CHAPTER 19

Oxidation-Reduction Reactions

Oxidation-reduction reactions propel rockets into space.

Oxidation and Reduction

SECTION 19-1

OBJECTIVES

- Assign oxidation numbers to reactant and product species.
- Define *oxidation* and *reduction.*
- Explain what an oxidation-reduction reaction (redox reaction) is.

Oxidation-reduction reactions involve a transfer of electrons. Oxidation involves the loss of electrons, whereas reduction involves the gain of electrons. Reduction and oxidation half-reactions must occur simultaneously. These processes can be identified through the understanding and use of oxidation numbers (oxidation states).

Oxidation States

Oxidation states were defined in Chapter 7. The oxidation number assigned to an element in a molecule is based on the distribution of electrons in that molecule. The rules by which oxidation numbers are assigned were given in Chapter 7. These rules are summarized in Table 19-1.

TABLE 19-1 ***Rules for Assigning Oxidation Numbers***

Rule	Example
1. The oxidation number of any uncombined element is 0.	The oxidation number of Na(*s*) is 0.
2. The oxidation number of a monatomic ion equals the charge on the ion.	The oxidation number of Cl^- is –1.
3. The more electronegative element in a binary compound is assigned the number equal to the charge it would have if it were an ion.	The oxidation number of O in NO is –2.
4. The oxidation number of fluorine in a compound is always –1.	The oxidation number of F in LiF is –1.
5. Oxygen has an oxidation number of –2 unless it is combined with F, when it is +2, or it is in a peroxide, such as H_2O_2, when it is –1.	The oxidation number of O in NO_2 is –2.
6. The oxidation state of hydrogen in most of its compounds is +1 unless it is combined with a metal, in which case it is –1.	The oxidation number of H in LiH is –1.
7. In compounds, Group 1 and 2 elements and aluminum have oxidation numbers of +1, +2, and +3, respectively.	The oxidation number of Ca in $CaCO_3$ is +2.
8. The sum of the oxidation numbers of all atoms in a neutral compound is 0.	The oxidation number of C in $CaCO_3$ is +4.
9. The sum of the oxidation numbers of all atoms in a polyatomic ion equals the charge of the ion.	The oxidation number of P in $H_2PO_4^-$ is +5.

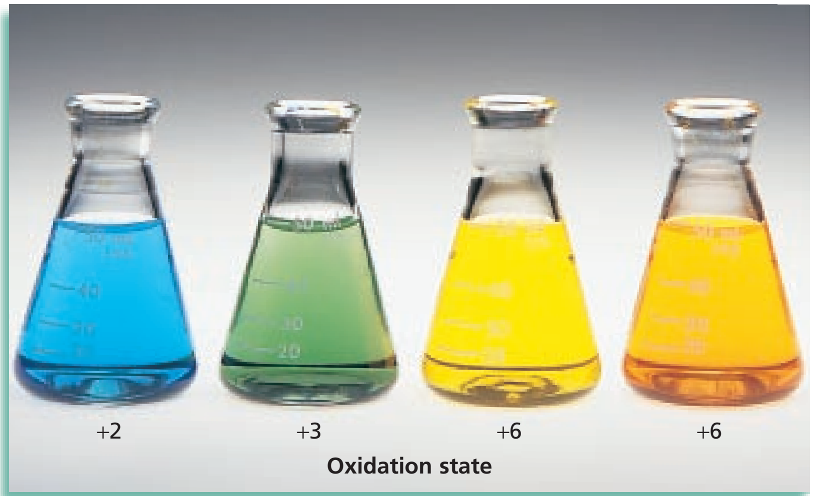

FIGURE 19-1 The color of solutions containing chromium compounds changes with the oxidation state of chromium.

Chromium provides a very visual example of different oxidation numbers. Different oxidation states of chromium have dramatically different colors, as can be seen in Figure 19-1. The chromium(II) chloride solution is blue, chromium(III) chloride solution is green, potassium chromate solution is yellow, and potassium dichromate solution is orange.

Oxidation

Reactions in which the atoms or ions of an element experience an increase in oxidation state are **oxidation** *processes.* The combustion of metallic sodium in an atmosphere of chlorine gas is shown in Figure 19-2. The sodium ions and chloride ions produced during this strongly exothermic reaction form a cubic crystal lattice in which sodium cations are ionically bonded to chloride anions. The chemical equation for this reaction is written as follows.

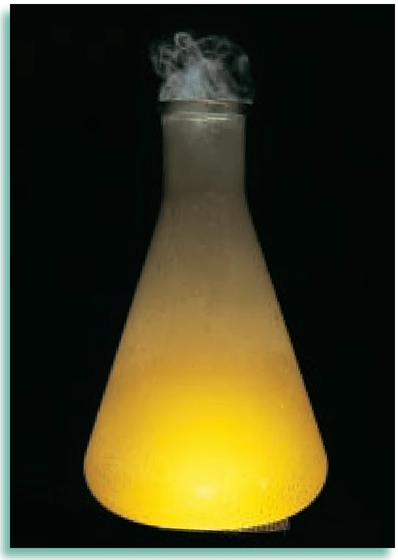

FIGURE 19-2 Sodium and chlorine react violently to form NaCl. The synthesis of NaCl from its elements illustrates the oxidation-reduction process.

$$2\text{Na}(s) + \text{Cl}_2(g) \longrightarrow 2\text{NaCl}(s)$$

The formation of sodium ions illustrates an oxidation process because each sodium atom loses an electron to become a sodium ion. The oxidation state is represented by placing an oxidation number above the symbol of the atom and the ion.

$$\overset{0}{\text{Na}} \longrightarrow \overset{+1}{\text{Na}^+} + e^-$$

The oxidation state of sodium has changed from 0, its elemental state, to the +1 state of the ion (Rules 1 and 7, Table 19-1). *A species whose oxidation number increases is* **oxidized.** The sodium atom is *oxidized* to a sodium ion.

Reduction

Reactions in which the oxidation state of an element decreases are **reduction** *processes.* Consider the behavior of chlorine in its reaction with sodium. Each chlorine atom accepts an electron and becomes a chloride ion. The oxidation state of chlorine decreases from 0 to –1 for the chloride ion (Rules 1 and 2, Table 19-1).

$$\overset{0}{\mathrm{Cl}_2} + 2e^- \longrightarrow 2\overset{-1}{\mathrm{Cl}^-}$$

A species that undergoes a decrease in oxidation state is **reduced.** The chlorine atom is reduced to the chloride ion.

FIGURE 19-3 Copper is oxidized and nitrogen monoxide is produced when this penny is placed in a nitric acid solution.

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Oxidation and Reduction as a Process

Electrons are produced in oxidation and acquired in reduction. Therefore, for oxidation to occur during a chemical reaction, reduction must occur simultaneously. Furthermore, the number of electrons produced in oxidation must equal the number of electrons acquired in reduction. This makes sense when you recall that electrons are negatively charged and that for charge to be conserved, the number of electrons lost must equal the number of electrons gained. You learned in Chapter 8 that mass is conserved in any chemical reaction. Therefore, the masses of the elements that undergo oxidation and reduction and the electrons that are exchanged are conserved.

A transfer of electrons causes changes in the oxidation states of one or more elements. *Any chemical process in which elements undergo changes in oxidation number is an* **oxidation-reduction reaction.** This name is often shortened to **redox reaction.** An example of a redox reaction can be seen in Figure 19-3, in which copper is being oxidized and NO_3^- from nitric acid is being reduced. *The part of the reaction involving oxidation or reduction alone can be written as a* **half-reaction.** The overall equation for a redox reaction is the sum of two half-reactions. Because the number of electrons involved is the same for oxidation and reduction, they cancel each other out and do not appear in the overall chemical equation. Equations for the reaction between nitric acid and copper illustrate the relationship between half-reactions and the overall redox reaction.

$$\begin{array}{rl}
3\overset{0}{\mathrm{Cu}} \longrightarrow 3\overset{+2}{\mathrm{Cu}}{}^{2+} + 6e^- & \text{(oxidation half-reaction)} \\
2\overset{+5}{\mathrm{N}}\overset{-2}{\mathrm{O}}{}_3^- + 6e^- + 8\overset{+1}{\mathrm{H}}{}^+ \longrightarrow 2\overset{+2}{\mathrm{N}}\overset{-2}{\mathrm{O}} + 4\overset{+1}{\mathrm{H}}{}_2\overset{-2}{\mathrm{O}} & \text{(reduction half-reaction)} \\
\hline
3\overset{0}{\mathrm{Cu}} + 2\overset{+5}{\mathrm{N}}\mathrm{O}_3^- + 8\mathrm{H}^+ \longrightarrow 3\overset{+2}{\mathrm{Cu}}{}^{2+} + 2\overset{+2}{\mathrm{N}}\mathrm{O} + 4\mathrm{H}_2\mathrm{O} & \text{(redox reaction)}
\end{array}$$

Notice that electrons lost in oxidation appear on the product side of the oxidation half-reaction. Electrons are gained in reduction and appear as reactants in the reduction half-reaction. When metallic copper reacts in nitric acid, three copper atoms are oxidized to Cu^{2+} ions as two nitrogen atoms are reduced from a +5 oxidation state to a +2 oxidation state. Atoms are conserved. This is illustrated by the balanced chemical equation for the reaction between copper and nitric acid.

If none of the atoms in a reaction change oxidation state, the reaction is *not* a redox reaction. For example, sulfur dioxide gas, SO_2, dissolves in water to form an acidic solution containing a low concentration of sulfur*ous* acid, H_2SO_3.

$$\overset{+4}{\mathrm{S}}\overset{-2}{\mathrm{O}_2} + \overset{+1}{\mathrm{H}_2}\overset{-2}{\mathrm{O}} \longrightarrow \overset{+1}{\mathrm{H}_2}\overset{+4}{\mathrm{S}}\overset{-2}{\mathrm{O}_3}$$

The oxidation states of all elemental species remain unchanged in this composition reaction. Therefore, it is *not* a redox reaction.

When a solution of sodium chloride is added to a solution of silver nitrate, an ion-exchange reaction occurs and white silver chloride precipitates.

$$\overset{+1}{\mathrm{Na}^+} + \overset{-1}{\mathrm{Cl}^-} + \overset{+1}{\mathrm{Ag}^+} + \overset{+5}{\mathrm{N}}\overset{-2}{\mathrm{O}_3^-} \longrightarrow \overset{+1}{\mathrm{Na}^+} + \overset{+5}{\mathrm{N}}\overset{-2}{\mathrm{O}_3^-} + \overset{+1}{\mathrm{Ag}}\overset{-1}{\mathrm{Cl}}$$

The oxidation state of each monatomic ion remains unchanged. Again, this reaction is not an oxidation-reduction reaction.

Redox Reactions and Covalent Bonds

Both the synthesis of NaCl from its elements and the reaction between copper and nitric acid involve ionic bonding. Substances with covalent bonds also undergo redox reactions. An oxidation number, unlike an ionic charge, has no physical meaning. That is, the oxidation number assigned to a particular atom is based on its electronegativity relative to the other atoms to which it is bonded in a given molecule; it is not based on any real charge on the atom. For example, an ionic charge of 1– results from the complete gain of one electron by an atom or other neutral species, whereas an oxidation state of –1 means an increased attraction for a bonding electron. A change in oxidation number does not require a change in actual charge.

When hydrogen burns in chlorine, a covalent bond forms from the sharing of two electrons. The two bonding electrons in the hydrogen chloride molecule are not shared equally. Rather, the pair of electrons is more strongly attracted to the chlorine atom because of its higher electronegativity.

$$\overset{0}{\mathrm{H}_2} + \overset{0}{\mathrm{Cl}_2} \longrightarrow 2\overset{+1}{\mathrm{H}}\overset{-1}{\mathrm{Cl}}$$

As specified by Rule 3 in Table 19-1, chlorine in HCl is assigned an oxidation number of –1. Thus, the oxidation number for the chlorine atoms changes from 0, its oxidation number in the elemental state, to –1; chlorine atoms are reduced. As specified by Rule 1, the oxidation number of each hydrogen atom in the hydrogen molecule is 0. As specified by Rule 6, the oxidation state of the hydrogen atom in the HCl molecule is +1;

the hydrogen atom is oxidized. No electrons have been totally lost or gained by either atom. Hydrogen has donated a share of its bonding electron to the chlorine; it has not completely transferred that electron. The assignment of oxidation numbers allows the determination of the partial transfer of electrons in compounds that are not ionic. Thus, increases or decreases in oxidation number can be seen in terms of complete or partial loss or gain of electrons.

Reactants and products in redox reactions are not limited to monatomic ions and uncombined elements. Elements in molecular compounds or polyatomic ions can also be oxidized and reduced if they have more than one non-zero oxidation state. An example of this is provided in the reaction between the copper penny and nitric acid when the nitrate ion, NO_3^-, is converted to nitrogen monoxide, NO. Nitrogen is reduced in this reaction. Usually we refer to the oxidation or reduction of the entire molecule or ion. Instead of saying the nitrogen atom is reduced, we say the nitrate ion is reduced to nitrogen monoxide.

$$\cdots + \overset{+5}{NO_3^-} \longrightarrow \overset{+2}{NO} + \cdots$$

SECTION REVIEW

1. How are oxidation numbers assigned?

2. Label each of the following half-reactions as either an oxidation or a reduction half-reaction:

a. $\overset{0}{Br_2} + 2e^- \longrightarrow 2\overset{-1}{Br^-}$

b. $\overset{0}{Na} \longrightarrow \overset{+1}{Na^+} + e^-$

c. $2\overset{-1}{Cl^-} \longrightarrow \overset{0}{Cl_2} + 2e^-$

d. $\overset{0}{Cl_2} + 2e^- \longrightarrow 2\overset{-1}{Cl^-}$

e. $\overset{+1}{Na^+} + e^- \longrightarrow \overset{0}{Na}$

f. $\overset{0}{Fe} \longrightarrow \overset{+2}{Fe^{2+}} + 2e^-$

g. $\overset{+2}{Cu^{2+}} + 2e^- \longrightarrow \overset{0}{Cu}$

h. $\overset{+3}{Fe^{3+}} + e^- \longrightarrow \overset{+2}{Fe^{2+}}$

3. Which of the following equations represent redox reactions?
a. $2KNO_3(s) \longrightarrow 2KNO_2(s) + O_2(g)$
b. $H_2(g) + CuO(s) \longrightarrow Cu(s) + H_2O(l)$
c. $NaOH(aq) + HCl(aq) \longrightarrow NaCl(aq) + H_2O(l)$
d. $H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$
e. $SO_3(g) + H_2O(l) \longrightarrow H_2SO_4(aq)$

4. For each redox equation identified in the previous question, determine which element is oxidized and which is reduced.

5. Use the equations below for the redox reaction between aluminum metal and sodium metal to answer the following.

$$\begin{array}{ll}
3\overset{0}{Na} \longrightarrow 3\overset{+1}{Na^+} + 3e^- & \text{(oxidation)} \\
\overset{+3}{Al^{3+}} + 3e^- \longrightarrow \overset{0}{Al} & \text{(reduction)} \\
\hline
3\overset{0}{Na} + \overset{+3}{Al^{3+}} \longrightarrow 3\overset{+1}{Na^+} + \overset{0}{Al} & \text{(redox reaction)}
\end{array}$$

a. Explain how this reaction illustrates that charge is conserved in a redox reaction.
b. Explain how this reaction illustrates that mass is conserved in a redox reaction.
c. Explain why electrons do not appear as reactants or products in the combined equation.

Skunk-Spray Remedy

So that pretty black cat with the white stripe down its back wasn't a cat after all? Well, hold off on dumping Fido into a tomato-juice bath. Chemistry has a much better way of conquering skunk spray.

Paul Krebaum, the inventor of a new deskunking formula, says that while working as a materials engineer, he constantly had to deal with the less-than-pleasant smell of the hydrogen sulfide gas that was released from one of his experiments. Mr. Krebaum was losing popularity with his neighbors, and venting off the gas only partially solved the problem. A better solution, he decided, would be to find a way to eliminate the smell entirely.

Mr. Krebaum rifled through his old chemistry books and found that hydrogen peroxide could oxidize these sulfur-containing compounds to much less smelly components. He immediately whipped up a hydrogen peroxide mixture, and it worked like a charm.

The reaction by which the hydrogen sulfide was destroyed, producing sulfate compounds that do not have the unpleasant odor, can be seen in the following equation.

$$2NaOH + 4H_2O_2 + H_2S \longrightarrow Na_2SO_4 + 6H_2O$$

"The receptors that are in your nose are sensitive to sulfur in its low oxidation state," says Mr. Krebaum. "However, they are not sensitive to sulfur in its high oxidation state."

Skunk spray gets its odor from chemicals called mercaptans.

Some time later, a friend of Mr. Krebaum's complained to him that a skunk had sprayed his pet. Because the odor in a skunk's spray also comes from compounds containing sulfur in a low oxidation state, Mr. Krebaum thought his solution might also work on this age-old problem. He mixed up a milder version to try out on the pet: 1 quart 3% hydrogen peroxide solution, 1/4 cup baking soda, and 1 teaspoon liquid soap. His friend tried it out, and the result was one wet and unhappy—but much less smelly—pet.

Mr. Krebaum says that the hydrogen peroxide in the remedy actually oxidizes the compounds, while the baking soda reduces the acidity of the mixture and the soap helps to wash out the greasy skunk spray. The reaction that occurs can be seen in the following equation. The symbol *R* represents all the other elements in the sulfur-containing compound found in skunk spray.

$$RSH + 3H_2O_2 + NaHCO_3 \longrightarrow RSO_3Na + 4H_2O + CO_2$$

The pet should be washed thoroughly with the mixture, taking care to avoid its eyes. If the mixture is left on for a few minutes—long enough for the reaction to occur—and then rinsed away with tap water, the smell will disappear.

The formula does not bleach or have any other negative side effects. Mr. Krebaum does have one warning: mix the formula just before using it because the mixture breaks down quickly. The reaction releases oxygen, so the formula should not be put into a sealed container; it will build up pressure and could eventually blow the top. For these reasons, bottles of "Krebaum's Skunkinator" will not be appearing on drug-store shelves any time soon.

How did Paul Krebaum's research into the properties of H_2S result in a benefit to dog owners?

SECTION 19-2

Balancing Redox Equations

OBJECTIVES

- Explain what must be conserved in redox equations.
- Balance redox equations by using the half-reaction method.

Equations for simple redox reactions can be balanced by inspection, which you learned to do in Chapter 8. Most redox equations, however, require more systematic methods. The equation-balancing process requires the use of oxidation numbers. In a balanced equation, both charge and mass are conserved. Although oxidation and reduction half-reactions occur together, their reaction equations are balanced separately, then combined to give the balanced redox-reaction equation.

Half-Reaction Method

The *half-reaction method,* or ion-electron method, for balancing redox equations consists of seven steps. Oxidation numbers are assigned to all atoms and polyatomic ions to determine which species are part of the redox process. The oxidation and reduction equations are balanced separately for mass and charge. They are then added together to produce a complete balanced equation. These seven steps are applied to balance the reaction of hydrogen sulfide and nitric acid. Sulfuric acid, nitrogen dioxide, and water are the products of the reaction.

1. ***Write the formula equation if it is not given in the problem. Then write the ionic equation.***

Formula equation: $H_2S + HNO_3 \longrightarrow H_2SO_4 + NO_2 + H_2O$

Ionic equation: $H_2S + H^+ + NO_3^- \longrightarrow 2H^+ + SO_4^{2-} + NO_2 + H_2O$

2. ***Assign oxidation numbers. Delete substances containing only elements that do not change oxidation state.***

$$\overset{+1\,-2}{H_2S} + \overset{+1}{H^+} + \overset{+5\,-2}{NO_3^-} \longrightarrow \overset{+1}{2H^+} + \overset{+6\,-2}{SO_4^{2-}} + \overset{+4\,-2}{NO_2} + \overset{+1\,-2}{H_2O}$$

The sulfur changes oxidation state from −2 to +6. The nitrogen changes oxidation state from +5 to +4. The other substances are deleted.

$$\overset{+1\,-2}{H_2S} + \overset{+5\,-2}{NO_3^-} \longrightarrow \overset{+6\,-2}{SO_4^{2-}} + \overset{+4\,-2}{NO_2}$$

The remaining species are used in step 3.

3. ***Write the half-reaction for oxidation.*** In this example, the sulfur is being oxidized.

$$H_2\overset{-2}{S} \longrightarrow \overset{+6}{S}O_4^{2-}$$

- ***Balance the atoms.*** To balance the oxygen in this half-reaction, H_2O must be added to the left side. This gives 10 extra hydrogen atoms on that side of the equation. Therefore, 10 hydrogen ions are added to the right side. In basic solution, OH^- ions and water may be used to balance atoms.

$$H_2\overset{-2}{S} + 4H_2O \longrightarrow \overset{+6}{S}O_4^{2-} + 10H^+$$

- ***Balance the charge.*** Electrons are added to the side having the greater positive net charge. The left side of the equation has no net charge; the right side has a net charge of 8+. For the charges to balance, each side must have the same net charge. Therefore, 8 electrons are added to the product side so that it has no charge and balances with the reactant side of the equation. Notice that the oxidation of sulfur from a state of –2 to +6 indicates a loss of 8 electrons.

$$H_2\overset{-2}{S} + 4H_2O \longrightarrow \overset{+6}{S}O_4^{2-} + 10H^+ + 8e^-$$

The oxidation half-reaction is now balanced.

4. ***Write the half-reaction for reduction.*** In this example, nitrogen is being reduced from a +5 state to a +4 state.

$$\overset{+5}{N}O_3^- \longrightarrow \overset{+4}{N}O_2$$

- ***Balance the atoms.*** H_2O must be added to the product side of the reaction to balance the oxygen atoms. Therefore, two hydrogen ions must be added to the reactant side to balance the hydrogen atoms.

$$\overset{+5}{N}O_3^- + 2H^+ \longrightarrow \overset{+4}{N}O_2 + H_2O$$

- ***Balance the charge.*** Electrons are added to the side having the greater positive net charge. The left side of the equation has a net charge of 1+. Therefore, 1 electron must be added to this side to balance the charge.

$$\overset{+5}{N}O_3^- + 2H^+ + e^- \longrightarrow \overset{+4}{N}O_2 + H_2O$$

The reduction half-reaction is now balanced.

5. ***Conserve charge by adjusting the coefficients in front of the electrons so that the number lost in oxidation equals the number gained in reduction.*** Write the ratio of the number of electrons lost to the number of electrons gained.

$$\frac{e^- \text{ lost in oxidation}}{e^- \text{ gained in reduction}} = \frac{8}{1}$$

This ratio is already in its lowest terms. If it were not, it would need to be reduced. Multiply the oxidation half-reaction by 1 (it remains unchanged) and the reduction half-reaction by 8. The number of electrons lost now equals the number of electrons gained.

$$1\left(H_2\overset{-2}{S} + 4H_2O \longrightarrow \overset{+6}{S}O_4^{2-} + 10H^+ + 8e^-\right)$$

$$8\left(\overset{+5}{N}O_3^- + 2H^+ + e^- \longrightarrow \overset{+4}{N}O_2 + H_2O\right)$$

6. ***Combine the half-reactions, and cancel out anything common to both sides of the equation.***

$$H_2\overset{-2}{S} + 4H_2O \longrightarrow \overset{+6}{S}O_4^{2-} + 10H^+ + 8e^-$$

$$8\overset{+5}{N}O_3^- + 16H^+ + 8e^- \longrightarrow 8\overset{+4}{N}O_2 + 8H_2O$$

$$8\overset{+5}{N}O_3^- + \overset{6}{\cancel{16}}H^+ + \cancel{8e^-} + H_2\overset{-2}{S} + \cancel{4H_2O} \longrightarrow$$

$$8\overset{+4}{N}O_2 + \overset{4}{\cancel{8}}H_2O + \overset{+6}{S}O_4^{2-} + \cancel{10H^+} + \cancel{8e^-}$$

Each side of the above equation has $10H^+$, $8e^-$, and $4H_2O$. These cancel each other out and do not appear in the balanced equation.

$$8\overset{+5}{N}O_3^- + H_2\overset{-2}{S} + 6H^+ \longrightarrow 8\overset{+4}{N}O_2 + 4H_2O + \overset{+6}{S}O_4^{2-}$$

7. ***Combine ions to form the compounds shown in the original formula equation. Check to ensure that all other ions balance.*** The NO_3^- ion appeared as nitric acid in the original equation. There are only 6 hydrogen ions to pair with the 8 nitrate ions. Therefore, 2 hydrogen ions must be added to complete this formula. If 2 hydrogen ions are added to the left side of the equation, 2 hydrogen ions must also be added to the right side of the equation.

$$8HNO_3 + H_2S \longrightarrow 8NO_2 + 4H_2O + SO_4^{2-} + 2H^+$$

The sulfate ion appeared as sulfuric acid in the original equation. The hydrogen ions added to the right side are used to complete the formula for sulfuric acid.

$$8HNO_3 + H_2S \longrightarrow 8NO_2 + 4H_2O + H_2SO_4$$

A final check must be made to ensure that all elements are correctly balanced.

FIGURE 19-4 As a $KMnO_4$ solution is titrated into an acidic solution of $FeSO_4$, deep purple MnO_4^- ions are reduced to colorless Mn^{2+} ions. When all Fe^{2+} ions are oxidized, MnO_4^- ions are no longer reduced to colorless Mn^{2+} ions. Thus, the first faint appearance of the MnO_4^- color indicates the end point of the titration.

SAMPLE PROBLEM 19-1

Write a balanced equation for the reaction shown in Figure 19-4. A deep purple solution of potassium permanganate is titrated into a colorless solution of iron(II) sulfate and sulfuric acid. The products are iron(III) sulfate, manganese(II) sulfate, potassium sulfate, and water—all of which are colorless.

SOLUTION

1. *Write the formula equation if it is not given in the problem. Then write the ionic equation.*

$$KMnO_4 + FeSO_4 + H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + MnSO_4 + K_2SO_4 + H_2O$$

$$K^+ + MnO_4^- + Fe^{2+} + SO_4^{2-} + 2H^+ + SO_4^{2-} \longrightarrow$$
$$2Fe^{3+} + 3SO_4^{2-} + Mn^{2+} + SO_4^{2-} + 2K^+ + SO_4^{2-} + H_2O$$

2. *Assign oxidation numbers to each element and ion. Delete substances containing an element that does not change oxidation state.*

$$\overset{+1}{K}{}^+ + \overset{+7}{Mn}\overset{-2}{O}{}_4^- + \overset{+2}{Fe}{}^{2+} + \overset{+6}{S}\overset{-2}{O}{}_4^{2-} + 2\overset{+1}{H}{}^+ + \overset{+6}{S}\overset{-2}{O}{}_4^{2-} \longrightarrow$$
$$2\overset{+3}{Fe}{}^{3+} + 3\overset{+6}{S}\overset{-2}{O}{}_4^{2-} + \overset{+2}{Mn}{}^{2+} + \overset{+6}{S}\overset{-2}{O}{}_4^{2-} + 2\overset{+1}{K}{}^+ + \overset{+6}{S}\overset{-2}{O}{}_4^{2-} + \overset{+1}{H}{}_2\overset{-2}{O}$$

Only ions or molecules whose oxidation numbers change are retained.

$$\overset{+7}{Mn}\overset{-2}{O}{}_4^- + \overset{+2}{Fe}{}^{2+} \longrightarrow \overset{+3}{Fe}{}^{3+} + \overset{+2}{Mn}{}^{2+}$$

3. *Write the half-reaction for oxidation.* The iron shows the increase in oxidation number. Therefore, it is oxidized.

$$\overset{+2}{Fe}{}^{2+} \longrightarrow \overset{+3}{Fe}{}^{3+}$$

- *Balance the mass.* The mass is already balanced.

- *Balance the charge.*

$$\overset{+2}{Fe}{}^{2+} \longrightarrow \overset{+3}{Fe}{}^{3+} + e^-$$

4. *Write the half-reaction for reduction.* Manganese shows a change in oxidation number from +7 to +2. It is reduced.

$$\overset{+7}{Mn}O_4^- \longrightarrow \overset{+2}{Mn}{}^{2+}$$

- *Balance the mass.* Water and hydrogen ions must be added to balance the oxygen atoms in the permanganate ion.

$$\overset{+7}{Mn}O_4^- + 8H^+ \longrightarrow \overset{+2}{Mn}{}^{2+} + 4H_2O$$

- *Balance the charge.*

$$\overset{+7}{Mn}O_4^- + 8H^+ + 5e^- \longrightarrow \overset{+2}{Mn}{}^{2+} + 4H_2O$$

5. *Adjust the coefficients to conserve charge.*

$$\frac{e^- \text{ lost in oxidation}}{e^- \text{ gained in reduction}} = \frac{1}{5}$$

$$5(Fe^{2+} \longrightarrow Fe^{3+} + e^-)$$
$$1(MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O)$$

6. *Combine the half-reactions and cancel.*

$$
\begin{array}{r}
5\mathrm{Fe}^{2+} \longrightarrow 5\mathrm{Fe}^{3+} + 5e^- \\
\mathrm{MnO}_4^- + 8\mathrm{H}^+ + 5e^- \longrightarrow \mathrm{Mn}^{2+} + 4\mathrm{H}_2\mathrm{O} \\
\hline
\mathrm{MnO}_4^- + 5\mathrm{Fe}^{2+} + 8\mathrm{H}^+ + \cancel{5e^-} \longrightarrow \mathrm{Mn}^{2+} + 5\mathrm{Fe}^{3+} + 4\mathrm{H}_2\mathrm{O} + \cancel{5e^-}
\end{array}
$$

7. *Combine ions to form compounds from the original equation.* The iron(III) product appears in the original equation as $\mathrm{Fe}_2(\mathrm{SO}_4)_3$. Every iron(III) sulfate molecule requires two iron ions. Therefore, the entire equation must be multiplied by 2 to provide an even number of iron ions.

$$
\begin{array}{c}
2(5\mathrm{Fe}^{2+} + \mathrm{MnO}_4^- + 8\mathrm{H}^+ \longrightarrow 5\mathrm{Fe}^{3+} + \mathrm{Mn}^{2+} + 4\mathrm{H}_2\mathrm{O}) \\
10\mathrm{Fe}^{2+} + 2\mathrm{MnO}_4^- + 16\mathrm{H}^+ \longrightarrow 10\mathrm{Fe}^{3+} + 2\mathrm{Mn}^{2+} + 8\mathrm{H}_2\mathrm{O}
\end{array}
$$

The iron(II), iron(III), manganese(II), and 2 hydrogen ions in the original equation are paired with sulfate ions. Iron(II) sulfate requires 10 sulfate ions, and sulfuric acid requires 8 sulfate ions. To balance the equation, 18 sulfate ions must be added to each side. On the product side, 15 of these ions form iron(III) sulfate, and 2 of them form manganese(II) sulfate. That leaves 1 sulfate ion unaccounted for. The permanganate ion requires the addition of 2 potassium ions to each side. These 2 potassium ions form potassium sulfate on the product side of the reaction.

$$10\mathrm{FeSO}_4 + 2\mathrm{KMnO}_4 + 8\mathrm{H}_2\mathrm{SO}_4 \longrightarrow 5\mathrm{Fe}_2(\mathrm{SO}_4)_3 + 2\mathrm{MnSO}_4 + \mathrm{K}_2\mathrm{SO}_4 + 8\mathrm{H}_2\mathrm{O}$$

Final inspection shows that atoms and charges are balanced.

PRACTICE

1. Copper reacts with hot, concentrated sulfuric acid to form copper(II) sulfate, sulfur dioxide, and water. Write and balance the equation for this reaction.	*Answer* $\mathrm{Cu} + 2\mathrm{H}_2\mathrm{SO}_4 \longrightarrow \mathrm{CuSO}_4 + \mathrm{SO}_2 + 2\mathrm{H}_2\mathrm{O}$
2. Write and balance the equation for the reaction between nitric acid and potassium iodide. The products are potassium nitrate, iodine, nitrogen monoxide, and water.	*Answer* $8\mathrm{HNO}_3 + 6\mathrm{KI} \longrightarrow 6\mathrm{KNO}_3 + 3\mathrm{I}_2 + 2\mathrm{NO} + 4\mathrm{H}_2\mathrm{O}$
3. Rust occurs when iron reacts with oxygen and water to form iron(III) hydroxide. Write and balance the equation for this reaction.	*Answer* $4\mathrm{Fe} + 3\mathrm{O}_2 + 6\mathrm{H}_2\mathrm{O} \longrightarrow 4\mathrm{Fe(OH)}_3$

SECTION REVIEW

1. What two quantities are conserved in redox equations?

2. Why do we add H^+ and $\mathrm{H}_2\mathrm{O}$ to some half-reactions and OH^- and $\mathrm{H}_2\mathrm{O}$ to others?

3. Balance the following oxidation-reduction reaction:

$$\mathrm{Na}_2\mathrm{SnO}_2 + \mathrm{Bi(OH)}_3 \longrightarrow \mathrm{Bi} + \mathrm{Na}_2\mathrm{SnO}_3 + \mathrm{H}_2\mathrm{O}$$

SECTION 19-3

Oxidizing and Reducing Agents

OBJECTIVES

- Relate chemical activity to oxidizing and reducing strength.
- Explain the concept of auto-oxidation.

A **reducing agent** *is a substance that has the potential to cause another substance to be reduced.* Reducing agents lose electrons; they attain a more positive oxidation state during an oxidation-reduction reaction. Therefore, the reducing agent is the oxidized substance.

An **oxidizing agent** *is a substance that has the potential to cause another substance to be oxidized.* Oxidizing agents gain electrons and attain a more negative oxidation state during an oxidation-reduction reaction. The oxidizing agent is the reduced substance. Table 19-2 helps clarify the terms describing the oxidation-reduction process.

Strengths of Oxidizing and Reducing Agents

Different substances can be compared and rated on their relative potential as reducing and oxidizing agents. For example, the order of the elements in the activity series, found in Table 8-3 on page 266, is related to each element's tendency to lose electrons. Elements in this series lose electrons to the positively charged ions of any element below them in the series. The more active an element is, the greater its tendency to lose electrons and the better a reducing agent it is. The greater the distance is between two elements in the list, the more likely it is that a redox reaction will take place between them.

These elements and some other familiar substances are arranged in Table 19-3 according to their activity as oxidizing and reducing agents. The fluorine atom is the most highly electronegative atom. It is also the

TABLE 19-2 *Oxidation-Reduction Terminology*

Term	Change in oxidation number	Change in electron population
Oxidation	in a positive direction	loss of electrons
Reduction	in a negative direction	gain of electrons
Oxidizing agent	in a negative direction	gains electrons
Reducing agent	in a positive direction	loses electrons

most active oxidizing agent. Because of its strong attraction for its own electrons, the fluoride ion is the weakest reducing agent. The negative ion of a strong oxidizing agent is a weak reducing agent.

The positive ion of a strong reducing agent is a weak oxidizing agent. As shown in Table 19-3, Li atoms are strong reducing agents because Li is a very active metal. When Li atoms oxidize, they produce Li^+ ions, which are unlikely to reacquire electrons, so Li^+ ions are weak oxidizing agents.

The left column of each pair also shows the relative abilities of metals listed in the table to displace other metals from their compounds. Zinc, for example, appears above copper. Thus, zinc is the more active reducing agent, and it displaces copper ions from solutions of copper compounds, as illustrated in Figure 19-5. The copper(II) ion, on the other hand, is a more active oxidizing agent than the zinc ion.

Nonmetals and some important ions also are included in the series in Table 19-3. Any reducing agent is oxidized by the oxidizing agents below it. Observe that F_2 displaces Cl^-, Br^-, and I^- ions from their solutions. Cl_2 displaces Br^- and I^- ions, and Br_2 displaces I^- ions. The equation for the displacement of Br^- by Cl_2 is as follows.

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

$$2\overset{-1}{Br^-} \longrightarrow \overset{0}{Br_2} + 2e^- \qquad \text{(oxidation)}$$

$$\overset{0}{Cl_2} + 2e^- \longrightarrow 2\overset{-1}{Cl^-} \qquad \text{(reduction)}$$

In every redox reaction, there is one reducing agent and one oxidizing agent. In the preceding example, Br^- is the reducing agent and Cl_2 is the oxidizing agent.

FIGURE 19-5 Zinc displaces copper ions from a copper(II) sulfate solution. Metallic copper precipitates.

TABLE 19-3 *Relative Strength of Oxidizing and Reducing Agents*

↑ Increasing strength

Reducing agents	Oxidizing agents
Li	Li^+
K	K^+
Ca	Ca^{2+}
Na	Na^+
Mg	Mg^{2+}
Al	Al^{3+}
Zn	Zn^{2+}
Cr	Cr^{3+}
Fe	Fe^{2+}
Ni	Ni^{2+}
Sn	Sn^{2+}
Pb	Pb^{2+}
H_2	H_3O^+
H_2S	S
Cu	Cu^{2+}
I^-	I_2
MnO_4^{2-}	MnO_4^-
Fe^{2+}	Fe^{3+}
Hg	Hg_2^{2+}
Ag	Ag^+
NO_2^-	NO_3^-
Br^-	Br_2
Mn^{2+}	MnO_2
SO_2	H_2SO_4 (conc.)
Cr^{3+}	$Cr_2O_7^{2-}$
Cl^-	Cl_2
Mn^{2+}	MnO_4^-
F^-	F_2

Increasing strength ↓

Quick LAB

Redox Reactions

Wear Safety Goggles and an Apron.

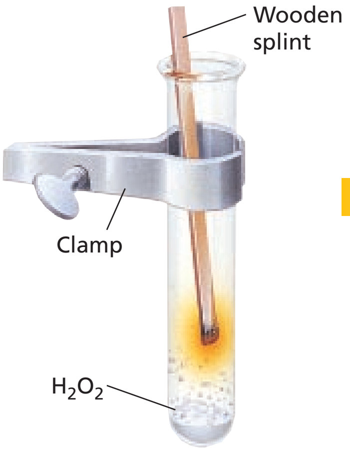
Materials

- aluminum foil
- beaker, 250 mL
- 1 M copper(II) chloride solution, $CuCl_2$
- 3% hydrogen peroxide
- manganese dioxide
- metric ruler
- scissors
- test-tube clamp
- test tube, 16 × 150 mm
- wooden splint

Procedure

Record all your results in a data table.

1. Put 10 mL of hydrogen peroxide in a test tube, and add a small amount of manganese dioxide (equal to the size of about half a pea). What is the result?



2. Insert a glowing wooden splint into the test tube (see diagram). What is the result? If oxygen is produced, a glowing wooden splint inserted into the test tube will glow brighter.
3. Fill the 250 mL beaker halfway with the copper(II) chloride solution.
4. Cut foil into 2 cm × 12 cm strips.
5. Add the aluminum strips to the copper(II) chloride solution. Use a glass rod to stir the mixture, and observe for 12 to 15 minutes. What is the result?

Discussion

1. Write balanced equations showing what happened in each of the reactions.
2. Write a conclusion for the two experiments.

Autooxidation

Some substances can be both reduced and oxidized easily. For example, peroxide ions, O_2^{2-}, have a relatively unstable covalent bond between the two oxygen atoms. The electron-dot formula is written as follows.

$$\left[:\underset{\cdot\cdot}{\ddot{O}}:\underset{\cdot\cdot}{\ddot{O}}:\right]^{2-}$$

Each oxygen atom has an oxidation number of −1. The peroxide ion structure represents an intermediate oxidation state between O_2 and O^{2-}. Therefore, the peroxide ion is highly reactive.

Hydrogen peroxide, H_2O_2, contains the reactive peroxide ion. It decomposes into water and molecular oxygen, as shown in the equation below.

$$2H_2\overset{-1}{O}_2 \longrightarrow 2H_2\overset{-2}{O} + \overset{0}{O}_2$$

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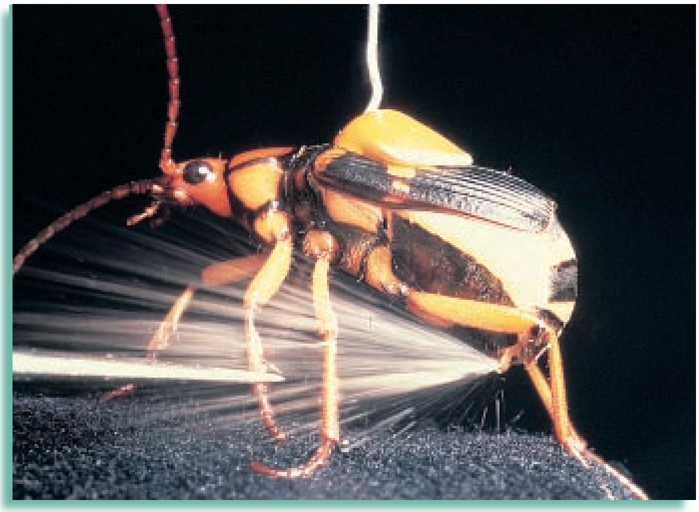

FIGURE 19-6 A bombardier beetle can repel large predators such as frogs with a chemical defense mechanism that uses the autooxidation of hydrogen peroxide.

Notice that in this reaction, hydrogen peroxide is both oxidized and reduced. Oxygen atoms that become part of gaseous oxygen molecules are oxidized. The oxidation number of theses oxygen atoms increases from –1 to 0. Oxygen atoms that become part of water are reduced. The oxidation number of these oxygen atoms decreases from –1 to –2. *A process in which a substance acts as both an oxidizing agent and a reducing agent is called* **autooxidation.** A substance that undergoes autooxidation is both *self-oxidizing* and *self-reducing.*

The bombardier beetle defends itself by spraying its enemies with an unpleasant hot chemical mixture as shown in Figure 19-6. The catalyzed autooxidation of hydrogen peroxide produces hot oxygen gas. This gas gives the insect an ability to eject irritating chemicals from its abdomen with explosive force.

SECTION REVIEW

1. Describe the chemical activity of the alkali metals and of the halogens on the basis of oxidizing and reducing strength.

2. The photo on the left depicts two redox reactions. Use them to answer the following questions:
   a. When zinc is wrapped around an iron nail, is the iron reduced or oxidized?
   b. When copper is wrapped around an iron nail, is the iron reduced or oxidized?
3. Would Cl_2 be reduced by I^-? Explain.
4. Which is the stronger oxidizing agent in each of the following pairs? Cu^{2+} or Al^{3+}, H_2 or H_3O^+, Cr or Cu?
5. What is meant by *autooxidation*?

SECTION 19-4

Electrochemistry

OBJECTIVES

- Explain what is required for an electrochemical cell.
- Describe the nature of voltaic cells.
- Describe the nature of electrolytic cells.
- Explain the process of electroplating.
- Describe the chemistry of a rechargeable cell.
- Calculate cell potentials from a table of standard electrode potentials.

Oxidation-reduction reactions involve energy changes. Because these reactions involve electron transfer, the net *release* or net *absorption* of energy can occur in the form of electrical energy rather than as heat. This property allows for a great many practical applications of redox reactions. It also makes possible quantitative predictions and comparisons of the oxidizing and reducing abilities of different substances. *The branch of chemistry that deals with electricity-related applications of oxidation-reduction reactions is called* **electrochemistry.**

Electrochemical Cells

Oxidation-reduction reactions involve a transfer of electrons from the substance oxidized to the substance reduced. If the two substances are in contact with one another, a transfer of energy as heat accompanies the electron transfer. In Figure 19-7 a zinc strip is in contact with a copper(II) sulfate solution. The zinc strip loses electrons to the copper(II) ions in solution. Copper(II) ions accept the electrons and fall out of solution as copper atoms. As electrons are transferred between zinc atoms and copper(II) ions, energy is released as heat, as indicated by the rise in temperature.

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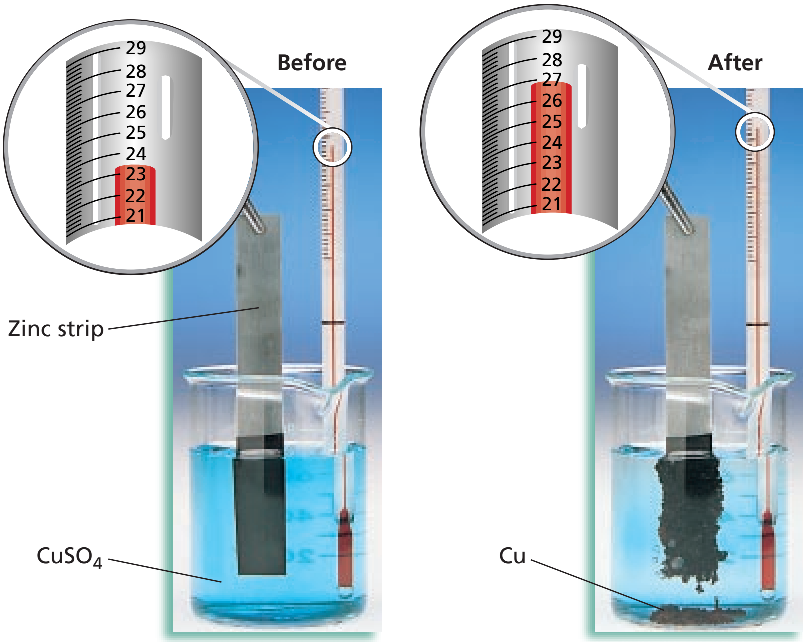

FIGURE 19-7 Heat energy given off when electrons are transferred directly from Zn atoms to Cu^{2+} ions causes the temperature of the aqueous $CuSO_4$ solution to rise.

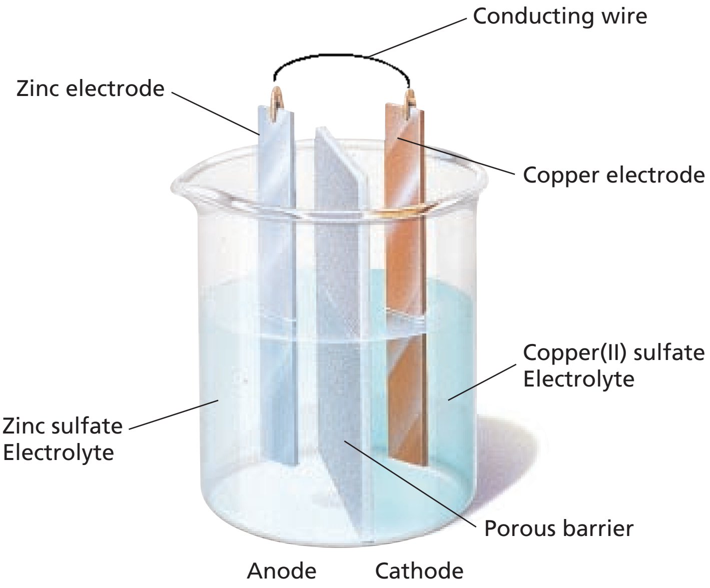

FIGURE 19-8 An electrochemical cell consists of two electrodes. Each electrode is in contact with an electrolyte; the electrode and the electrolyte make up a half-cell. The two electrodes are connected by a wire, and a porous barrier separates the two electrolytes.

If, however, we separate the substance that is oxidized during the reaction from the substance that is reduced during the reaction, the electron transfer is accompanied by a transfer of electrical energy instead of heat. One means of separating oxidation and reduction half-reactions is with a *porous barrier.* This barrier prevents the metal atoms of one half-reaction from mixing with the ions of the other half-reaction. Ions in the two solutions can move through the porous barrier. Electrons can be transferred from one side to the other through an external connecting wire. Electric current moves in a closed loop path, or *circuit,* so this movement of electrons through the wire is balanced by the movement of ions in solution.

Altering the system in Figure 19-7 so that electrical current is produced instead of heat would simply involve separating the copper and zinc, as shown in Figure 19-8. The Zn strip is in an aqueous solution of $ZnSO_4$. The Cu strip is in an aqueous solution of $CuSO_4$. Both solutions conduct electricity, so, as you learned in Chapter 14, they are classified as electrolytes. *An* **electrode** *is a conductor used to establish electrical contact with a nonmetallic part of a circuit, such as an electrolyte*. In Figure 19-8, the Zn and Cu strips are electrodes. *A single electrode immersed in a solution of its ions is a* **half-cell.** The Zn strip in aqueous $ZnSO_4$ is an **anode,** *the electrode where oxidation takes place*. The Cu strip in $CuSO_4$ is a **cathode,** *the electrode where reduction takes place*. The copper half-cell can be written as Cu^{2+}/Cu, and the zinc half-cell can be written as Zn^{2+}/Zn. The two half-cells together make an electrochemical cell. *An* **electrochemical cell** is a *system of electrodes and electrolytes in which either chemical reactions produce electrical energy or an electric current produces chemical change*. An electrochemical cell may be represented by the following notation: anode | cathode. For the example, the cell made up of zinc and copper could be written as Zn | Cu. There are two types of electrochemical cells: voltaic (also called galvanic) and electrolytic.

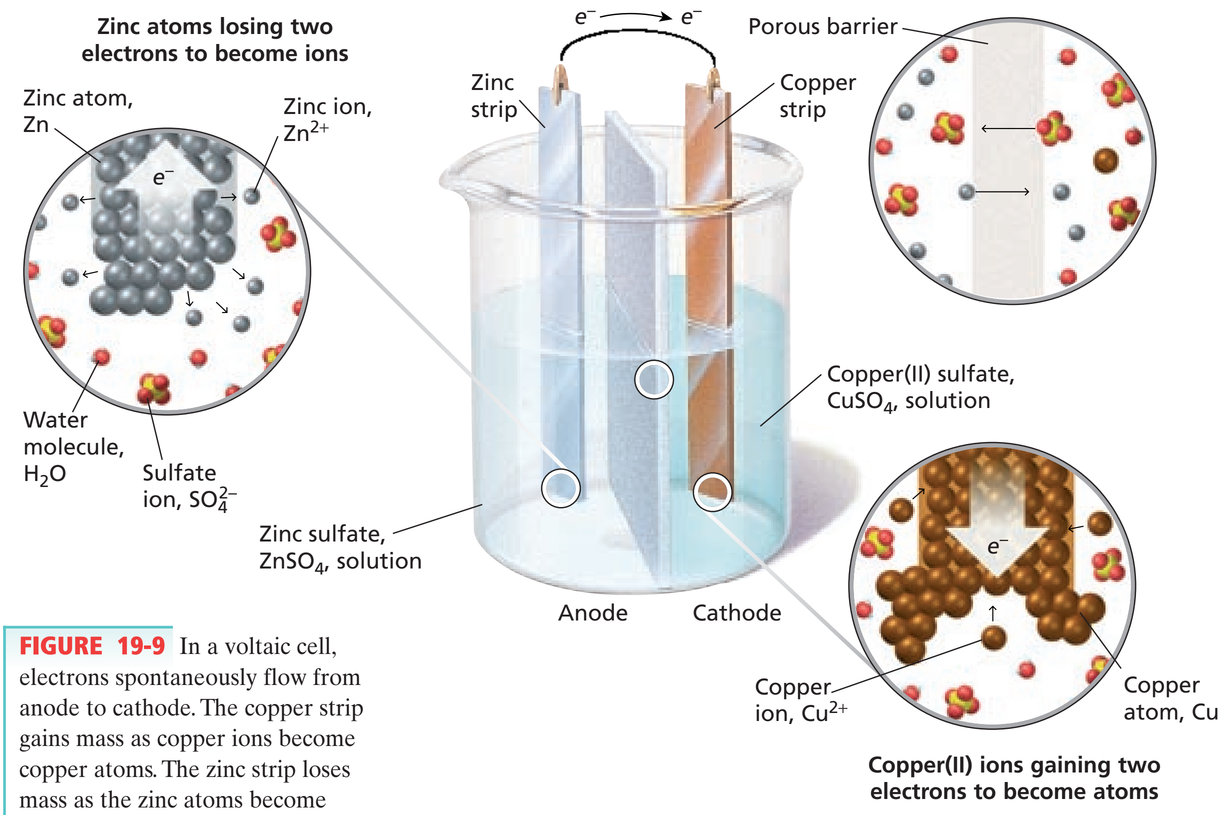

FIGURE 19-9 In a voltaic cell, electrons spontaneously flow from anode to cathode. The copper strip gains mass as copper ions become copper atoms. The zinc strip loses mass as the zinc atoms become zinc ions.

CHEMISTRY INTERACTIVE TUTOR

Module 10: Electrochemical Cells

Voltaic Cells

If the redox reaction in an electrochemical cell occurs spontaneously and produces electrical energy, the cell is a **voltaic cell.** Cations in the solution are reduced when they gain electrons at the surface of the cathode to become metal atoms. This half-reaction for the voltaic cell shown in Figure 19-9 is as follows.

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

The half-reaction occurring at the anode is as follows.

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

Electrons given up at the anode pass along the external connecting wire to the cathode.

The movement of electrons through the wire must be balanced by a movement of ions in the solution. Anions move toward the anode to replace the negatively charged electrons that are moving away. Cations move toward the cathode as positive charge is lost through reduction. Thus, in Figure 19-9, sulfate ions in the $CuSO_4$ solution can move through the barrier into the $ZnSO_4$ solution. Likewise, the Zn^{2+} ions pass through the barrier into the $CuSO_4$ solution.

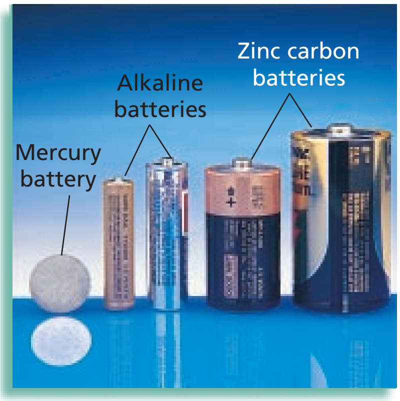

FIGURE 19-10 Many common batteries are simple voltaic dry cells.

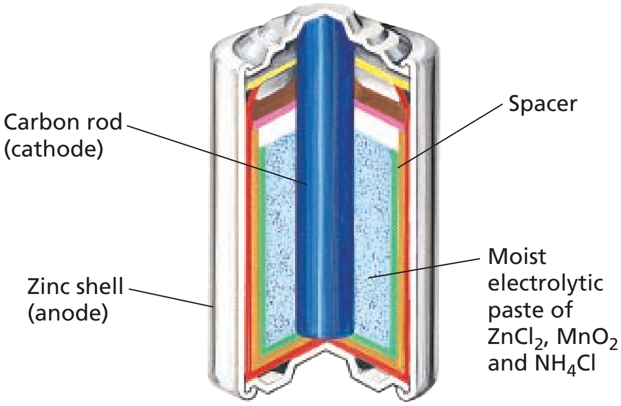

FIGURE 19-11 In a zinc dry cell, zinc is oxidized to Zn^{2+} at the anode, and manganese(IV) is reduced to manganese(III) at the cathode.

The dry cells pictured in Figure 19-10 are common sources of electrical energy. Like the wet cell previously described, dry cells are voltaic cells. The three most common types of dry cells are the zinc-carbon battery, the alkaline battery, and the mercury battery. They differ in the substances being oxidized and reduced.

Zinc-Carbon Dry Cells

Batteries such as those used in flashlights are zinc-carbon dry cells. These cells consist of a zinc container, which serves as the anode, filled with a moist paste of MnO_2, graphite, and NH_4Cl, as illustrated in Figure 19-11. When the external circuit is closed, zinc atoms are oxidized at the negative electrode, or anode.

$$\overset{0}{\mathrm{Zn}}(s) \longrightarrow \overset{+2}{\mathrm{Zn}}{}^{2+}(aq) + 2e^-$$

Electrons move across the circuit and reenter the cell through the carbon rod. The carbon rod is the cathode or positive electrode. Here MnO_2 is reduced in the presence of H_2O according to the following half-reaction.

$$2\overset{+4}{\mathrm{Mn}}\mathrm{O_2}(s) + \mathrm{H_2O}(l) + 2e^- \longrightarrow \overset{+3}{\mathrm{Mn}}{}_2\mathrm{O_3}(s) + 2\mathrm{OH}^-(aq)$$

Alkaline Batteries

The batteries found in a small, portable cassette player or other small electronic device are frequently alkaline dry cells. These cells do not have a carbon rod cathode, as in the zinc-carbon cell. The absence of the carbon rod allows them to be smaller. Figure 19-12 shows a model of an alkaline battery. This cell uses a paste of Zn metal and potassium hydroxide instead of a solid metal anode. The half-reaction at the anode is as follows.

$$\overset{0}{\mathrm{Zn}}(s) + 2\mathrm{OH}^-(aq) \longrightarrow \overset{+2}{\mathrm{Zn}}(\mathrm{OH})_2(s) + 2e^-$$

The reduction half-reaction, the reaction at the cathode, is exactly the same as that for the zinc-carbon dry cell.

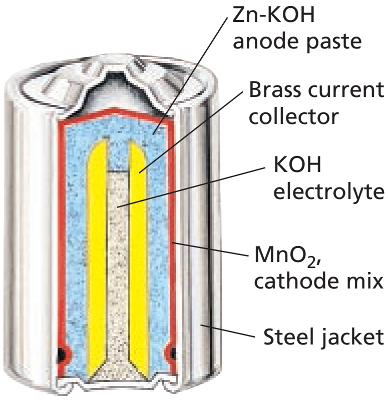

FIGURE 19-12 KOH makes the electrolyte paste in this battery basic. Thus, it is called an alkaline dry cell.

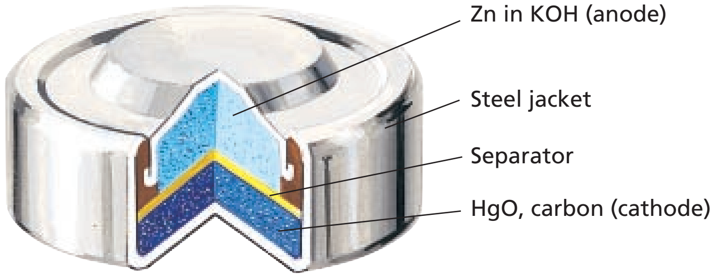

FIGURE 19-13 It is important that mercury batteries be recycled and not just discarded because mercury is a poisonous substance.

Mercury Batteries

The tiny batteries found in hearing aids, calculators, and camera flashes are mercury batteries, as shown in Figure 19-13. The anode half-reaction is identical to that found in the alkaline dry cell. However, the cathode, or reduction, half-reaction is different. The cathode half-reaction is described by the following equation.

$$\overset{+2}{\mathrm{Hg}}\mathrm{O}(s) + \mathrm{H_2O}(l) + 2e^- \longrightarrow \overset{0}{\mathrm{Hg}}(l) + 2\mathrm{OH}^-(aq)$$

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Module 10: Electrochemical Cells

Electrolytic Cells

Some oxidation-reduction reactions do not occur spontaneously, but can be driven by electrical energy. *The process in which an electric current is used to produce an oxidation-reduction reaction is* **electrolysis.** *If electrical energy is required to produce a redox reaction and bring about a chemical change in an electrochemical cell, it is an* **electrolytic cell.** Most commercial uses of redox reactions make use of electrolytic cells.

An electrolytic cell is depicted in Figure 19-14. The electrode of the cell connected to the negative terminal of the battery acquires an excess of electrons and becomes the cathode of the electrolytic cell. The electrode of the cell connected to the positive terminal of the battery loses electrons to the battery; it is the anode of the electrolytic cell. The battery can be thought of as an electron pump simultaneously supplying electrons to the cathode and recovering electrons from the anode. This energy input from the battery drives the electrode reactions in the electrolytic cell.

A comparison of electrolytic and voltaic cells can be seen in Figure 19-14. The voltaic cell shown in Figure 19-14 has a copper cathode and a zinc anode. If a battery is connected so that the positive terminal contacts the copper electrode and the negative terminal contacts the zinc electrode, the electrons flow in the opposite direction. The battery forces the cell to reverse its reaction; the zinc electrode becomes the cathode, and the copper electrode becomes the anode. The half-reaction at the anode, in which copper metal is oxidized, can be written as follows.

$$\overset{0}{\mathrm{Cu}} \longrightarrow \overset{+2}{\mathrm{Cu}}{}^{2+} + 2e^-$$

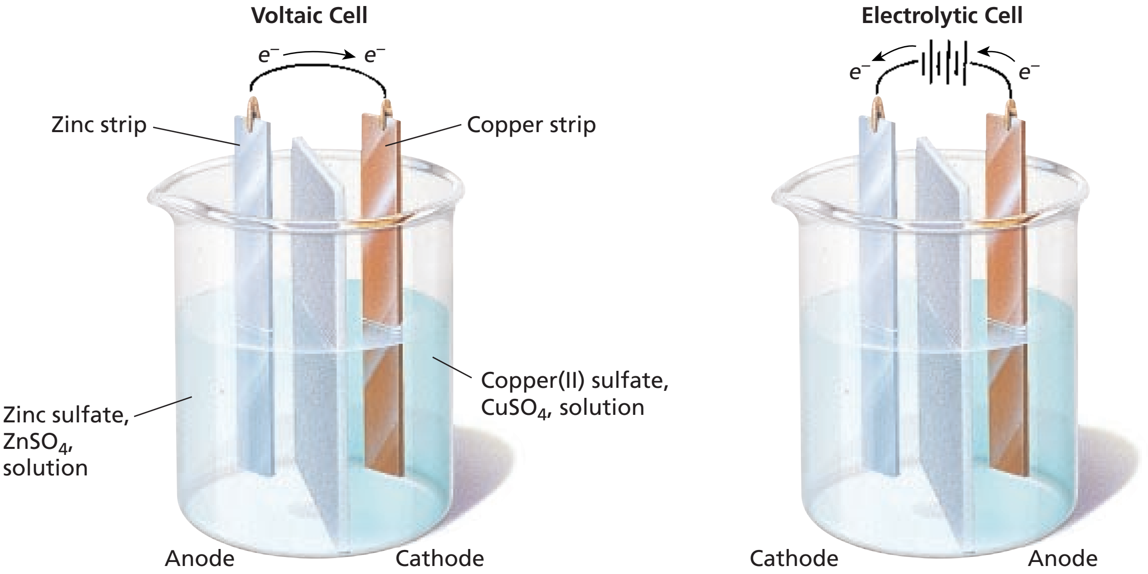

FIGURE 19-14 The direction in which the electrons move reverses if a voltaic cell is connected to a direct current source to become an electrolytic cell.

The reduction half-reaction of zinc at the cathode is written as follows.

$$\overset{+2}{\mathrm{Zn}}^{2+} + 2e^- \longrightarrow \overset{0}{\mathrm{Zn}}$$

There are two important differences between the voltaic cell and the electrolytic cell.

1. The anode and cathode of an electrolytic cell are connected to a battery or other direct-current source, whereas a voltaic cell serves as a source of electrical energy.

2. Electrolytic cells are those in which electrical energy from an external source causes *nonspontaneous* redox reactions to occur. Voltaic cells are those in which *spontaneous* redox reactions produce electricity. In an electrolytic cell, electrical energy is converted to chemical energy; in a voltaic cell, chemical energy is converted to electrical energy.

Electroplating

Metals such as copper, silver, and gold are difficult to oxidize. In an electrolytic cell, these inactive metals form ions at an anode that are easily reduced at a cathode. This type of cell allows solid metal from one electrode to be deposited on the other electrode. *An electrolytic process in which a metal ion is reduced and a solid metal is deposited on a surface is called* **electroplating.**

An electroplating cell contains a solution of a salt of the plating metal. It has an object to be plated (the cathode) and a piece of the plating metal (the anode). A silver-plating cell contains a solution of a soluble silver salt and a silver anode. The cathode is the object to be plated. The silver anode is connected to the positive electrode of a battery or to some other source of direct current. The object to be plated is connected to the negative electrode.

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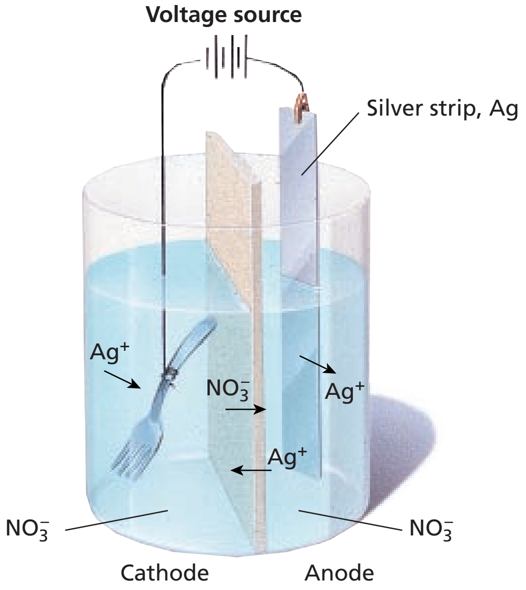
FIGURE 19-15 Electroplating is often used to avoid corrosion (a redox reaction) at the object's surface by putting a layer of an inactive metal on a more-active metal.



A cell in which silver is being electroplated onto a fork can be seen in Figure 19-15. Silver ions are reduced at the cathode according to the following equation and deposited as metallic silver when electrons flow through the circuit.

$$\overset{+1}{Ag^+} + e^- \longrightarrow \overset{0}{Ag}$$

Meanwhile, metallic silver is removed from the anode as ions. Silver atoms are oxidized at the anode according to the following half-reaction.

$$\overset{0}{Ag} \longrightarrow \overset{+1}{Ag^+} + e^-$$

This action maintains the Ag^+ ion concentration of the solution. Thus, in effect, silver is transferred from the anode to the cathode of the cell.

Rechargeable Cells

A rechargeable cell combines the oxidation-reduction chemistry of both voltaic cells and electrolytic cells. When a rechargeable cell converts chemical energy to electrical energy, it operates as a voltaic cell. But when the cell is recharged, it operates as an electrolytic cell, converting electrical energy to chemical energy.

The standard 12 V automobile battery, shown in Figure 19-16, is a set of six rechargeable cells. The anode in each cell is lead submerged in a solution of H_2SO_4. The anode half-reaction is described by the following equation.

$$Pb(s) + SO_4^{2-}(aq) \longrightarrow PbSO_4(s) + 2e^-$$

Electrons move through the circuit to the cathode, where PbO_2 is reduced according to the following equation.

$$PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O(l)$$

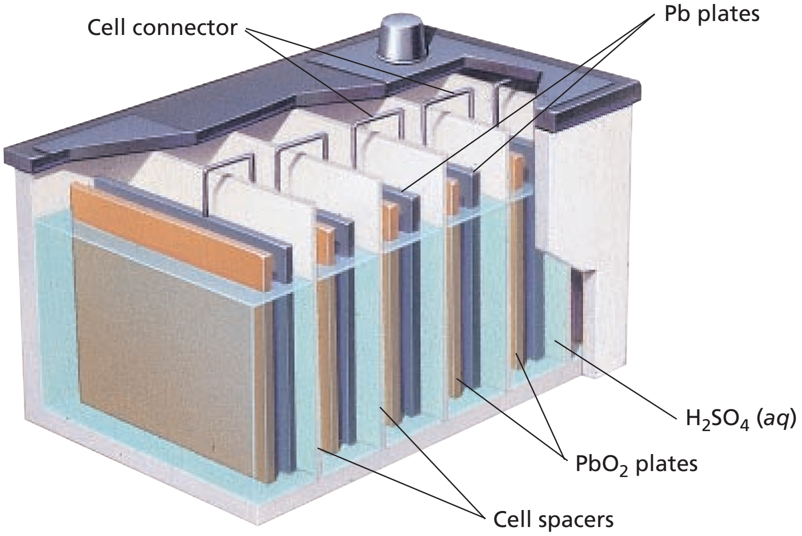


FIGURE 19-16 The rechargeable cells of a car battery produce electricity from reactions between lead(IV) oxide, lead, and sulfuric acid.

The net oxidation-reduction reaction for the discharge cycle is described by the following chemical equation.

$$Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \longrightarrow 2PbSO_4(s) + 2H_2O(l)$$

A car's battery produces the electric energy needed to start its engine. Sulfuric acid, present as its ions, is consumed, and lead(II) sulfate accumulates as a white powder on the electrodes. Once the car is running, the half-reactions are reversed by a voltage produced by the alternator. The Pb, PbO_2, and H_2SO_4 are regenerated. A battery can be recharged as long as all reactants necessary for the electrolytic reaction are present, and all reactions are reversible.

Electrode Potentials

Reconsider the voltaic cell shown in Figure 19-9. There are two electrodes, Zn and Cu. According to Table 19-3, these two metals each have different tendencies for accepting electrons. *This tendency for the half-reaction of either copper or zinc to occur as a reduction half-reaction in an electrochemical cell can be quantified as a* **reduction potential.** There are two half-cells in Figure 19-9: a strip of zinc placed in a solution of $ZnSO_4$ and a strip of copper placed in a solution of $CuSO_4$. *The difference in potential between an electrode and its solution is known as its* **electrode potential.** When these two half-cells are connected and the reaction begins, a difference in potential is observed between the electrodes. This potential difference, or voltage, is a measure of the energy required to move a certain electric charge between the electrodes. Potential difference is measured in volts. A voltmeter connected across the Cu | Zn voltaic cell measures a potential difference of about 1.10 V when the solution concentrations of Zn^{2+} and Cu^{2+} ions are each 1 M.

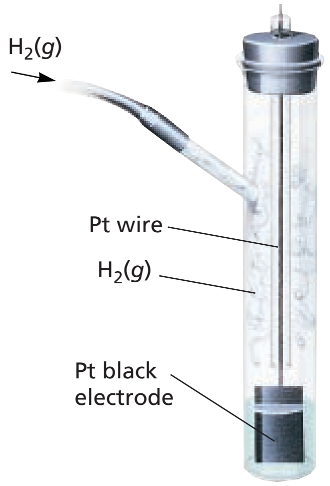


FIGURE 19-17 A hydrogen electrode is the standard reference electrode for measuring electrode potentials. The electrode surface in contact with the solution is actually a layer of hydrogen adsorbed onto the surface of the platinum.

The potential difference measured across the complete voltaic cell roughly equals the sum of the electrode potentials for the two half-reactions. But while the potential difference across a voltaic cell is easily measured, there is no way to measure an individual electrode potential directly. This is because there can be no transfer of electrons unless both the anode and the cathode are connected to form a complete circuit. A relative value for the potential of a half-reaction can be determined by connecting it to a standard half-cell as a reference. This standard half-cell, shown in Figure 19-17, is called a standard hydrogen electrode, or SHE. It consists of a platinum electrode dipped into a 1.00 M acid solution surrounded by hydrogen gas at 1 atm pressure and 25°C. Other electrodes are ranked according to their ability to reduce hydrogen under these conditions.

The anodic reaction for the standard hydrogen electrode is described by the forward half-reaction in the following equilibrium equation.

$$\overset{0}{H_2}(g) \rightleftharpoons 2\overset{+1}{H}{}^+(aq) + 2e^-$$

The cathodic half-reaction is the reverse. An arbitrary potential of 0.00 V is assigned to both of these half-reactions. Therefore, any voltage measurement obtained is attributed to the half-cell connected to the SHE. *A half-cell potential measured relative to a potential of zero for the standard hydrogen electrode is a* **standard electrode potential,** E^0. Electrode potentials are expressed as potentials for reduction. These reduction potentials provide a reliable indication of the tendency of a substance to be reduced. Half-reactions for some common electrodes and their standard electrode potentials are listed in Table 19-4.

Positive E^0 values indicate that hydrogen is more willing to give up its electrons than the other electrode. Half-reactions with positive reduction potentials are favored. Effective oxidizing agents, such as Cu and F_2, have positive E^0 values. Half-reactions with negative reduction potentials are not favored; these half-reactions prefer oxidation over reduction. Negative E^0 values indicate that the metal or other electrode is more willing to give up electrons than hydrogen. Effective reducing agents, such as Li and Zn, have negative E^0 values. When a half-reaction

FIGURE 19-18 The electrode potentials of zinc and copper half-cells are measured by coupling them with a standard hydrogen electrode.

TABLE 19-4 ***Standard Reduction Potentials***

Half-cell reaction	Standard electrode potential, E^0 (in volts)	Half-cell reaction	Standard electrode potential, E^0 (in volts)
$F_2 + 2e^- \rightleftharpoons 2F^-$	+2.87	$Fe^{3+} + 3e^- \rightleftharpoons Fe$	−0.04
$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$	+1.50	$Pb^{2+} + 2e^- \rightleftharpoons Pb$	−0.13
$Au^{3+} + 3e^- \rightleftharpoons Au$	+1.50	$Sn^{2+} + 2e^- \rightleftharpoons Sn$	−0.14
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+1.36	$Ni^{2+} + 2e^- \rightleftharpoons Ni$	−0.26
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$	+1.23	$Co^{2+} + 2e^- \rightleftharpoons Co$	−0.28
$MnO_2 + 4H^+ + 2e^- \rightleftharpoons Mn^{2+} + 2H_2O$	+1.22	$Cd^{2+} + 2e^- \rightleftharpoons Cd$	−0.40
$Br_2 + 2e^- \rightleftharpoons 2Br^-$	+1.07	$Fe^{2+} + 2e^- \rightleftharpoons Fe$	−0.45
$Hg^{2+} + 2e^- \rightleftharpoons Hg$	+0.85	$S + 2e^- \rightleftharpoons S^{2-}$	−0.48
$Ag^+ + e^- \rightleftharpoons Ag$	+0.80	$Cr^{3+} + 3e^- \rightleftharpoons Cr$	−0.74
$Hg_2^{2+} + 2e^- \rightleftharpoons 2Hg$	+0.80	$Zn^{2+} + 2e^- \rightleftharpoons Zn$	−0.76
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+0.77	$Al^{3+} + 3e^- \rightleftharpoons Al$	−1.66
$MnO_4^- + e^- \rightleftharpoons MnO_4^{2-}$	+0.56	$Mg^{2+} + 2e^- \rightleftharpoons Mg$	−2.37
$I_2 + 2e^- \rightleftharpoons 2I^-$	+0.54	$Na^+ + e^- \rightleftharpoons Na$	−2.71
$Cu^{2+} + 2e^- \rightleftharpoons Cu$	+0.34	$Ca^{2+} + 2e^- \rightleftharpoons Ca$	−2.87
$Cu^{2+} + e^- \rightleftharpoons Cu^+$	+0.15	$Ba^{2+} + 2e^- \rightleftharpoons Ba$	−2.91
$S + 2H^+(aq) + 2e^- \rightleftharpoons H_2S(aq)$	+0.14	$K^+ + e^- \rightleftharpoons K$	−2.93
$2H^+(aq) + 2e^- \rightleftharpoons H_2$	0.00	$Li^+ + e^- \rightleftharpoons Li$	−3.04

is written as an oxidation reaction, the sign of its electrode potential is changed as shown for the oxidation and reduction half-reactions for zinc.

$$Zn^{2+} + 2e^- \longrightarrow Zn \qquad E^0 = -0.76\ \text{V}$$
$$Zn \longrightarrow Zn^{2+} + 2e^- \qquad E^0 = +0.76\ \text{V}$$

To measure the reduction potential of a zinc half-cell, it is connected to a standard hydrogen electrode, as in Figure 19-18. The potential difference across the cell is –0.76 V. The negative number indicates that electrons flow through the external circuit from the zinc electrode, where zinc is oxidized, to the hydrogen electrode, where aqueous hydrogen ions are reduced.

A copper half-cell coupled with the standard hydrogen electrode gives a potential difference measurement of +0.34 V. This positive number indicates that $Cu^{2+}(aq)$ ions are more readily reduced than $H^+(aq)$ ions.

Standard electrode potentials can be used to predict if a redox reaction will occur naturally. A naturally occurring reaction will have a positive value for $E^0{}_{cell}$, which is calculated using the following equation.

$$E^0{}_{cell} = E^0{}_{cathode} - E^0{}_{anode}$$

CHEMISTRY INTERACTIVE TUTOR

Module 10: Electrochemical Cells

When evaluating the two half-reactions in a voltaic cell, the half-reaction with the more negative standard reduction potential is the anode. Oxidation occurs at the anode, so the half-cell reaction is the reverse of the reduction reaction found in Table 19-4. When a reaction is reversed, the actual half-cell potential is the negative of the standard reduction potential. For this reason, the total potential of a cell is calculated by subtracting the standard reduction potential for the reaction at the anode (E^0_{anode}) from the standard reduction potential for the reaction at the cathode ($E^0_{cathode}$).

Consider cells made from Fe in a solution of $Fe(NO_3)_3$ and Ag in a solution of $AgNO_3$. Table 19-4 gives the following half-reactions and E^0 values for these half-cells.

$$\begin{array}{ll} Fe^{3+}(aq) + 3e^- \longrightarrow Fe(s) & E^0 = -0.04\ V \\ 3Ag^+(aq) + 3e^- \longrightarrow 3Ag(s) & E^0 = +0.80\ V \end{array}$$

Fe in $Fe(NO_3)_3$ is the anode because it has the lower reduction potential, and Ag in $AgNO_3$ is therefore the cathode. The overall cell reaction is

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

The reduction of silver ions is multiplied by 3 so that the number of electrons lost in that half-reaction equals the number of electrons gained in the oxidation of iron. The standard reduction potentials for the anode and cathode are as follows.

$$E^0_{anode} = -0.04\ V$$
$$E^0_{cathode} = +0.80\ V$$

Note that when a half-reaction is multiplied by a constant, the E^0 value is not multiplied but remains the same.

So the potential for this cell can be calculated as follows.

$$E^0_{cell} = E^0_{cathode} - E^0_{anode}$$
$$E^0_{cell} = +0.80\ V - (-0.04\ V) = 0.84\ V$$

If the calculated value for E^0_{cell} were negative, the reaction would not occur naturally in the direction written, so it would not occur in a voltaic cell. It could be made to occur in an electrolytic cell.

SECTION REVIEW

1. What is a voltaic cell?
2. Describe an electrolytic cell.
3. Explain the process of electroplating.
4. What is a rechargeable cell?
5. What is electrode potential, and how is it used to calculate information about an electrochemical reaction?
6. Given the Na^+/Na and K^+/K half-cells, determine the overall electrochemical reaction that proceeds spontaneously and the E^0 value.

CHAPTER 19 REVIEW

CHAPTER SUMMARY

19-1

- Oxidation numbers are assigned by the set of rules listed in Table 19-1.
- Oxidation-reduction reactions consist of two half-reactions that must occur simultaneously.
- Oxidation-reduction reactions are identified by examining the reactants and products for changes in oxidation numbers of their constituent atoms.
- Oxidation involves the loss of electrons, and reduction involves the gain of electrons.

Vocabulary

half-reaction (593)
oxidation (592)
oxidation-reduction reaction (593)
oxidized (592)
redox reaction (593)
reduced (593)
reduction (593)

19-2

- Both charge and mass are conserved in a balanced redox equation.
- In the half-reaction method for balancing equations, oxidation and reduction equations are balanced separately for atoms and charge. Then they are combined to give a complete balanced equation.

19-3

- In redox reactions, the substance that is *reduced* acts as an *oxidizing agent* because it *acquires* electrons from the substance oxidized.
- The substance that is *oxidized* in a redox reaction is the *reducing agent* because it *supplies* the electrons to the substance reduced.

Vocabulary

autooxidation (605)
oxidizing agent (602)
reducing agent (602)

19-4

- Some oxidation-reduction reactions that occur naturally can be sources of electrical energy in voltaic cells. Other oxidation-reduction reactions that do not occur naturally can be driven by an external source of electrical energy in electrolytic cells; this process is called electrolysis.
- An electrode and its electrolyte in an electrochemical cell are called a half-cell.
- The potential difference between the electrode and its solution is called the electrode potential. The sum of the electrode potentials of the two half-reactions of an electrochemical cell is roughly equal to the potential difference across the cell.
- Standard electrode potentials are measured relative to a standard hydrogen electrode. They indicate the relative strengths of substances as oxidizing and reducing agents.

Vocabulary

anode (607)
cathode (607)
electrochemical cell (607)
electrochemistry (606)
electrode (607)
electrode potential (613)
electrolysis (610)
electrolytic cell (610)
electroplating (611)
half-cell (607)
reduction potential (613)
standard electrode potential (614)
voltaic cell (608)

REVIEWING CONCEPTS

1. a. Distinguish between the processes of oxidation and reduction.
b. Write an equation to illustrate each. (19-1)

2. Which of the following are redox reactions?
a. $2Na + Cl_2 \longrightarrow 2NaCl$
b. $C + O_2 \longrightarrow CO_2$
c. $2H_2O \longrightarrow 2H_2 + O_2$
d. $NaCl + AgNO_3 \longrightarrow AgCl + NaNO_3$
e. $NH_3 + HCl \longrightarrow NH_4^+ + Cl^-$
f. $2KClO_3 \longrightarrow 2KCl + 3O_2$
g. $H_2 + Cl_2 \longrightarrow 2HCl$
h. $H_2SO_4 + 2KOH \longrightarrow K_2SO_4 + 2H_2O$
i. $Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu$ (19-1)

3. For each oxidation-reduction reaction in the previous question, identify what is oxidized and what is reduced. (19-1)

4. a. Identify the most active reducing agent among all common elements.
b. Why are all of the elements in its group in the periodic table very active reducing agents?
c. Identify the most active oxidizing agent among the common elements. (19-3)

5. Based on Table 19-3, identify the strongest and weakest reducing agents among the substances listed within each of the following groupings:
a. Ca, Ag, Sn, Cl^-
b. Fe, Hg, Al, Br^-
c. F^-, Pb, Mn^{2+}, Na
d. Cr^{3+}, Cu^{2+}, NO_3^-, K^+
e. Cl_2, S, Zn^{2+}, Ag^+
f. Li^+, F_2, Ni^{2+}, Fe^{3+} (19-3)

6. Use Table 19-3 to respond to each of the following:
a. Would Al be oxidized by Ni^{2+}?
b. Would Cu be oxidized by Ag^+?
c. Would Pb be oxidized by Na^+?
d. Would F_2 be reduced by Cl^-?
e. Would Br_2 be reduced by Cl^-? (19-3)

7. Distinguish between a voltaic cell and an electrolytic cell in terms of the nature of the reaction involved. (19-4)

8. a. What is electroplating?
b. Distinguish between the nature of the anode and cathode in such a process. (19-4)

9. a. Explain what is meant by the potential difference between the two electrodes in an electrochemical cell.
b. How, and in what units, is this potential difference measured? (19-4)

10. The standard hydrogen electrode is assigned an electrode potential of 0.00 V. Explain why this voltage is assigned. (19-4)

11. a. What information is provided by the electrode potential of a given half-cell?
b. What does the relative value of the potential of a given half-reaction indicate about its oxidation-reduction tendency? (19-4)

PROBLEMS

Redox Equations

12. Each of the following atom/ion pairs undergoes the oxidation number change indicated below. For each pair, determine whether oxidation or reduction has occurred, and then write the electronic equation indicating the corresponding number of electrons lost or gained.
a. $K \longrightarrow K^+$
b. $S \longrightarrow S^{2-}$
c. $Mg \longrightarrow Mg^{2+}$
d. $F^- \longrightarrow F_2$
e. $H_2 \longrightarrow H^+$
f. $O_2 \longrightarrow O^{2-}$
g. $Fe^{3+} \longrightarrow Fe^{2+}$
h. $Mn^{2+} \longrightarrow MnO_4^-$

13. Identify the following reactions as redox or nonredox:
a. $2NH_4Cl(aq) + Ca(OH)_2(aq) \longrightarrow 2NH_3(aq) + 2H_2O(l) + CaCl_2(aq)$
b. $2HNO_3(aq) + 3H_2S(g) \longrightarrow 2NO(g) + 4H_2O(l) + 3S(s)$
c. $[Be(H_2O)_4]^{2+}(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + [Be(H_2O)_3OH]^+(aq)$

14. Arrange the following in order of increasing oxidation number of the xenon atom:
$CsXeF_8$, Xe, XeF_2, $XeOF_2$, XeO_3, XeF

15. Determine the oxidation number of each atom indicated in the following:
- a. H_2
- b. H_2O
- c. Al
- d. MgO
- e. Al_2S_3
- f. HNO_3
- g. H_2SO_4
- h. $Ca(OH)_2$
- i. $Fe(NO_3)_2$
- j. O_2

16. Balance the oxidation-reduction equation below by using the half-reaction method in response to each requested step. (Hint: See Sample Problem 19-1.)

$$K + H_2O \longrightarrow KOH + H_2$$

- a. Write the ionic equation, and assign oxidation numbers to all atoms to determine what is oxidized and what is reduced.
- b. Write the equation for the reduction, and balance it for both atoms and charge.
- c. Write the equation for the oxidation, and balance it for both atoms and charge.
- d. Adjust the oxidation and reduction equations by multiplying the coefficients as needed so that electrons lost equal electrons gained, and add the two resulting equations.
- e. Add species as necessary to balance the overall formula equation.

17. Use the method in the previous problem to balance each of the reactions below.
- a. $HI + HNO_2 \longrightarrow NO + I_2 + H_2O$
- b. $FeCl_3 + H_2S \longrightarrow FeCl_2 + HCl + S$

18. Balance the equation for the reaction in which hot, concentrated sulfuric acid reacts with zinc to form zinc sulfate, hydrogen sulfide, and water.

Voltaic and Electrolytic Cells

19. For each of the following pairs of half-cells, determine the overall electrochemical reaction that proceeds spontaneously:
- a. Cu^{2+}/Cu, Ag^+/Ag
- b. Cd^{2+}/Cd, Co^{2+}/Co
- c. Na^+/Na, Ni^{2+}/Ni
- d. I_2/I^-, Br_2/Br^-

20. Determine the values of E^0 for the cells in the previous problem.

21. Suppose chemists had chosen to make the $I_2 + 2e^- \rightleftharpoons 2I^-$ half-cell the standard electrode and had assigned it a potential of zero volts.
- a. What would be the E^0 value for the $Br_2 + 2e^- \rightleftharpoons 2Br^-$ half-cell?
- b. What would be the E^0 value for the $Al^{3+} + 3e^- \rightleftharpoons Al$ half-cell?
- c. How much change would be observed in the E^0 value for the reaction involving $Br_2 + I^-$ using the I_2 half-cell as the standard?

22. If a strip of Ni were dipped into a solution of $AgNO_3$, what would be expected to occur? Explain, using E^0 values and equations.

23.
- a. What would happen if an aluminum spoon were used to stir a solution of $Zn(NO_3)_2$?
- b. Could a strip of Zn be used to stir a solution of $Al(NO_3)_3$? Explain, using E^0 values.

24. How do the redox reactions for each of the following types of batteries differ?
- a. zinc-carbon
- b. alkaline
- c. mercury

25.
- a. Why are some standard reduction potentials positive and some negative?
- b. Compare the E^0 value for a metal with the reactivity of that metal.

MIXED REVIEW

26. Predict whether each of the following reactions will occur spontaneously as written by determining the E^0 value for potential reaction. Write and balance the overall equation for each reaction that does occur.
- a. $Mg + Sn^{2+} \longrightarrow$
- b. $K + Al^{3+} \longrightarrow$
- c. $Li^+ + Zn \longrightarrow$
- d. $Cu + Cl_2 \longrightarrow$

27. Why is it possible for alkaline batteries to be smaller than zinc-carbon dry cells?

28. Draw a diagram of a voltaic cell whose two half-reactions consist of Ag in $AgNO_3$ and Ni in $NiSO_4$. Identify the anode and cathode, and indicate the directions in which the electrons and ions are moving.

29. Identify the following reactions as redox or nonredox:

a. $Mg(s) + ZnCl_2(aq) \longrightarrow Zn(s) + MgCl_2(aq)$
b. $2H_2(g) + OF_2(g) \longrightarrow H_2O(g) + 2HF(g)$
c. $2KI(aq) + Pb(NO_3)_2(aq) \longrightarrow PbI_2(s) + 2KNO_3(aq)$
d. $CaO(s) + H_2O(l) \longrightarrow Ca(OH)_2(aq)$
e. $3CuCl_2(aq) + 2(NH_4)_3PO_4(aq) \longrightarrow 6NH_4Cl(aq) + Cu_3(PO_4)_2(s)$
f. $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g)$

30. Can a solution of $Sn(NO_3)_2$ be stored in an aluminum container? Explain, using E^0 values.

31. A voltaic cell is made up of a cadmium electrode in a solution of $CdSO_4$ and a zinc electrode in a solution of $ZnSO_4$. The two half-cells are separated by a porous barrier.

a. Which is the cathode, and which is the anode?
b. In which direction are the electrons flowing?
c. Write balanced equations for the two half-reactions, and write a net equation for the combined reaction.

32. Would the following pair of electrodes make a good battery? Explain.

$$Cd \longrightarrow Cd^{2+} + 2e^-$$
$$Fe \longrightarrow Fe^{2+} + 2e^-$$

33. Arrange the following in order of decreasing oxidation number of the nitrogen atom: N_2, NH_3, N_2O_4, N_2O, N_2H_4, NO_3^-

34. Balance the following redox equations:

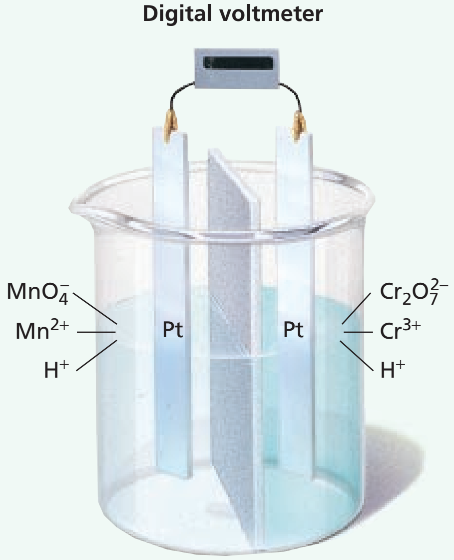
a. $SbCl_5 + KI \longrightarrow KCl + I_2 + SbCl_3$
b. $Ca(OH)_2 + NaOH + ClO_2 + C \longrightarrow NaClO_2 + CaCO_3 + H_2O$

CRITICAL THINKING

35. Applying Models Explain how the oxidation-reduction chemistry of both the voltaic cell and the electrolytic cell are combined in the chemistry of rechargeable cells.

36. Applying Ideas In lead/acid batteries, such as your car battery, the degree of discharge of the battery can be determined by measuring the density of the battery fluid. Explain how this is possible.

37. Interpreting Graphics A voltaic cell is pictured below. Identify the species that is oxidized if current is allowed to flow.



TECHNOLOGY & LEARNING

38. Graphing Calculator: Calculate the Equilibrium Constant, Using the Standard Cell Voltage

The graphing calculator can run a program that calculates the equilibrium constant for an electrochemical cell using an equation called the Nernst equation, given the standard potential and the number of electrons transferred. Given that the standard potential is 2.041 V and that two electrons are transferred, you will calculate the equilibrium constant. The program will be used to make the calculations.

Go to Appendix C. If you are using a TI 83 Plus, you can download the program and data and run the application as directed. If you are using another calculator, your teacher will provide you with keystrokes and data sets to use.

Remember that you will need to name the program and check the display, as explained in Appendix C. You will then be ready to run the program. After you have graphed the data, answer these questions.

a. What is the equilibrium constant when the standard potential is .099?
b. What is the equilibrium constant when the standard potential is 1.125?
c. What is the equilibrium constant when the standard potential is 2.500?

HANDBOOK SEARCH

39. Several reactions of aluminum are shown in the common reactions section for Group 13 of the *Elements Handbook*. Use these reactions to answer the following.
  a. Which of the five reactions shown are oxidation-reduction reactions? How do you know?
  b. For the redox reactions you listed for item a, identify what is oxidized and what is reduced.
  c. Write half-reactions for each equation you listed in item a.

40. Aluminum is described in Group 13 of the *Elements Handbook* as a self-protecting metal. This property of aluminum results from a redox reaction.
  a. Write the redox equation for the oxidation of aluminum.
  b. Write the half-reactions for this reaction showing the number of electrons transferred.
  c. What problems are associated with the buildup of aluminum oxide on electrical wiring made of aluminum?

RESEARCH & WRITING

41. Go to the library and find out what you can about the electroplating industry in the United States. What are the top three metals used for plating, and how many metric tons of each are used in the United States each year for electroplating?

42. Investigate the types of batteries being considered for electric cars. Write a report on the advantages and disadvantages of these types of batteries.

ALTERNATIVE ASSESSMENT

43. **Performance** Take an inventory of the types of batteries used in your home. Find out the voltage supplied by each battery and what electrochemical reaction each uses. Suggest why that electrochemical reaction is used in each case.

44. In our portable society, batteries have become a necessary power supply. As consumers, we want to purchase batteries that will last as long as possible. Advertisements tell us that some batteries last longer than others, but do they really? Design an investigation to answer the question. Is there a difference in longevity among the major brands of AA batteries? Add a cost-effectiveness component to your design.

45. When someone with a silver filling in a tooth bites down on an aluminum gum wrapper, saliva acts as an electrolyte. The system is an electrochemical cell which produces a small jolt of pain. Explain what occurs, using half-cell reactions and $E°$ values.