in Earth's crust.

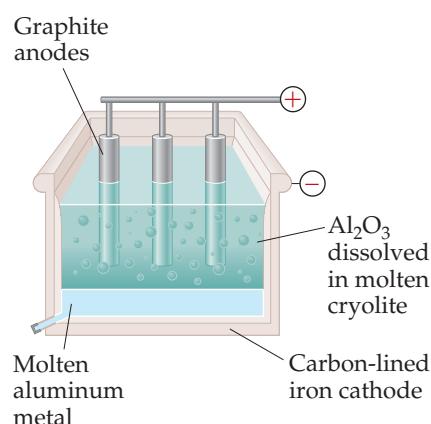
Hall, who was 21 years old when he began his research, utilized handmade and borrowed equipment in his studies and used a woodshed near his Ohio home as his laboratory. In about a year's time, he developed an electrolytic procedure using an ionic compound that melts to form a conducting medium that dissolves Al_2O_3 but does not interfere with the electrolysis reactions. The ionic compound he selected was the relatively rare mineral cryolite (Na_3AlF_6). Héroult, who was the same age as Hall, independently made the same

discovery in France at about the same time. Because of the research of these two unknown young scientists, large-scale production of aluminum became commercially feasible, and aluminum became a common and familiar metal. Indeed, the factory that Hall subsequently built to produce aluminum evolved into Alcoa Corporation.

In the Hall-Héroult process, Al_2O_3 is dissolved in molten cryolite, which melts at 1012°C and is an effective electrical conductor (Figure 20.32). Graphite rods are employed as anodes and are consumed in the electrolysis:



A large amount of electrical energy is needed in the Hall-Héroult process, with the result that many aluminum plants are close to cheap sources of electricity, such as hydroelectric power plants. Because recycled aluminum requires only 5% of the energy needed to produce “new” aluminum, considerable energy savings can be realized by increasing the amount of aluminum recycled. Approximately 65% of aluminum beverage containers are recycled in the United States.



▲ Figure 20.32 The Hall-Héroult process. Because molten aluminum is denser than the mixture of cryolite (Na_3AlF_6) and Al_2O_3 , the metal collects at the bottom of the cell.

Self-Assessment Exercise

- 20.45** An electrolytic cell contains a solution of MCl_3 . A total charge of 3610 C is passed through the cell, depositing 0.648 g of the metal, M, at the cathode. What is the identity of the metal, M?

- (a) V
- (b) Cr
- (c) Mn
- (d) Co

Exercises

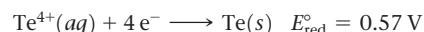
- 20.46** (a) What is an *electrolytic cell*? (b) The negative terminal of a voltage source is connected to an electrode of an electrolytic cell. Is the electrode the anode or the cathode of the cell? Explain. (c) The electrolysis of water is often done with a small amount of sulfuric acid added to the water. What is the role of the sulfuric acid? (d) Why are active metals such as Al obtained by electrolysis using molten salts rather than aqueous solutions?

- 20.47** Metallic magnesium can be made by the electrolysis of molten MgCl_2 . (a) What mass of Mg is formed by passing a current of 4.55 A through molten MgCl_2 , for 4.50 days? (b) How many minutes are needed to plate out 25.00 g Mg from molten MgCl_2 using 3.50 A of current?

- 20.48** Elemental calcium is produced by the electrolysis of molten CaCl_2 . (a) What mass of calcium can be produced

by this process if a current of $7.5 \times 10^3\text{ A}$ is applied for 48 h ? Assume that the electrolytic cell is 68% efficient. (b) What is the minimum voltage needed to cause the electrolysis?

- 20.49** A mixture of copper and gold metals that is subjected to electrorefining contains tellurium as an impurity. The standard reduction potential between tellurium and its lowest common oxidation state, Te^{4+} , is



Given this information, describe the probable fate of tellurium impurities during electrorefining. Do the impurities fall to the bottom of the refining bath, unchanged, as copper is oxidized, or do they go into solution as ions? If they go into solution, do they plate out on the cathode?

20.45 (b)

Answers to Self-Assessment Exercises



Sample Integrative Exercise

Putting Concepts Together

The K_{sp} at 298 K for iron(II) fluoride is 2.4×10^{-6} . (a) Write a half-reaction that gives the likely products of the two-electron reduction of $\text{FeF}_2(s)$ in water. (b) Use the K_{sp} value and the standard reduction potential of $\text{Fe}^{2+}(aq)$ to calculate the standard reduction potential for the half-reaction in part (a). (c) Rationalize the difference between the reduction potential in part (a) and the reduction potential for $\text{Fe}^{2+}(aq)$.

Continued

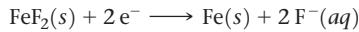
SOLUTION

Analyze We are going to combine what we know about equilibrium constants and electrochemistry to obtain reduction potentials.

Plan For (a) we need to determine which ion, Fe^{2+} or F^- , is more likely to be reduced by two electrons and complete the overall

Solve

(a) Iron(II) fluoride is an ionic substance that consists of Fe^{2+} and F^- ions. We are asked to predict where two electrons could be added to FeF_2 . We cannot envision adding the electrons to the F^- ions to form F^{2-} , so it seems likely that we could reduce the Fe^{2+} ions to $\text{Fe}(s)$. We therefore predict the half-reaction:



(b) The K_{sp} for FeF_2 refers to the following equilibrium:



We were also asked to use the standard reduction potential of Fe^{2+} , whose half-reaction and standard reduction potentials are listed in Appendix E:



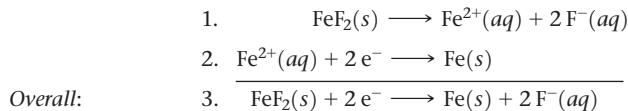
According to Hess's law, if we can add chemical equations to get a desired equation, then we can add their associated thermodynamic state functions, like ΔH or ΔG , to determine the thermodynamic quantity for the desired reaction. So we need to consider whether the three equations we are working with can be combined in a similar fashion. Notice that if we add the K_{sp} reaction to the standard reduction half-reaction for Fe^{2+} , we get the half-reaction we want:

Reaction 3 is still a half-reaction, so we do see the free electrons.

If we knew ΔG° for reactions 1 and 2, we could add them to get ΔG° for reaction 3. We can relate ΔG° to E° by $\Delta G^\circ = -nFE^\circ$ (Equation 20.12) and to K by $\Delta G^\circ = -RT \ln K$ (Equation 19.20; see also Figure 20.13). Furthermore, we know that K for reaction 1 is the K_{sp} of FeF_2 , and we know E° for reaction 2. Therefore, we can calculate ΔG° for reactions 1 and 2: (Recall that 1 volt is 1 joule per coulomb.)

Then ΔG° for reaction 3, the one we want, is the sum of the ΔG° values for reactions 1 and 2:

We can convert this to E° from the relationship $\Delta G^\circ = -nFE^\circ$:

**Reaction 1:**

$$\Delta G^\circ = -RT \ln K = -(8.314 \text{ J/K mol})(298 \text{ K}) \ln(2.4 \times 10^{-6}) = 3.21 \times 10^4 \text{ J/mol}$$

Reaction 2:

$$\Delta G^\circ = -nFE^\circ = -(2)(96,485 \text{ C/mol})(-0.440 \text{ J/C}) = 8.49 \times 10^4 \text{ J/mol}$$

$$3.21 \times 10^4 \text{ J/mol} + 8.49 \times 10^4 \text{ J/mol} = 1.17 \times 10^5 \text{ J/mol}$$

$$1.17 \times 10^5 \text{ J/mol} = -(2)(96,485 \text{ C/mol})E^\circ$$

$$E^\circ = \frac{1.17 \times 10^5 \text{ J/mol}}{-(2)(96,485 \text{ C/mol})} = -0.606 \text{ J/C} = -0.606 \text{ V}$$

(c) The standard reduction potential for $\text{FeF}_2(-0.606 \text{ V})$ is more negative than that for $\text{Fe}^{2+}(-0.440 \text{ V})$, telling us that the reduction of FeF_2 is the less favorable process. When FeF_2 is reduced, we not only reduce the Fe^{2+} but also break up the ionic solid. Because this additional energy must be overcome, the reduction of FeF_2 is less favorable than the reduction of Fe^{2+} .

reaction $\text{FeF}_2 + 2 \text{e}^- \longrightarrow ?$. For (b) we need to write the chemical equation associated with the K_{sp} and see how it relates to E° for the reduction half-reaction in (a). For (c) we need to compare E° from (b) with the value for the reduction of Fe^{2+} .

Chapter Summary and Key Terms

OXIDATION STATES AND OXIDATION–REDUCTION REACTIONS (INTRODUCTION AND SECTION 20.1) In this chapter, we have focused on **electrochemistry**, the branch of chemistry that relates electricity and chemical reactions. Electrochemistry involves oxidation–reduction reactions, also called redox reactions. These reactions involve a change in the oxidation state of one or more elements. In every oxidation–reduction reaction one substance is oxidized (its oxidation state, or number, increases) and one substance is reduced (its oxidation state, or number, decreases). The substance that is oxidized is referred to as a **reducing agent**, or **reductant**, because it causes the reduction of some other substance. Similarly, the substance that is reduced is referred to as an **oxidizing agent**, or **oxidant**, because it causes the oxidation of some other substance.

BALANCING REDOX EQUATIONS (SECTION 20.2) An oxidation–reduction reaction can be balanced by dividing the reaction into two **half-reactions**, one for oxidation and one for reduction. A half-reaction is a balanced chemical equation that includes electrons. In oxidation half-reactions, the electrons are on the product (right) side of the equation. In reduction half-reactions, the electrons are on the reactant (left) side of the equation. Each half-reaction is balanced separately, and the two are brought together with proper coefficients to balance the electrons on each side of the equation, so the electrons cancel when the half-reactions are added.

VOLTAIC CELLS (SECTION 20.3) A **voltaic** (or **galvanic**) **cell** uses a spontaneous oxidation–reduction reaction to generate electricity. In a voltaic cell the oxidation and reduction half-reactions often occur in separate half-cells. Each half-cell has a solid surface called an **electrode**, where the half-reaction occurs. The electrode where oxidation occurs is called the **anode**, and the electrode where reduction occurs is called the **cathode**. The electrons released at the anode flow through an external circuit (where they do electrical work) to the cathode. Electrical neutrality in the solution is maintained by the migration of ions between the two half-cells through a device such as a salt bridge.

CELL POTENTIALS UNDER STANDARD CONDITIONS (SECTION 20.4) A voltaic cell generates an **electromotive force (emf)** that moves the electrons from the anode to the cathode through the external circuit. The origin of emf is a difference in the electrical potential energy of the two electrodes in the cell. The emf of a cell is called its **cell potential**, E_{cell} and is measured in volts ($1 \text{ V} = 1 \text{ J/C}$). The cell potential under standard conditions is called the **standard emf**, or the **standard cell potential**, and is denoted E_{cell}° .

A **standard reduction potential**, E_{red}° , can be assigned for an individual half-reaction. This is achieved by comparing the potential of the half-reaction to that of the **standard hydrogen electrode (SHE)**, which is defined to have $E_{\text{red}}^{\circ} = 0 \text{ V}$.

The standard cell potential of a voltaic cell is the difference between the standard reduction potentials of the half-reactions that occur at the cathode and the anode:

$$E_{\text{cell}}^{\circ} = E_{\text{red}}^{\circ}(\text{cathode}) - E_{\text{red}}^{\circ}(\text{anode}).$$

The value of E_{cell}° is positive for a voltaic cell.

For a reduction half-reaction, E_{red}° is a measure of the tendency of the reduction to occur; the more positive the value for E_{red}° , the greater the tendency of the substance to be reduced. Substances that are easily reduced act as strong oxidizing agents; thus, E_{red}° provides a measure of the oxidizing strength of a substance.

Substances that are strong oxidizing agents produce products that are weak reducing agents and vice versa.

FREE ENERGY AND REDOX REACTIONS (SECTION 20.5) The emf, E , is related to the change in the Gibbs free energy, $\Delta G = -nFE$, where n is the number of moles of electrons transferred during the redox process and F is the **Faraday constant**, defined as the quantity of electrical charge on one mole of electrons: $F = 96,485 \text{ C/mol}$. Because E is related to ΔG , the sign of E indicates whether a redox process is spontaneous: $E > 0$ indicates a spontaneous process, and $E < 0$ indicates a nonspontaneous one. Because ΔG is also related to the equilibrium constant for a reaction ($\Delta G^{\circ} = -RT \ln K$), we can relate E to K as well.

CELL POTENTIALS UNDER NONSTANDARD CONDITIONS (SECTION 20.6) The emf of a redox reaction varies with temperature and with the concentrations of reactants and products. The **Nernst equation** relates the emf under nonstandard conditions to the standard emf and the reaction quotient Q :

$$E = E^{\circ} - (RT/nF) \ln Q = E^{\circ} - (0.0592/n) \log Q$$

The factor 0.0592 is valid when $T = 298 \text{ K}$. A **concentration cell** is a voltaic cell in which the same half-reaction occurs at both the anode and the cathode but with different concentrations of reactants in each half-cell. At equilibrium, $Q = K$ and $E = 0$.

BATTERIES AND FUEL CELLS (SECTION 20.7) A **battery** is a self-contained electrochemical power source that contains one or more voltaic cells. Batteries are based on a variety of different redox reactions. Batteries that cannot be recharged are called **primary cells**, while those that can be recharged are called **secondary cells**. The common alkaline dry cell battery is an example of a primary cell battery. Lead-acid, nickel–cadmium, nickel–metal hydride, and lithium-ion batteries are examples of secondary cells. **Fuel cells** are voltaic cells that utilize redox reactions in which reactants such as H_2 have to be continuously supplied to the cell to generate voltage.

CORROSION (SECTION 20.8) Electrochemical principles help us understand **corrosion**, undesirable redox reactions in which a metal is attacked by some substance in its environment. The corrosion of iron into rust is caused by the presence of water and oxygen, and it is accelerated by the presence of electrolytes, such as road salt. The protection of a metal by putting it in contact with another metal that more readily undergoes oxidation is called **cathodic protection**. Galvanized iron, for example, is coated with a thin layer of zinc; because zinc is oxidized more readily than iron, the zinc serves as a sacrificial anode in the redox reaction.

ELECTROLYSIS (SECTION 20.9) An **electrolysis reaction**, which is carried out in an **electrolytic cell**, employs an external source of electricity to drive a nonspontaneous electrochemical reaction. The current-carrying medium within an electrolytic cell may be either a molten salt or an electrolyte solution. The electrodes in an electrolytic cell can be inert or active, meaning that the electrode can be involved in the electrolysis reaction. Active electrodes are important in electroplating and in metallurgical processes.

The quantity of substances formed during electrolysis can be calculated by considering the number of electrons involved in the redox reaction and the amount of electrical charge that passes into the cell. The amount of electrical charge is measured in coulombs and is related to the magnitude of the current and the time it flows ($1 \text{ C} = 1 \text{ A}\cdot\text{s}$).

Learning Outcomes

After studying this chapter, you should be able to:

- Identify oxidation, reduction, oxidizing agent, and reducing agent in a chemical equation. (Section 20.1)
Related Exercises: 20.2, 20.62, 20.65
- Complete and balance redox equations using the method of half-reactions. (Section 20.2) *Related Exercises: 20.9, 20.68*
- Sketch a voltaic cell and identify its cathode, anode, and the directions in which electrons and ions move. (Section 20.3)
Related Exercises: 20.12, 20.70
- Calculate standard emfs (cell potentials), E_{cell}° , from standard reduction potentials. (Section 20.4) *Related Exercises: 20.15, 20.16, 20.17, 20.75, 20.76*
- Use reduction potentials to predict whether a redox reaction is spontaneous. (Section 20.4) *Related Exercises: 20.21, 20.82*
- Relate E_{cell}° to ΔG° and equilibrium constants. (Section 20.5)
Related Exercises: 20.23, 20.83

- Calculate emf under nonstandard conditions. (Section 20.6)
Related Exercises: 20.32, 20.91
- Identify the components of common batteries. (Section 20.7)
Related Exercises: 20.36, 20.94
- Describe the construction of a lithium-ion battery and explain how it works (Section 20.7) *Related Exercises: 20.39, 20.97*
- Describe the construction of a fuel cell and explain how it generates electrical energy. (Section 20.7)
Related Exercises: 20.40, 20.98
- Explain how corrosion occurs and how it is prevented by cathodic protection. (Section 20.8) *Related Exercises: 20.42, 20.99*
- Describe the reactions in electrolytic cells. (Section 20.9)
Related Exercises: 20.46, 20.102
- Relate amounts of products and reactants in redox reactions to electrical charge. (Section 20.9) *Related Exercises: 20.48, 20.104*

Key Equations

$$\bullet E_{\text{cell}} = E_{\text{red}}^{\circ}(\text{cathode}) - E_{\text{red}}^{\circ}(\text{anode}) \quad [20.8]$$

$$\bullet \Delta G = -nFE \quad [20.11]$$

$$\bullet E = E^{\circ} - \frac{0.0592 \text{ V}}{n} \log Q \quad (\text{at } 298 \text{ K}) \quad [20.18]$$

Relating standard emf to standard reduction potentials of the reduction (cathode) and oxidation (anode) half-reactions

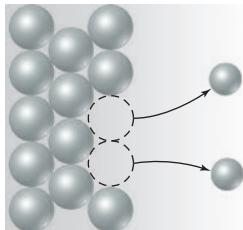
Relating free-energy change and emf

The Nernst equation, expressing the effect of concentration on cell potential

Exercises

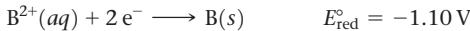
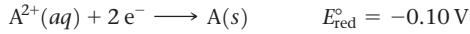
Visualizing Concepts

- 20.50** In the Brønsted–Lowry concept of acids and bases, acid–base reactions are viewed as proton-transfer reactions. The stronger the acid, the weaker is its conjugate base. If we were to think of redox reactions in a similar way, what particle would be analogous to the proton? Would strong oxidizing agents be analogous to strong acids or strong bases? [Sections 20.1 and 20.2]
- 20.51** You may have heard that “antioxidants” are good for your health. Is an “antioxidant” an oxidizing agent or a reducing agent? [Sections 20.1 and 20.2]
- 20.52** The diagram that follows represents a molecular view of a process occurring at an electrode in a voltaic cell.

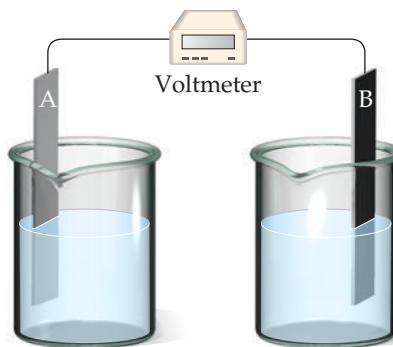


- (a) Does the process represent oxidation or reduction?
(b) Is the electrode the anode or cathode? (c) Why are the atoms in the electrode represented by larger spheres than those in the solution? [Section 20.3]

- 20.53** Assume that you want to construct a voltaic cell that uses the following half-reactions:



You begin with the incomplete cell pictured here in which the electrodes are immersed in water.



- (a) What additions must you make to the cell for it to generate a standard emf? (b) Which electrode functions as the cathode? (c) Which direction do electrons move through the external circuit? (d) What voltage will the cell generate under standard conditions? [Sections 20.3 and 20.4]

- 20.54** For a spontaneous reaction $A(aq) + B(aq) \rightarrow A^-(aq) + B^+(aq)$, answer the following questions:

- (a) If you made a voltaic cell out of this reaction, what half-reaction would be occurring at the cathode, and what half-reaction would be occurring at the anode?
 (b) Which half-reaction from (a) is higher in potential energy?
 (c) What is the sign of E_{cell}° ? [Section 20.3]

- 20.55** Consider the following table of standard electrode potentials for a series of hypothetical reactions in aqueous solution:

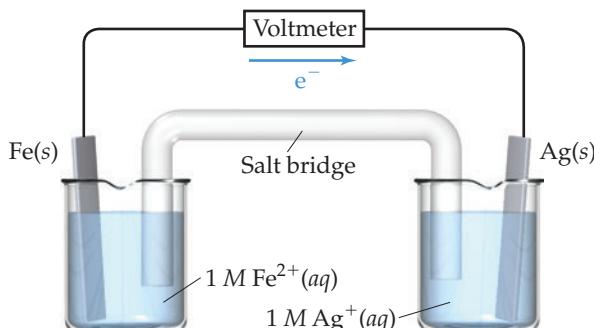
Reduction Half-Reaction	$E^\circ(V)$
$A^+(aq) + e^- \rightarrow A(s)$	1.33
$B^{2+}(aq) + 2e^- \rightarrow B(s)$	0.87
$C^{3+}(aq) + e^- \rightarrow C^{2+}(aq)$	-0.12
$D^{3+}(aq) + 3e^- \rightarrow D(s)$	-1.59

- (a) Which substance is the strongest oxidizing agent? Which is weakest?
 (b) Which substance is the strongest reducing agent? Which is weakest?
 (c) Which substance(s) can oxidize C^{2+} ? [Sections 20.4 and 20.5]

- 20.56** Consider a redox reaction for which E° is a negative number.

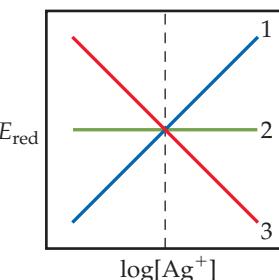
- (a) What is the sign of ΔG° for the reaction?
 (b) Will the equilibrium constant for the reaction be larger or smaller than 1?
 (c) Can an electrochemical cell based on this reaction accomplish work on its surroundings? [Section 20.5]

- 20.57** Consider the following voltaic cell:



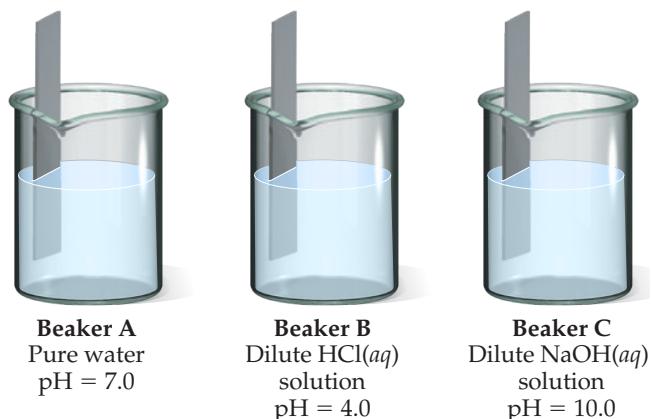
- (a) Which electrode is the cathode?
 (b) What is the standard emf generated by this cell?
 (c) What is the change in the cell voltage when the ion concentrations in the cathode half-cell are increased by a factor of 10?
 (d) What is the change in the cell voltage when the ion concentrations in the anode half-cell are increased by a factor of 10? [Sections 20.4 and 20.6]

- 20.58** Consider the half-reaction $\text{Ag}^+(aq) + e^- \rightarrow \text{Ag}(s)$.
 (a) Which of the lines in the following diagram indicates how the reduction potential varies with the concentration of $\text{Ag}^+(aq)$? (b) What is the value of E_{red} when $\log[\text{Ag}^+] = 0$? [Section 20.6]

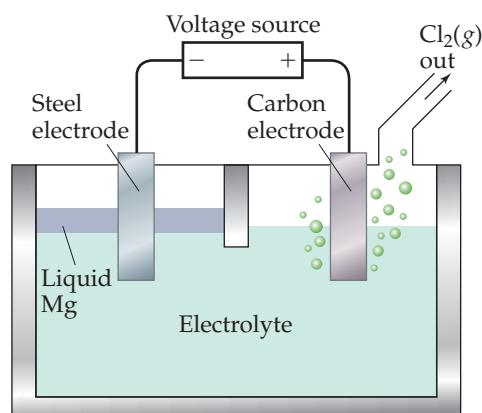


- 20.59** The electrodes in a silver oxide battery are silver oxide (Ag_2O) and zinc. (a) Which electrode acts as the anode?
 (b) Which battery do you think has an energy density most similar to the silver oxide battery: a Li-ion battery, a nickel-cadmium battery, or a lead-acid battery? [Section 20.7]

- 20.60** Bars of iron are put into each of the three beakers as shown here. In which beaker—A, B, or C—would you expect the iron to show the most corrosion? [Section 20.8]



- 20.61** Magnesium, the element, is produced commercially by electrolysis from a molten salt (the “electrolyte”) using a cell similar to the one shown here. (a) What is the most common oxidation number for Mg when it is part of a salt?
 (b) Chlorine gas is evolved as voltage is applied in the cell. Knowing this, identify the electrolyte. (c) Recall that in an electrolytic cell the anode is given the + sign and the cathode is given the - sign, which is the opposite of what we see in batteries. What half-reaction occurs at the anode in this electrolytic cell? (d) What half-reaction occurs at the cathode? [Section 20.9]



Oxidation–Reduction Reactions (Section 20.1)

20.62 (a) What is meant by the term *oxidation*? (b) On which side of an oxidation half-reaction do the electrons appear? (c) What is meant by the term *oxidant*? (d) What is meant by the term *oxidizing agent*?

20.63 Indicate whether each of the following statements is true or false:

- (a) If something is oxidized, it is formally losing electrons.
- (b) For the reaction $\text{Fe}^{3+}(aq) + \text{Co}^{2+}(aq) \longrightarrow \text{Fe}^{2+}(aq) + \text{Co}^{3+}(aq)$, $\text{Fe}^{3+}(aq)$ is the reducing agent and $\text{Co}^{2+}(aq)$ is the oxidizing agent.
- (c) If there are no changes in the oxidation state of the reactants or products of a particular reaction, that reaction is not a redox reaction.

20.64 For each of the following balanced oxidation–reduction reactions, (i) identify the oxidation numbers for all the elements in the reactants and products and (ii) state the total number of electrons transferred in each reaction.

- (a) $14\text{H}^+(aq) + 2\text{Mn}^{2+}(aq) + 5\text{NaBiO}_3(s) \longrightarrow 7\text{H}_2\text{O}(l) + 2\text{MnO}_4^-(aq) + 5\text{Bi}^{3+}(aq) + 5\text{Na}^+(aq)$
- (b) $2\text{KMnO}_4(aq) + 3\text{Na}_2\text{SO}_3(aq) + \text{H}_2\text{O}(l) \longrightarrow 2\text{MnO}_2(s) + 3\text{Na}_2\text{SO}_4(aq) + 2\text{KOH}(aq)$
- (c) $\text{Cu}(s) + 2\text{AgNO}_3(aq) \longrightarrow 2\text{Ag}(s) + \text{Cu}(\text{NO}_3)_2(aq)$

20.65 Indicate whether the following balanced equations involve oxidation–reduction. If they do, identify the elements that undergo changes in oxidation number.

- (a) $2\text{NO}_2(g) + \text{H}_2\text{O}_2(aq) \longrightarrow 2\text{HNO}_3(aq)$
- (b) $\text{FeS}(s) + 2\text{HCl}(aq) \longrightarrow \text{FeCl}_2(aq) + \text{H}_2\text{S}(g)$
- (c) $\text{Fe}(s) + 2\text{HNO}_3(aq) \longrightarrow \text{H}_2\text{O}(l) + 2\text{NO}_2(g) + \text{FeO}(s)$

Balancing Oxidation–Reduction Reactions (Section 20.2)

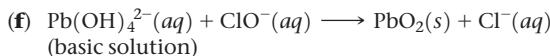
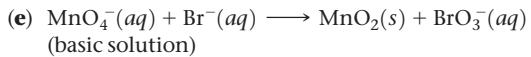
20.66 The purification process of silicon involves the reaction of silicon tetrachloride vapor ($\text{SiCl}_4(g)$) with hydrogen to 1250°C to form solid silicon and hydrogen chloride. (a) Write a balanced equation for this reaction. (b) What is being oxidized, and what is being reduced? (c) Which substance is the reductant, and which is the oxidant?

20.67 Complete and balance the following half-reactions. In each case, indicate whether the half-reaction is an oxidation or a reduction.

- (a) $\text{Cr}_2\text{O}_7^{2-}(aq) \longrightarrow \text{Cr}^{3+}(aq)$ (acidic solution)
- (b) $\text{Mn}^{2+}(aq) \longrightarrow \text{MnO}_4^-(aq)$ (acidic solution)
- (c) $\text{I}_2(s) \longrightarrow \text{IO}_3^-(aq)$ (acidic solution)
- (d) $\text{S}(s)(aq) \longrightarrow \text{H}_2\text{S}(g)$ (acidic solution)
- (e) $\text{NO}_3^-(aq) \longrightarrow \text{NO}_2^-(aq)$ (basic solution)
- (f) $\text{H}_2\text{O}_2(aq) \longrightarrow \text{OH}^-(aq)$ (basic solution)

20.68 Complete and balance the following equations, and identify the oxidizing and reducing agents:

- (a) $\text{Cr}_2\text{O}_7^{2-}(aq) + \text{I}^-(aq) \longrightarrow \text{Cr}^{3+}(aq) + \text{IO}_3^-(aq)$ (acidic solution)
- (b) $\text{MnO}_4^-(aq) + \text{CH}_3\text{OH}(aq) \longrightarrow \text{Mn}^{2+}(aq) + \text{HCOOH}(aq)$ (acidic solution)
- (c) $\text{I}_2(s) + \text{OCl}^-(aq) \longrightarrow \text{IO}_3^-(aq) + \text{Cl}^-(aq)$ (acidic solution)
- (d) $\text{As}_2\text{O}_3(s) + \text{NO}_3^-(aq) \longrightarrow \text{H}_3\text{AsO}_4(aq) + \text{N}_2\text{O}_3(aq)$ (acidic solution)



Voltaic Cells (Section 20.3)

20.69 Indicate whether each statement is true or false: (a) The cathode is the electrode at which oxidation takes place. (b) A galvanic cell is another name for a voltaic cell. (c) Electrons flow spontaneously from anode to cathode in a voltaic cell.

20.70 A voltaic cell similar to that shown in Figure 20.5 is constructed. One electrode half-cell consists of a magnesium strip placed in a solution of MgCl_2 , and the other has a nickel strip placed in a solution of NiCl_2 . The overall cell reaction is



- (a) What is being oxidized, and what is being reduced?
- (b) Write the half-reactions that occur in the two half-cells.
- (c) Which electrode is the anode, and which is the cathode?
- (d) Indicate the signs of the electrodes. (e) Do electrons flow from the magnesium electrode to the nickel electrode or from the nickel to the magnesium? (f) In which directions do the cations and anions migrate through the solution?

Cell Potentials under Standard Conditions (Section 20.4)

20.71 (a) What is the definition of the *volt*? (b) Do all voltaic cells produce a positive cell potential?

20.72 (a) Write the half-reaction that occurs at an oxygen electrode in acidic aqueous solution when it serves as the cathode of a voltaic cell. (b) Write the half-reaction that occurs at an oxygen electrode in acidic aqueous solution when it serves as the anode of a voltaic cell. (c) What is standard about the standard oxygen electrode?

20.73 (a) What conditions must be met for a reduction potential to be a *standard reduction potential*? (b) What is the standard reduction potential of a standard hydrogen electrode? (c) Why is it impossible to measure the standard reduction potential of a single half-reaction?

20.74 A voltaic cell that uses the reaction

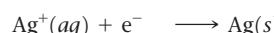
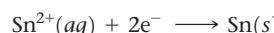
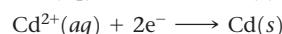
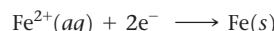


has a measured standard cell potential of $+1.19\text{ V}$. (a) Write the two half-cell reactions. (b) By using data from Appendix E, determine E_{red}° for the reduction of $\text{Tl}^{3+}(aq)$ to $\text{Tl}^+(aq)$. (c) Sketch the voltaic cell, label the anode and cathode, and indicate the direction of electron flow.

20.75 Using standard reduction potentials (Appendix E), calculate the standard emf for each of the following reactions:

- (a) $\text{Cl}_2(g) + 2\text{I}^-(aq) \longrightarrow 2\text{Cl}^-(aq) + \text{I}_2(s)$
- (b) $\text{Ni}(s) + 2\text{Ce}^{4+}(aq) \longrightarrow \text{Ni}^{2+}(aq) + 2\text{Ce}^{3+}(aq)$
- (c) $\text{Fe}(s) + 2\text{Fe}^{3+}(aq) \longrightarrow 3\text{Fe}^{2+}(aq)$
- (d) $2\text{NO}_3^-(aq) + 8\text{H}^+(aq) + 3\text{Cu}(s) \longrightarrow 2\text{NO}(g) + 4\text{H}_2\text{O}(l) + 3\text{Cu}^{2+}(aq)$

20.76 The standard reduction potentials of the following half-reactions are given in Appendix E:



(a) Determine which combination of these half-cell reactions leads to the cell reaction with the largest positive cell potential and calculate the value. (b) Determine which combination of these half-cell reactions leads to the cell reaction with the smallest positive cell potential and calculate the value.

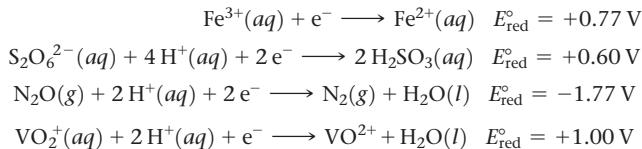
- 20.77** A 1 M solution of AgNO_3 is placed in a beaker with a strip of Ag metal. A 1 M solution of $\text{Cu}(\text{NO}_3)_2$ is placed in a second beaker with a strip of Cu metal. A salt bridge connects the two beakers, and wires to a voltmeter link the two metal electrodes. (a) Which electrode serves as the anode, and which as the cathode? (b) Which electrode gains mass, and which loses mass as the cell reaction proceeds? (c) Write the equation for the overall cell reaction. (d) What is the emf generated by the cell under standard conditions?

Strengths of Oxidizing and Reducing Agents (Section 20.4)

- 20.78** From each of the following pairs of substances, use data in Appendix E to choose the one that is the stronger reducing agent:
 (a) $\text{Al}(s)$ or $\text{Mg}(s)$
 (b) $\text{Fe}(s)$ or $\text{Ni}(s)$
 (c) $\text{H}_2(g)$, acidic solution or $\text{Sn}(s)$
 (d) $\text{I}^-(aq)$ or $\text{Br}^-(aq)$
- 20.79** By using the data in Appendix E, determine whether each of the following substances is likely to serve as an oxidant or a reductant: (a) $\text{H}_2(g)$, basic, (b) $\text{Cr}_2\text{O}_7^{2-}(aq)$, acidic, (c) $\text{F}_2(g)$, (d) $\text{Li}(s)$.
- 20.80** (a) Assuming standard conditions, arrange the following in order of increasing strength as oxidizing agents in acidic solution: $\text{MnO}_4^-(aq)$, $\text{O}_3(g)$, $\text{HSO}_4^-(aq)$, $\text{O}_2(g)$, $\text{HClO}(aq)$. (b) Arrange the following in order of increasing strength as reducing agents in basic solution: $\text{Cr(OH)}_3(s)$, $\text{Fe}(s)$, $\text{Ca}(s)$, $\text{H}_2(g)$, $\text{Mn}(s)$.
- 20.81** Based on the data in Appendix E, (a) which of the following is the strongest oxidizing agent, and which is the weakest in acidic solution: Br_2 , H_2O_2 , Zn , $\text{Cr}_2\text{O}_7^{2-}$? (b) Which of the following is the strongest reducing agent, and which is the weakest in acidic solution: F^- , Zn , N_2H_5^+ , I_2 , NO ?
- 20.82** The standard reduction potential of $\text{Eu}^{2+}(aq)$ is -0.43 V . Using Appendix E, which of the following substances is capable of reducing $\text{Eu}^{3+}(aq)$ to $\text{Eu}^{2+}(aq)$ under standard conditions: Al, Co, H_2O_2 , N_2H_5^+ , $\text{H}_2\text{C}_2\text{O}_4$?

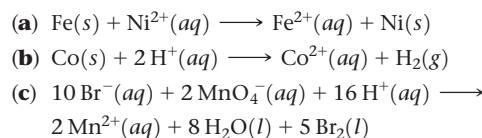
Free Energy and Redox Reactions (Section 20.5)

- 20.83** Given the following reduction half-reactions:



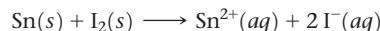
(a) Write balanced chemical equations for the oxidation of $\text{Fe}^{2+}(aq)$ by $\text{S}_2\text{O}_6^{2-}(aq)$, by $\text{N}_2\text{O}(aq)$, and by $\text{VO}_2^+(aq)$. (b) Calculate ΔG° for each reaction at 298 K. (c) Calculate the equilibrium constant K for each reaction at 298 K.

- 20.84** If the equilibrium constant for a one-electron redox reaction at 298 K is 2.2×10^{-5} , calculate the corresponding ΔG° and E° .
- 20.85** Using the standard reduction potentials listed in Appendix E, calculate the equilibrium constant for each of the following reactions at 298 K:



- 20.86** A cell has a standard cell potential of $+0.257\text{ V}$ at 298 K. What is the value of the equilibrium constant for the reaction (a) if $n = 1$? (b) if $n = 2$? (c) if $n = 3$?

- 20.87** A voltaic cell is based on the reaction



Under standard conditions, what is the maximum electrical work, in joules, that the cell can accomplish if 75.0 g of Sn is consumed?

Cell EMF under Nonstandard Conditions (Section 20.6)

- 20.88** (a) In the Nernst equation, what is the numerical value of the reaction quotient, Q , under standard conditions? (b) Can the Nernst equation be used at temperatures other than room temperature?

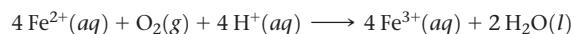
- 20.89** What is the effect on the emf of the cell shown in Figure 20.5, which has the overall reaction $\text{Zn}(s) + \text{Cu}^{2+}(aq) \longrightarrow \text{Cu}(s) + \text{Zn}^{2+}(aq)$, for each of the following changes? (a) Zinc chloride is added to the anode half-cell. (b) Copper chloride is added to the anode half-cell. (c) The surface area of the anode is cut to half. (d) The cell operates for one hour.

- 20.90** A voltaic cell is constructed that uses the following reaction and operates at 298 K:



- (a) What is the emf of this cell under standard conditions? (b) What is the emf of this cell when $[\text{Ni}^{2+}] = 3.00\text{ M}$ and $[\text{Zn}^{2+}] = 0.100\text{ M}$? (c) What is the emf of the cell when $[\text{Ni}^{2+}] = 0.200\text{ M}$ and $[\text{Zn}^{2+}] = 0.900\text{ M}$?

- 20.91** A voltaic cell utilizes the following reaction:



- (a) What is the emf of this cell under standard conditions? (b) What is the emf of this cell when $[\text{Fe}^{2+}] = 1.3\text{ M}$, $[\text{Fe}^{3+}] = 0.010\text{ M}$, $P_{\text{O}_2} = 50.0\text{ kPa}$, and the pH of the solution in the cathode half-cell is 3.50?

- 20.92** A voltaic cell is constructed with two Cu^{2+} – Cu electrodes. The two half-cells have $[\text{Cu}^{2+}] = 0.100\text{ M}$ and $[\text{Cu}^{2+}] = 1.00 \times 10^{-4}\text{ M}$, respectively. (a) Which electrode is the cathode of the cell? (b) What is the standard emf of the cell? (c) What is the cell emf for the concentrations given? (d) For each electrode, predict whether $[\text{Cu}^{2+}]$ will increase, decrease, or stay the same as the cell operates.

- 20.93** The cell in Figure 20.9 could be used to provide a measure of the pH in the cathode half-cell. Calculate the pH of the cathode half-cell solution if the cell emf at 298 K is measured to be $+0.663\text{ V}$ when $[\text{Zn}^{2+}] = 0.10\text{ M}$ and $P_{\text{H}_2} = 101.3\text{ kPa}$.

Batteries and Fuel Cells (Section 20.7)

- 20.94** During a period of discharge of a lead–acid battery, 300 g of $\text{PbO}_2(s)$ from the cathode is converted into $\text{PbSO}_4(s)$. (a) What mass of $\text{Pb}(s)$ is oxidized at the anode during this same period? (b) How many coulombs of electrical charge are transferred from Pb to PbO_2 ?

- 20.95** Heart pacemakers are often powered by lithium–silver chromate “button” batteries. The overall cell reaction is



- (a)** Lithium metal is the reactant at one of the electrodes of the battery. Is it the anode or the cathode? **(b)** Choose the two half-reactions from Appendix E that *most closely approximate* the reactions that occur in the battery. What standard emf would be generated by a voltaic cell based on these half-reactions? **(c)** The battery generates an emf of +3.5 V. How close is this value to the one calculated in part (b)? **(d)** Calculate the emf that would be generated at body temperature, 37 °C. How does this compare to the emf you calculated in part (b)?
- 20.96** **(a)** Suppose that an alkaline battery was manufactured using cadmium metal rather than zinc. What effect would this have on the cell emf? **(b)** What environmental advantage is provided by the use of nickel–metal hydride batteries over nickel–cadmium batteries?
- 20.97** In a Li-ion battery the composition of the cathode is LiCoO₂ when completely discharged. On charging, approximately 50% of the Li⁺ ions can be extracted from the cathode and transported to the graphite anode where they intercalate between the layers. **(a)** What is the composition of the cathode when the battery is fully charged? **(b)** If the LiCoO₂ cathode has a mass of 10 g (when fully discharged), how many coulombs of electricity can be delivered on completely discharging a fully charged battery?
- 20.98** **(a)** Which reaction is spontaneous in the hydrogen fuel cell: hydrogen gas plus oxygen gas makes water, or water makes hydrogen gas plus oxygen gas? **(b)** Using the standard reduction potentials in Appendix E, calculate the standard voltage generated by the hydrogen fuel cell in acidic solution.

Corrosion (Section 20.8)

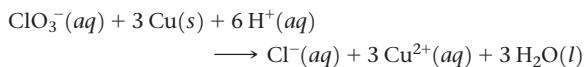
- 20.99** **(a)** Based on standard reduction potentials, would you expect copper metal to oxidize under standard conditions in the presence of oxygen and hydrogen ions? **(b)** When the Statue of Liberty was refurbished, Teflon spacers were placed between the iron skeleton and the copper metal on the surface of the statue. What role do these spacers play?

Additional Exercises

- 20.106** A disproportionation reaction is an oxidation–reduction reaction in which the same substance is oxidized and reduced. Complete and balance the following disproportionation reactions:
- (a)** Fe²⁺(aq) → Fe(s) + Fe³⁺(aq)
- (b)** Br₂(l) → Br[−](aq) + BrO₃[−](aq) (acidic solution)
- (c)** Cr³⁺(aq) → Cr₂O₇^{2−}(aq) + Cr(s) (acidic solution)
- (d)** NO(g) → N₂(g) + NO₃[−](aq) (acidic solution)
- 20.107** A common shorthand way to represent a voltaic cell is

anode|anode solution || cathode solution |cathode

A double vertical line represents a salt bridge or a porous barrier. A single vertical line represents a change in phase, such as from solid to solution. **(a)** Write the half-reactions and overall cell reaction represented by Fe|Fe²⁺||Ag⁺|Ag; calculate the standard cell emf using data in Appendix E. **(b)** Write the half-reactions and overall cell reaction represented by Zn|Zn²⁺||H⁺|H₂; calculate the standard cell emf using data in Appendix E and use Pt for the hydrogen electrode. **(c)** Using the notation just described, represent a cell based on the following reaction:



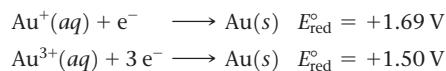
- 20.100** **(a)** Aluminum metal is used as a sacrificial anode to protect offshore pipelines in salt water from corrosion. Why is the aluminum referred to as a “sacrificial anode”? **(b)** Looking in Appendix E, suggest what metal the pipelines could be made from in order for aluminum to be successful as a sacrificial anode.
- 20.101** Iron corrodes to produce rust, Fe₂O₃, but other corrosion products that can form are Fe(O)(OH), iron oxyhydroxide, and magnetite, Fe₃O₄. **(a)** What is the oxidation number of Fe in iron oxyhydroxide, assuming oxygen’s oxidation number is −2? **(b)** The oxidation number for Fe in magnetite was controversial for a long time. If we assume that oxygen’s oxidation number is −2, and Fe has a unique oxidation number, what is the oxidation number for Fe in magnetite? **(c)** It turns out that there are two different kinds of Fe in magnetite that have different oxidation numbers. Suggest what these oxidation numbers are and what their relative stoichiometry must be, assuming oxygen’s oxidation number is −2.

Electrolysis (Section 20.9)

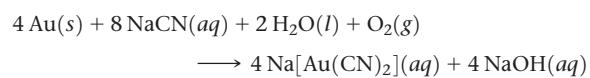
- 20.102** **(a)** What is electrolysis? **(b)** Are electrolysis reactions thermodynamically spontaneous? **(c)** What process occurs at the anode in the electrolysis of molten NaCl? **(d)** Why is sodium metal not obtained when an aqueous solution of NaCl undergoes electrolysis?
- 20.103** **(a)** A Cr³⁺(aq) solution is electrolyzed, using a current of 7.60 A. What mass of Cr(s) is plated out after 2.00 days? **(b)** What amperage is required to plate out 0.250 mol Cr from a Cr³⁺ solution in a period of 8.00 h?
- 20.104** **(a)** Calculate the mass of Li formed by electrolysis of molten LiCl by a current of 7.5×10^4 A flowing for a period of 24 h. Assume the electrolytic cell is 85% efficient. **(b)** What is the minimum voltage required to drive the reaction?
- 20.105** Metallic gold is collected from below the anode when a mixture of copper and gold metals is refined by electrolysis. Explain this behavior.

Pt is used as an inert electrode in contact with the ClO₃[−] and Cl[−]. Calculate the standard cell emf given: ClO₃[−](aq) + 6 H⁺(aq) + 6 e[−] → Cl[−](aq) + 3 H₂O(l); $E^\circ = 1.45$ V.

- 20.108** Predict whether the following reactions will be spontaneous in acidic solution under standard conditions: **(a)** oxidation of Cu to Cu²⁺ by I₂ (to form I[−]), **(b)** reduction of Fe²⁺ to Fe by H₂ (to form H⁺), **(c)** reduction of I₂ to I[−] by H₂O₂, **(d)** reduction of Ni²⁺ to Ni by Sn²⁺ (to form Sn⁴⁺).
- 20.109** Gold exists in two common positive oxidation states, +1 and +3. The standard reduction potentials for these oxidation states are

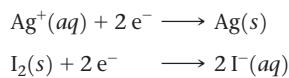


(a) Can you use these data to explain why gold does not tarnish in the air? **(b)** Suggest several substances that should be strong enough oxidizing agents to oxidize gold metal. **(c)** Miners obtain gold by soaking gold-containing ores in an aqueous solution of sodium cyanide. A very soluble complex ion of gold forms in the aqueous solution because of the redox reaction



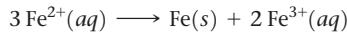
What is being oxidized, and what is being reduced in this reaction? (d) Gold miners then react the basic aqueous product solution from part (c) with Zn dust to get gold metal. Write a balanced redox reaction for this process. What is being oxidized, and what is being reduced?

- 20.110** A voltaic cell is constructed from an $\text{Cd}^{2+}(aq) - \text{Cd}(s)$ half-cell and an $\text{Ag}^+(aq) - \text{Ag}(s)$ half-cell. The initial concentration of $\text{Cd}^{2+}(aq)$ in the $\text{Cd}^{2+}(aq) - \text{Cd}(s)$ half-cell is $[\text{Cd}^{2+}] = 0.0200\text{ M}$. The initial cell voltage is $+1.102\text{ V}$. (a) By using data in Appendix E, calculate the standard emf of this voltaic cell. (b) Will the concentration of $\text{Cd}^{2+}(aq)$ increase or decrease as the cell operates? (c) What is the initial concentration of $\text{Ag}^+(aq)$ in the $\text{Ag}^+(aq) - \text{Ag}(s)$ half-cell?
- 20.111** A voltaic cell is constructed that uses the following half-cell reactions:

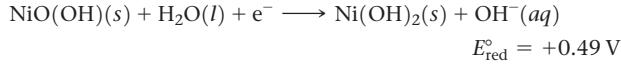
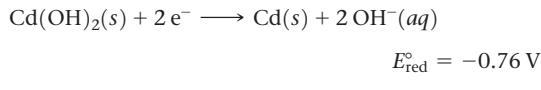


The cell is operated at 298 K with $[\text{Ag}^+] = 0.15\text{ M}$ and $[\text{I}^-] = 0.035\text{ M}$. (a) Determine E for the cell at these concentrations. (b) Which electrode is the anode of the cell? (c) Is the answer to part (b) the same as it would be if the cell were operated under standard conditions? (d) With $[\text{Ag}^+]$ equal to 0.15 M , at what concentration of I^- would the cell have zero potential?

- 20.112** Using data from Appendix E, calculate the equilibrium constant for the disproportionation of the iron(II) ion at room temperature:



- 20.113** (a) Write the reactions for the discharge and charge of a nickel–cadmium (nicad) rechargeable battery. (b) Given the following reduction potentials, calculate the standard emf of the cell:



(c) A typical nicad voltaic cell generates an emf of $+1.30\text{ V}$. Why is there a difference between this value and the one you calculated in part (b)? (d) Calculate the equilibrium constant for the overall nicad reaction based on this typical emf value.

- 20.114** The capacity of batteries such as a lithium-ion battery is expressed in units of milliamp-hours (mAh). A typical battery of this type yields a nominal capacity of 2000 mAh. (a) What quantity of interest to the consumer is being expressed by the units of mAh? (b) The starting voltage of a fresh lithium-ion battery is 3.60 V . The voltage decreases

during discharge and is 3.20 V when the battery has delivered its rated capacity. If we assume that the voltage declines linearly as current is withdrawn, estimate the total maximum electrical work the battery could perform during discharge.

- 20.115** Disulfides are compounds that have S–S bonds, like peroxides have O–O bonds. Thiols are organic compounds that have the general formula R–SH, where R is a generic hydrocarbon. The SH^- ion is the sulfur counterpart of hydroxide, OH^- . Two thiols can react to make a disulfide, R–S–S–R. (a) What is the oxidation state of sulfur in a thiol? (b) What is the oxidation state of sulfur in a disulfide? (c) If you react two thiols to make a disulfide, are you oxidizing or reducing the thiols? (d) If you wanted to convert a disulfide to two thiols, should you add a reducing agent or oxidizing agent to the solution? (e) Suggest what happens to the H's in the thiols when they form disulfides.

- 20.116** (a) How many coulombs are required to plate a layer of chromium metal 0.15 mm thick on an auto bumper with a total area of 0.40 m^2 from a solution containing CrO_4^{2-} ? The density of chromium metal is 7.20 g/cm^3 . (b) What current flow is required for this electroplating if the bumper is to be plated in 20.0 s ? (c) If the external source has an emf of $+5.5\text{ V}$ and the electrolytic cell is 60% efficient, how much electrical energy is expended to electroplate the bumper?

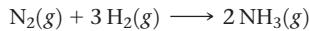
- 20.117** Magnesium is obtained by electrolysis of molten MgCl_2 . (a) Why is an aqueous solution of MgCl_2 not used in the electrolysis? (b) Several cells are connected in parallel by very large copper bars that convey current to the cells. Assuming that the cells are 96% efficient in producing the desired products in electrolysis, what mass of Mg is formed by passing a current of $97,000\text{ A}$ for a period of 24 h ?

- 20.118** Calculate the number of kilowatt-hours of electricity required to produce 500 kg of aluminum by electrolysis of Al^{3+} if the applied voltage is 5.00 V and the process is 50% efficient.

- 20.119** Some years ago a unique proposal was made to raise the *Titanic*. The plan involved placing pontoons within the ship using a surface-controlled submarine-type vessel. The pontoons would contain cathodes and would be filled with hydrogen gas formed by the electrolysis of water. It has been estimated that it would require about $7 \times 10^8\text{ mol}$ of H_2 to provide the buoyancy to lift the ship (*J. Chem. Educ.*, 1973, Vol. 50, 61). (a) How many coulombs of electrical charge would be required? (b) What is the minimum voltage required to generate H_2 and O_2 if the pressure on the gases at the depth of the wreckage (3 km) is 30 MPa ? (c) What is the minimum electrical energy required to raise the *Titanic* by electrolysis? (d) What is the minimum cost of the electrical energy required to generate the necessary H_2 if the electricity costs 85 cents per kilowatt-hour to generate at the site?

Integrative Exercises

- 20.120** The Haber process is the principal industrial route for converting nitrogen into ammonia:



(a) What is being oxidized, and what is being reduced? (b) Using the thermodynamic data in Appendix C, calculate the equilibrium constant for the process at room temperature. (c) Calculate the standard emf of the Haber process at room temperature.

- 20.121** In a galvanic cell the cathode is an $\text{Ag}^+(1.00\text{ M})/\text{Ag}(s)$ half-cell. The anode is a standard hydrogen electrode

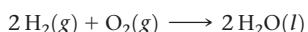
immersed in a buffer solution containing 0.10 M benzoic acid ($\text{C}_6\text{H}_5\text{COOH}$) and 0.050 M sodium benzoate ($\text{C}_6\text{H}_5\text{COO}^-\text{Na}^+$). The measured cell voltage is 1.030 V . What is the pK_a of benzoic acid?

- 20.122** Aqueous solutions of ammonia (NH_3) and bleach (active ingredient NaOCl) are sold as cleaning fluids, but bottles of both of them warn: “Never mix ammonia and bleach, as toxic gases may be produced.” One of the toxic gases that can be produced is chloroamine, NH_2Cl . (a) What is the oxidation number of chlorine in bleach? (b) What is the oxidation number of chlorine in chloroamine? (c) Is Cl oxidized,

reduced, or neither, upon the conversion of bleach to chloramine? (d) Another toxic gas that can be produced is nitrogen trichloride, NCl_3 . What is the oxidation number of N in nitrogen trichloride? (e) Is N oxidized, reduced, or neither, upon the conversion of ammonia to nitrogen trichloride?

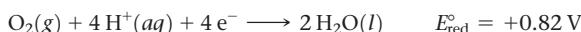
- 20.123** A voltaic cell is based on $\text{Cu}^{2+}(aq)/\text{Cu}(s)$ and $\text{Br}_2(l)/\text{Br}^-(aq)$ half-cells. (a) What is the standard emf of the cell? (b) Which reaction occurs at the cathode and which at the anode of the cell? (c) Use S° values in Appendix C and the relationship between cell potential and free-energy change to predict whether the standard cell potential increases or decreases when the temperature is raised above 25 °C. (The standard entropy of $\text{Cu}^{2+}(aq)$ is $S^\circ = -99.6 \text{ J/K}$)

- 20.124** Hydrogen gas has the potential for use as a clean fuel in reaction with oxygen. The relevant reaction is



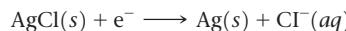
Consider two possible ways of utilizing this reaction as an electrical energy source: (i) Hydrogen and oxygen gases are combusted and used to drive a generator, much as coal is currently used in the electric power industry; (ii) hydrogen and oxygen gases are used to generate electricity directly by using fuel cells that operate at 85 °C. (a) Use data in Appendix C to calculate ΔH° and ΔS° for the reaction. We will assume that these values do not change appreciably with temperature. (b) Based on the values from part (a), what trend would you expect for the magnitude of ΔG for the reaction as the temperature increases? (c) What is the significance of the change in the magnitude of ΔG with temperature with respect to the utility of hydrogen as a fuel? (d) Based on the analysis here, would it be more efficient to use the combustion method or the fuel-cell method to generate electrical energy from hydrogen?

- 20.125** Cytochrome, a complicated molecule that we will represent as CyFe^{2+} , reacts with the air we breathe to supply energy required to synthesize adenosine triphosphate (ATP). The body uses ATP as an energy source to drive other reactions (Section 19.7). At pH 7.0 the following reduction potentials pertain to this oxidation of CyFe^{2+} :



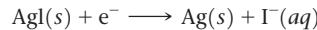
- (a) What is ΔG for the oxidation of CyFe^{2+} by air? (b) If the synthesis of 1.00 mol of ATP from adenosine diphosphate (ADP) requires a ΔG of 37.7 kJ, how many moles of ATP are synthesized per mole of O_2 ?

- 20.126** The standard potential for the reduction of $\text{AgCl}(s)$ is +0.222 V.



Using this value and the electrode potential for $\text{Ag}^+(aq)$, calculate the K_{sp} for AgCl .

- 20.127** The K_{sp} value for $\text{Agl}(s)$ is 8.3×10^{-17} . By using this value together with an electrode potential from Appendix E, determine the value of the standard reduction potential for the reaction



- 20.128** A student designs an ammeter (device that measures electrical current) that is based on the electrolysis of water into hydrogen and oxygen gases. When electrical current of unknown magnitude is run through the device for 90 min, 32.5 mL of water-saturated $\text{H}_2(g)$ is collected. The temperature of the system is 20 °C, and the atmospheric pressure is 101.3 kPa. What is the magnitude of the average current in amperes?

Design an Experiment

You are asked to construct a voltaic cell that would simulate an alkaline battery by providing an electrical output of 1.50 V at the beginning of its discharge. After you complete it, your voltaic cell will be used to power an external device that draws a constant current of 0.50 amperes for 2.0 hours. You are given the following supplies: electrodes of each transition metal from manganese to zinc, the chloride salts of the +2 transition metal ions from Mn^{2+} to Zn^{2+} (MnCl_2 , FeCl_2 , CoCl_2 , NiCl_2 , CuCl_2 , and ZnCl_2), two 100 mL beakers, a salt bridge, a voltmeter, and wires to make electrical connections between the electrodes and the voltmeter. (a) Sketch out your

voltaic cell labeling the metal used for each electrode and the type and concentration of the solutions in which each electrode is immersed. Be sure to describe how many grams of the salt are dissolved and the total volume of solution in each beaker. (b) What will be the concentrations of the transition metal ion in each solution at the end of the 2 h discharge? (c) What voltage will the cell register at the end of the discharge? (d) How long would your cell run before it died because the reactant in one of the half-cells was completely consumed? Assume the current stays constant throughout the discharge.