Applications of Oxidation-Reduction Reactions

SECTION 16.2

SECTION PREVIEW

Objectives

- Analyze common redox processes to identify the oxidizing and reducing agents.
- Identify some redox reactions that take place in living cells.

Natural redox reactions are going on around you every day, everywhere. This is partly due to the abundance of oxygen, which acts as the oxidizing agent as it is reduced in some redox reactions. Other oxidizing agents take part in different redox reactions, especially in environments where not much oxygen gas is found. Near the vents of volcanoes, where sulfur compounds explode out from deep within Earth, enormous deposits of solid yellow sulfur are found. The element sulfur acts both as an oxidizing agent and as a reducing agent in the reaction that forms the sulfur deposits. Can you tell which sulfur compound serves each function in this reaction?

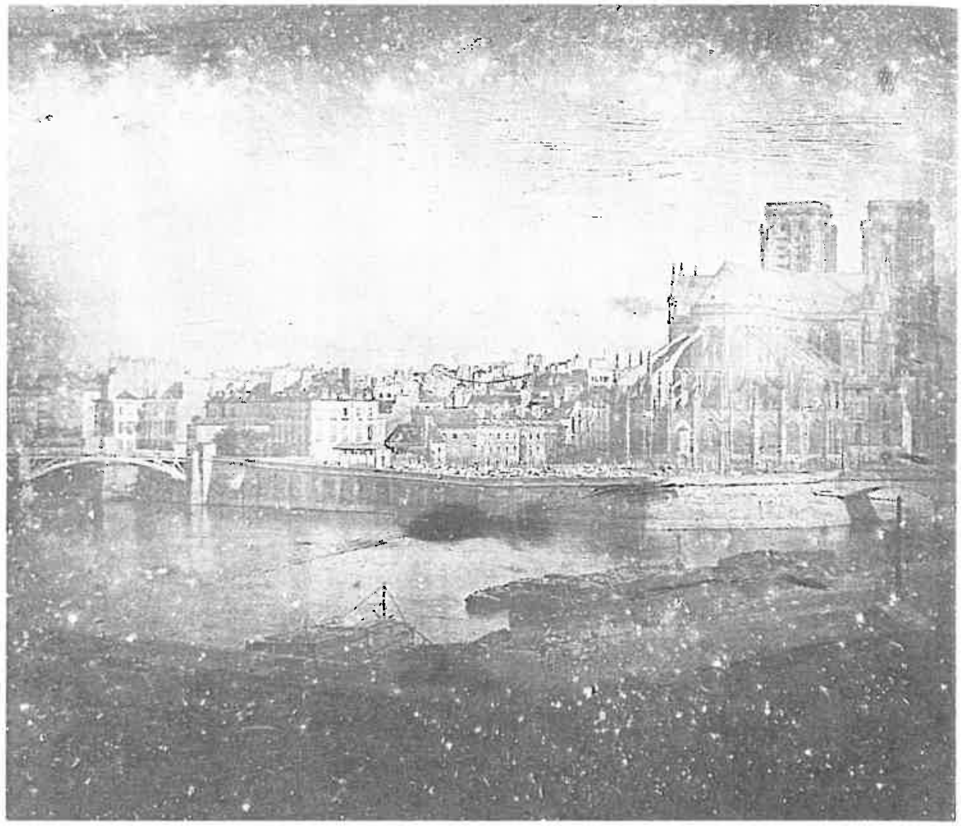
$$2H_2S(g) + SO_2(g) \rightarrow 3S(s) + 2H_2(g) + O_2(g)$$

Note that more than one element in a reaction can be oxidized or reduced. The sulfur in hydrogen sulfide and the oxygen in sulfur dioxide both are oxidized. Sulfur in sulfur dioxide and hydrogen in hydrogen sulfide both are reduced. Each reactant acts as both a reducing agent and an oxidizing agent.

Say Cheese: Redox in Photography

Understanding natural redox reactions such as the one that occurs in sulfur volcanoes has allowed chemists to develop many processes that make use of oxidation and reduction reactions. Without them, photographs or steel wouldn't exist, and stains would be much harder to remove from clothing.

Figure 16.7
Early Photos
In a daguerreotype, a redox reaction between silver and iodine fumes produced a layer of light-sensitive silver iodide on the surface of the polished photographic plate. Exposure to light caused decomposition of the silver iodide into elemental silver, which was then treated with the fumes of heated mercury to form bright amalgam areas. The image of Paris shown here was made by Daguerre himself.



WORD ORIGIN

photograph:
photos **(GK) light**
graphein **(GK) to write**
Light is used to record the image of an object in a photograph.

GO TO CD-ROM Use the Interactive Virtual Experiment *Titrate Using Redox* found on Disc 3 of the CD-ROM.

Leonardo da Vinci described a primitive "camera" before 1519, in which someone had to trace images focused on a glass plate inside a box. However, it wasn't until 1838 that the French inventor L.J.M. Daguerre successfully fixed the images in a camera on highly polished, silver-plated copper to make the first photographs. These early photographs were called daguerreotypes in his honor, **Figure 16.7.**

Modern photographic film is made of a plastic backing covered with a layer of gelatin, in which millions of grains of silver bromide are embedded. When light strikes a grain, silver and bromide ions are converted into their elemental forms through a redox reaction. The equation for this redox reaction is as follows.

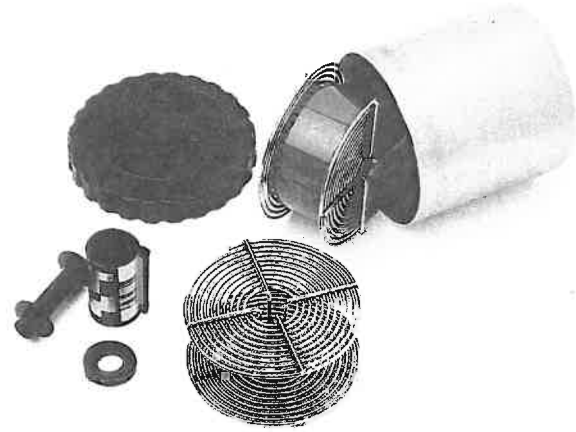
$$2Ag^{+} + 2Br^{-} \rightarrow 2Ag + Br_2$$

The reaction begins when the shutter on a camera is opened. Light from the scene being photographed passes through the camera's lens and shutter and strikes the light-sensitive silver bromide on the film. The light energy causes electrons to be ejected from a few of the bromide ions, oxidizing them to elemental bromine. The electrons are transferred to silver ions, reducing them to metallic silver atoms. These grains are now activated. The developing chemicals continue the redox reaction by causing the activated grains to be converted to metallic silver. In areas where the light is brightest, more grains are activated, and after developing, they become the darker areas. No silver atoms form in areas of the film that are not struck by light, and that part of the film remains transparent. The exposed film is then developed into a negative, during which time the remaining AgBr and Br_2 is washed away. **Figure 16.8** describes the developing and printing processes.

Figure 16.8

Developing and Printing Pictures

Making photographic negatives by developing exposed film involves several steps. The process describes how black-and-white pictures are made. For color photos, light-sensitive dyes are combined with the silver bromide in layers on the film.

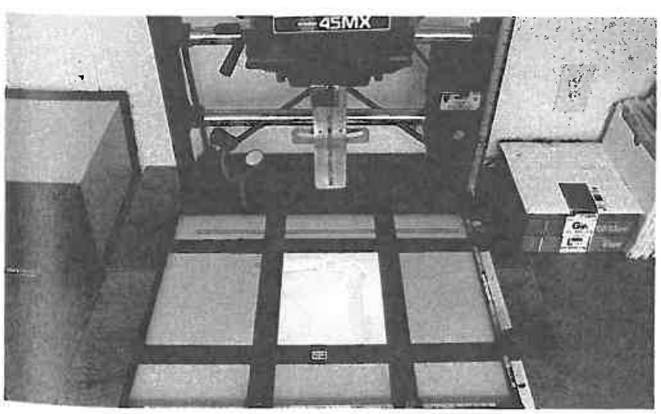


1. The exposed film is transferred to a canister, where it is developed using a solution of a reducing agent, or developer. The organic compound hydroquinone is usually used for this purpose. The developer reduces all the silver ions to silver atoms in any grain of silver bromide that was hit by light, but it does not react with silver ions in grains that were not exposed to light. Because metallic silver is dark and silver bromide is light, an image having light and dark areas is produced.

2. After the film has been developed, a solution of a fixer containing thiosulfate ions is added. Thiosulfate ions react with unreduced silver ions to form a soluble complex, which is washed away. This prevents unreduced silver ions from becoming reduced and darkening slowly over time. The reaction follows.

$$AgBr(s) + 2S_2O_3^{2-}(aq) \rightarrow [Ag(S_2O_3)_2]^{3-}(aq) + Br^-(aq)$$

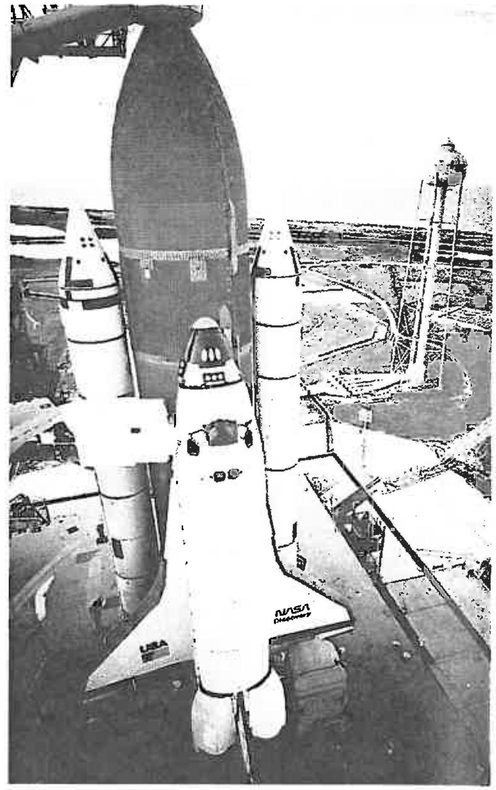
3. The fixed film is washed to remove any remaining developer or fixer solution. The photographic negative is the reverse of the image photographed; that is, light areas in the scene are dark on the film, and vice versa.



4. When light is shone through the negative onto light-sensitive photographic paper, a photographic print is made. The print is positive; light and dark areas are identical to those in the scene.

PHYSICS CONNECTION

Solid Rocket Booster Engines



If you have ever built and launched a model rocket, you probably noticed that the rocket engine was made of a solid, highly combustible material packed into a cardboard tube. After ignition, the expansion and expulsion of the gases produced enough downward force to launch the lightweight rocket quickly into the air. Space shuttles use a similar type of technology, but on a much larger scale.

Engine systems The space shuttle has two different engine systems. The three main engines attached directly to the shuttle operate on liquid hydrogen and liquid oxygen reservoirs carried in the large, centrally located disposable fuel tank. The two smaller, reusable, strap-on booster rockets on either side of the main fuel tank are loaded with a solid fuel, which undergoes a powerful, thrust-producing, oxidation-reduction reaction that helps boost the shuttle into orbit.

Solid rocket fuel The solid rocket fuel is a mixture containing 12 percent aluminum powder, 74 percent ammonium perchlorate, and 12 percent polymer binder. Once ignited, the engine cannot be extinguished. The extremely reactive ammonium perchlorate supplies oxygen to the easily oxidized aluminum powder, providing a greatly exothermic and fast reaction. The purpose of the polymer binder is to hold the mixture together and to help it burn evenly. The overall redox reaction is shown here.

$$24e^-$$

$$8Al + 3NH_4ClO_4 \rightarrow 4Al_2O_3 + 3NH_4Cl$$

Shuttle forces Each solid rocket booster weighs 591 000 kg at liftoff, produces 11.5 million N of force, and operates for about two minutes into the flight. For comparison, a 1000-kg car accelerating from 0 to 26.8 m/s (60 mph) in 7 seconds would require a force of only 3830 N. The tremendous release of chemical energy and expansion of hot gases due to the oxidation-reduction reaction through the engine of the solid rocket booster produces the tremendous thrust needed to get the 2 million-kg shuttle from 0 to almost 700 m/s (1500 mph) in just 132 seconds.

Connecting to Chemistry

1. **Applying** Powdered aluminum is used in another greatly exothermic reaction, the thermite reaction, which is used for welding metals. The reaction is as shown.

   $$2Al + Fe_2O_3 \rightarrow Al_2O_3 + 2Fe$$

   What role does the powdered aluminum play in this reaction?

2. **Acquiring Information** Investigate the lives and research of Robert Goddard and Werner Von Braun, who both experimented with rockets in the 1930s and helped guide the United States into the space age. Write a short report about these men.

Having a Blast: Redox in a Blast Furnace

Iron is seldom found in the elemental form needed to make steel. Metallic iron must be separated and purified from iron ore—usually hematite, Fe_2O_3. This process takes place in a blast furnace in a series of redox reactions. The major reaction in which iron ore is reduced to iron metal uses carbon monoxide gas as a reducing agent.

First, a blast of hot air causes coke, a form of carbon, to burn, producing CO_2 and heat. Limestone, $CaCO_3$, which is mixed with the iron ore in the furnace, decomposes to form lime (CaO) and more carbon dioxide. The carbon dioxide then oxidizes the coke in a redox reaction to form carbon monoxide, which is used to reduce the iron ore to iron. The process is outlined here and illustrated in **Figure 16.9.**

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

$$CO_2(g) + C(s) \rightarrow 2CO(g)$$

$$2\overset{3+}{Fe}(s) + 3\overset{2-}{O}(s) + 3CO(g) \rightarrow 2\overset{0}{Fe}(l) + 3CO_2(g) \quad (6e^-)$$

Fact of the Matter

The Stone, Bronze, and Iron Ages are historical periods named after the most common material that was used for making tools during each time. The Bronze Age came before the Iron Age because copper and tin, the elements that are melted together to form the alloy bronze, were both widely available and easily accessible metals. Bronze is stronger than either copper or tin alone. The Iron Age came later because iron is harder to reduce to elemental form. It requires smelting at a higher temperature than bronze.

Redox in Bleaching Processes

Bleaches can be used to remove stains from clothing. Where do the stains go? Bleach does not actually remove the chemicals in stains from the fabric; it reacts with them to form colorless compounds. In chlorine bleaches, an ionic chlorine compound in the bleach reacts with the compounds responsible for the stain. This ionic compound is sodium hypochlorite (NaOCl). The hypochlorite ions oxidize the molecules that cause dark stains.

$$OCl^-(aq) + \underset{\text{(colored)}}{\text{stain molecule(s)}} \rightarrow Cl^-(aq) + \underset{\text{(colorless)}}{\text{oxidized stain molecule(s)}}$$

▲ **Molten iron is drawn off at the bottom of the furnace. A combination of by-products known as slag is also removed at the bottom.**

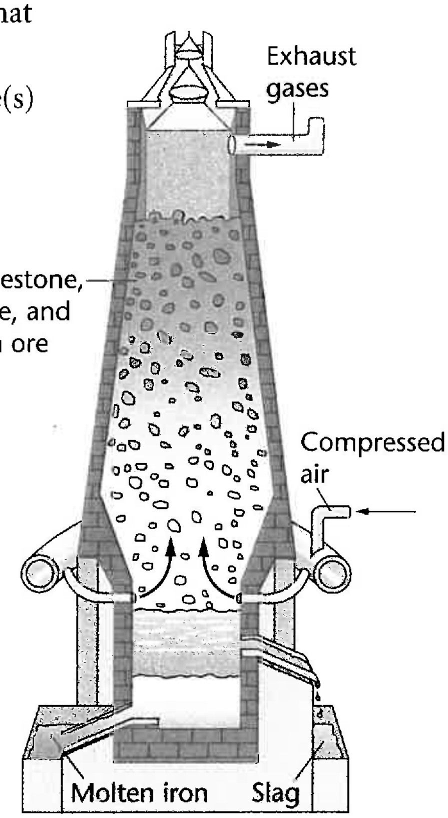


Figure 16.9
Blast Furnace
Iron ore (Fe_2O_3), coke (C), and limestone ($CaCO_3$) are added at the top of the furnace. Hot air at about 900°C, blasted into the bottom of the furnace, burns the coke in an exothermic reaction. This reaction causes temperatures in a blast furnace to reach about 2000°C. ▶

miniLAB 2

Testing for Alcohol by Redox

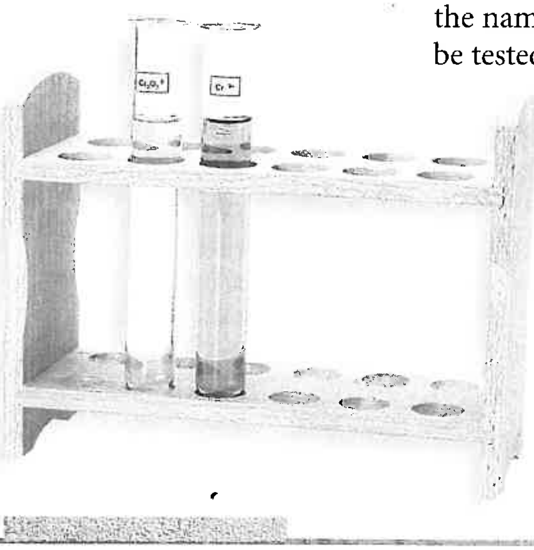
Organic alcohols react with orange dichromate ions, producing blue-green chromium(III) ions. This reaction is used in a Breathalyzer test to test for the presence of alcohol in a person's breath. In this MiniLab, you will use this reaction to test for the presence of alcohol in a number of household hygiene, cosmetic, and cleaning products.

Procedure

1. Label five small test tubes with the names of the products to be tested.
2. Place approximately 1 mL of each product in the appropriate tube.
3. Wearing apron and goggles, add three drops of dichromate reagent to each tube, and stir to mix the solutions.

CAUTION: *Do not allow dichromate reagent to come into contact with skin. Wash with large volumes of water if it does.*

4. Observe and record any color changes that occur within one minute.



Analysis

1. Which of the products that you tested contain alcohol? Was the presence of alcohol noted on the label of the products?
2. If the orange $Cr_2O_7^{2-}$ ion reacts with alcohol to produce the blue-green Cr^{3+} ion, what substance is the reducing agent in the reaction?

Bleaches containing hypochlorite should be used carefully because hypochlorite is a powerful oxidizing agent that can damage delicate fabrics. These bleaches usually have a warning label telling the user to test an inconspicuous part of the fabric before using the product. In addition to acting as a bleaching agent, hypochlorite ions are also used as disinfectants, as **Figure 16.10** shows.

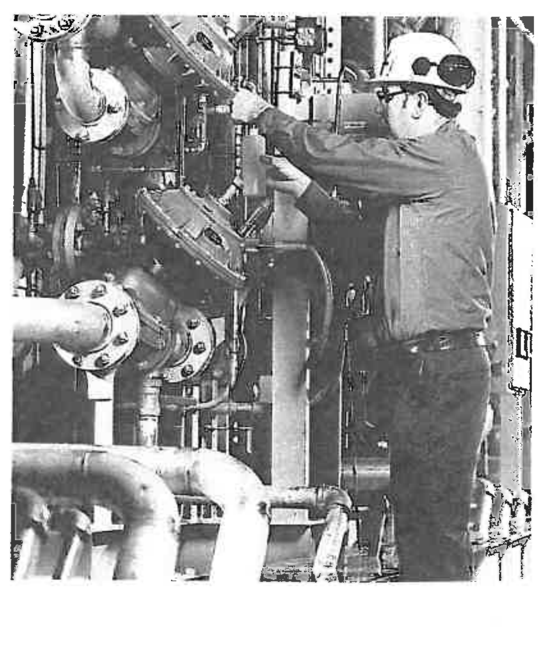


Figure 16.10

Hypochlorite as a Disinfectant

Hypochlorite is used in disinfectants to kill bacteria in swimming pools and in drinking water. In both cases, the hypochlorite ions act as oxidizing agents. Bacteria are killed when important compounds in them are destroyed by oxidation. In this photo, the amount of chlorine in the water is being monitored. Chlorine reacts with the water to form hypochlorite ions.

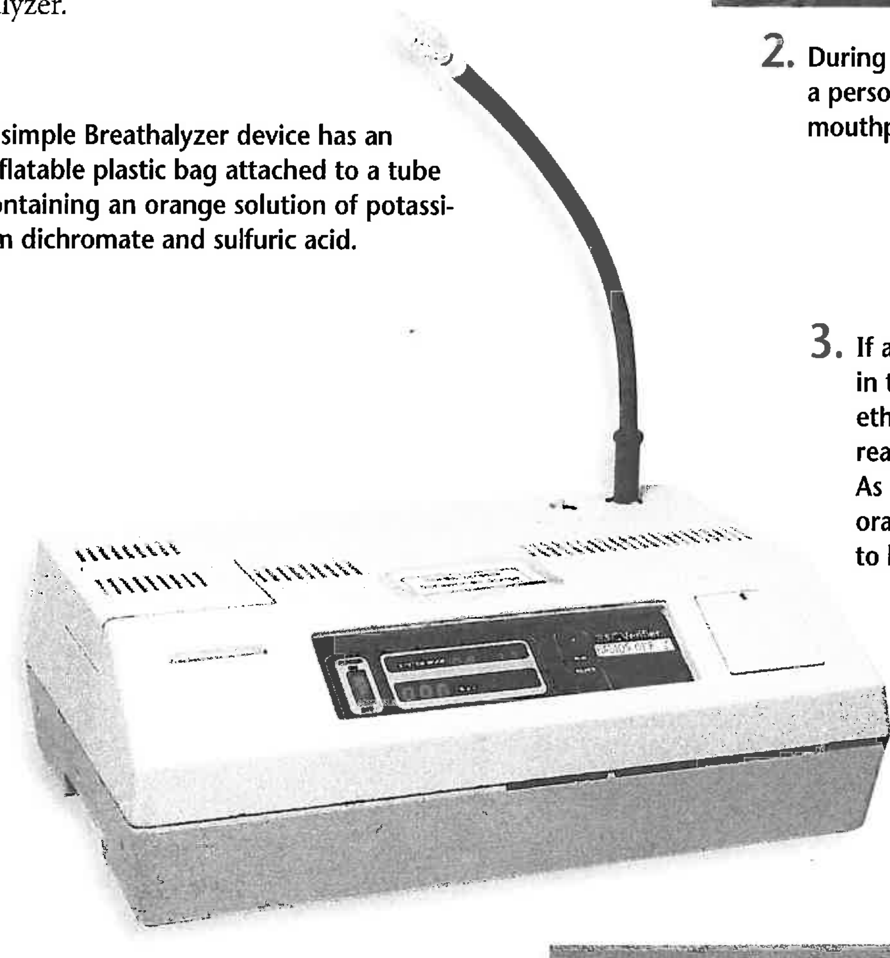
How it Works

Breathalyzer Test

The alcohol in beverages, hair spray, and mouthwashes is ethanol. Ethanol is a volatile liquid that evaporates rapidly at room temperature. Because of this volatility, drinking an alcoholic beverage results in a level of gaseous ethanol in the breath that is proportional to the level of alcohol in the bloodstream. About 50 percent of all automobile accidents that result in a fatality are caused by intoxicated drivers. Law officers can determine quickly whether a person is legally intoxicated by using an instrument called a breath analyzer, or Breathalyzer.

2. During a Breathalyzer test, a person blows into the mouthpiece of the bag.

1. A simple Breathalyzer device has an inflatable plastic bag attached to a tube containing an orange solution of potassium dichromate and sulfuric acid.



3. If alcohol vapors are present in the person's breath, ethanol undergoes a redox reaction with the dichromate. As ethanol is oxidized, the orange Cr^{6+} ions are reduced to blue-green Cr^{3+} ions.

4. The exact color produced depends on the amount of alcohol in the breath. The color change that is produced during the test is compared to standard color mixtures of the two chromium ions to get an estimate of the blood alcohol level.

Thinking Critically

1. Suppose a person used mouthwash shortly before taking a Breathalyzer test. What might be the result?
2. How would the color produced in a Breathalyzer test change as the ethanol content of the blood increases?

Figure 16.11
The Green Lady
The green color of the Statue of Liberty in New York Harbor is due to a layer of patina, or protective coating, that covers the copper sheets making up the statue. The presence of the patina helps keep the statue from corroding further because oxygen cannot get through the patina to reach the copper layers underneath.

Corrosion of Metals

Did you know that the Statue of Liberty is made of copper sheets attached to a steel skeleton? Why does it appear green rather than the reddish-brown color of copper? When copper is exposed to humid air that contains sulfur compounds, it undergoes a slow oxidation process. Under these conditions, the copper metal atoms each lose two electrons to produce Cu^{2+} ions, which form the compounds $CuSO_4 \cdot 3Cu(OH)_2$ and $Cu_2(OH)_2CO_3$. These compounds are responsible for the green coat or patina found on the surface of copper objects that have been exposed to air for long periods of time, **Figure 16.11.**

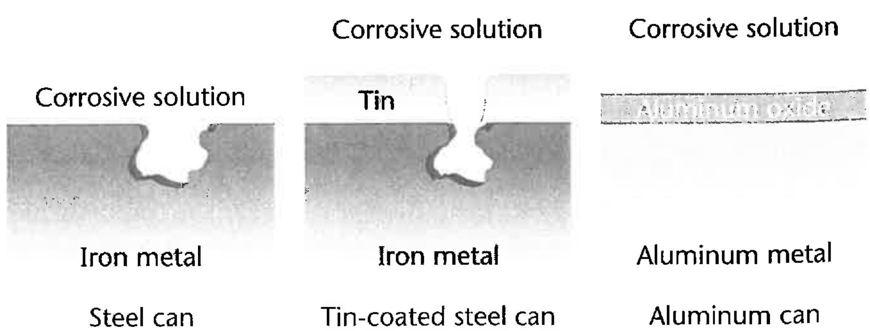
You have learned that iron is oxidized by oxygen in the air to form rust. Aluminum is a more active metal than iron. As a result of its greater activity, aluminum is oxidized more quickly than iron. If this is true, why does an aluminum can degrade much more slowly than a tin can, which is made of iron-containing steel that is coated with a thin layer of tin? The reason is that, like copper, aluminum is oxidized to form a compound that coats the metal and protects it from further corrosion, as shown in **Figure 16.12.** Aluminum reacts with oxygen to form aluminum oxide in a redox reaction.

$$4Al(s) + 3O_2(g) \rightarrow 2Al_2O_3(s)$$

A coating of aluminum oxide is tough and does not flake off easily, as iron oxide rust does. When rust flakes fall off a surface, additional metal is exposed to air and becomes corroded.

Figure 16.12
Corrosion of Iron and Aluminum
Because iron rust is porous and flaky, it does not form a good protective coating for itself. ▶

A tin coating offers some protection to the iron. However, if a hole or crack develops in the thin tin coating, the underlying iron corrodes rapidly. A tin-coated steel can will degrade completely in about 100 years. The aluminum oxide coating on an aluminum can is tough and closely packed. It protects the underlying aluminum from further corrosion so that the can will take about 400 years to degrade. ▶



Everyday Chemistry

Lightning-Produced Fertilizer

All plants need nutrients just as animals do, but did you know that one of the main nutrients needed is nitrogen? Even though the air surrounding Earth is almost 80 percent nitrogen, the nitrogen is in the form of N_2 molecules, a form that most plants and animals cannot use. Nitrogen from the air is converted to a form that plants can use by a process called nitrogen fixation. Plants can best use nitrogen when it is in the form of the ammonium ion, NH_4^+, where the nitrogen has an oxidation number of 3−, but they can also use the nitrate ion, NO_3^-, with nitrogen having an oxidation number of 5+.

Nitrogen fixation Nitrogen can be fixed for plants in three different ways: by lightning, by nitrogen-fixing bacteria living in the roots of certain plants or in the soil, and by commercial synthesis reactions such as the Haber ammonia process.

Nitrogen is a fairly inert gas because the triple bond of N_2 is strong and resists breaking. However, the exceptionally high energy and temperatures of lightning can easily break bonds and allow for recombination of gases in the atmosphere.

Lightning-driven reactions In the process of lightning-driven nitrogen fixation, nitrogen and oxygen combine to form nitrogen monoxide. Nitrogen monoxide then combines with more oxygen to form nitrogen dioxide. This nitrogen dioxide mixes with water in the air to form nitric acid and more nitrogen monoxide, which is available to continue the cycle.

$$N_2 + O_2 \rightarrow 2NO$$
$$2NO + O_2 \rightarrow 2NO_2$$
$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$$

Fertilizer production The pH of rainwater is naturally slightly acidic, and you can see that some of this acidity is due to the dissolved nitric acid, HNO_3, from nitrogen fixation. As the rain soaks into the soil, bacteria convert the nitrate ions into ammonium ions.

How does nature's manufacturing of fixed nitrogen compare with commercial production of fixed nitrogen? You may think that lightning isn't all that common, but it is estimated that there are approximately 10 000 lightning storms every day over the surface of Earth. Stated another way, lightning strikes 100 times a second on the planet as a whole. Approximately 10 billion kg of nitrogen are fixed yearly in the atmosphere. Biological agents such as bacteria fix about 100 billion kg of nitrogen yearly, and an amount equal to that is fixed through the manufacture of fertilizer and other industrial processes.

Exploring Further

1. **Classifying** Nitrogen fixation in the soil is accomplished by bacteria living in the roots of certain plants. Name some of these plants.
2. **Applying** In each of the three equations shown, what is oxidized and what is reduced?
3. **Acquiring Information** The process by which nitrogen is put back into the air is called denitrification. Find out what conditions are necessary for this process and what reaction occurs.

Silver Tarnish: A Redox Reaction

WORD ORIGIN

tarnish:
terne (OF) dull, wan

The shiny surfaces of many metal objects lose luster and become dull and tarnished as the metal atoms undergo oxidation.

Imagine if, along with your usual chores of taking out the trash, washing dishes, feeding your pets, and taking care of your younger siblings, you also had to polish the silver—as people did back in your great-grandparents' days. How would you find time for any fun? Fortunately, other materials such as stainless steel have replaced most "silverware." Why do silver utensils have to be polished, but those made of stainless steel or aluminum don't? Silver becomes tarnished through a redox reaction that is a form of corrosion, as rusting is. Tarnish is formed on the surface of a silver object when silver reacts with H_2S in air. The product, black silver sulfide, forms the coating of tarnish on the silver.

$$O_2(g) + 4Ag(s) + 2H_2S(g) \rightarrow 2Ag_2S(s) + 2H_2O(l)$$

Many commercial silver polishes contain abrasives that help to remove tarnish. Unfortunately, they also remove some of the silver. A more gentle way to remove tarnish from the surface of a silver object involves another redox reaction. In this reaction, aluminum foil scraps act as a reducing agent.

$$6e^-$$

$$2Al^0(s) + 6Ag^+(s) + 3S^{2-}(s) + 6H_2O(l) \rightarrow 6Ag^0(s) + 2Al^{3+}(aq) + 6OH^-(aq) + 3H_2S(g)$$

This reaction is essentially the reverse of the reaction that forms tarnish. Here, silver ions in the Ag_2S tarnish are reduced to silver atoms, while aluminum atoms in the foil are oxidized to aluminum ions. The tarnish-removing solution usually includes baking soda (sodium hydrogen carbonate) to help remove any aluminum oxide coating that forms and to make the cleaning solution more conductive. **Figure 16.13** shows how this method of silver cleaning is done.

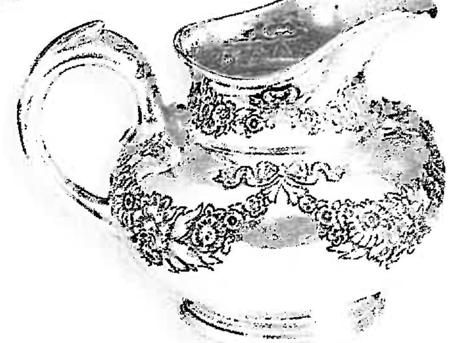


Figure 16.13
Removing Silver Tarnish
Even though corrosion is an unwanted redox reaction, removing the tarnish makes use of another redox reaction. A nest of crumpled aluminum foil scraps is made at the bottom of a large pot. The tarnished silver object is added, making sure the silver is in contact with the foil scraps. Baking soda is added, and the silver is covered with water. When the pot is heated on a stove, the silver sulfide tarnish is reduced to silver atoms, and the silver object becomes shiny and bright.

CHEMISTRY & TECHNOLOGY

Forensic Blood Detection

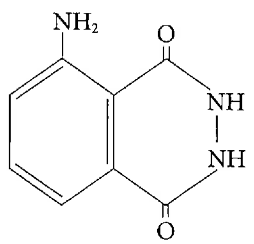
The gas station at the corner was robbed, and the cashier was shot. On television, police announce that Suspect A has been taken into custody. They have confiscated a jacket, allegedly worn by the suspect. After preliminary examination by the police department, the jacket is sent to a forensic laboratory for scientific investigation. One of the first tests a technician at the laboratory will carry out determines whether or not there are blood stains on the jacket.

The Luminol Test

The technician may choose from several chemical tests for blood, all based on the fact that the hemoglobin in blood catalyzes the oxidation of a number of organic indicators to produce a colored product that emits light, or luminesces.

The technician on this case chooses the luminol test. Luminol has an organic double-ring structure, shown below. In 1928, German chemists first observed the blue-green luminescence when the compound was oxidized in alkaline solution. It was soon found that a number of oxidizing agents, such as hydrogen peroxide, bring about the luminescence. Later, workers noted that the luminescence was greatly enhanced by the presence of blood, which led to its current use in forensic investigations.

Luminol



The technician carefully mixes an alkaline solution of luminol with aqueous sodium peroxide and, in a darkened workplace, sprays the solution onto suspected spots on the jacket. Bingo! An intense, blue-green chemiluminescence is emitted from several spots. Because the glow will last for a few minutes, the technician photographs the spots and their telltale light.

Ruling Out with Luminol

You may wonder if this relatively simple procedure will serve to convict Suspect A. Certainly not. However, if the test had been negative, Suspect A might have been cleared from suspicion. A negative result ensures that a stain is *not* blood. But, because this is not the case with the stains on the jacket, the luminol test is preliminary and will be used with other tests.

The luminol test is especially useful because it works well with both fresh and dried blood. Luminol has one particularly useful feature. The same stains can be made luminescent over and over again if the spray is allowed to dry and the stains are resprayed.

A positive test should not be taken as absolute proof of blood because luminol reacts with copper and cobalt ions, as well as with the iron in hemoglobin. However, it reacts much more strongly with hemoglobin. A large number of forensic authorities believe that the luminol test has value as a preliminary sorting technique.

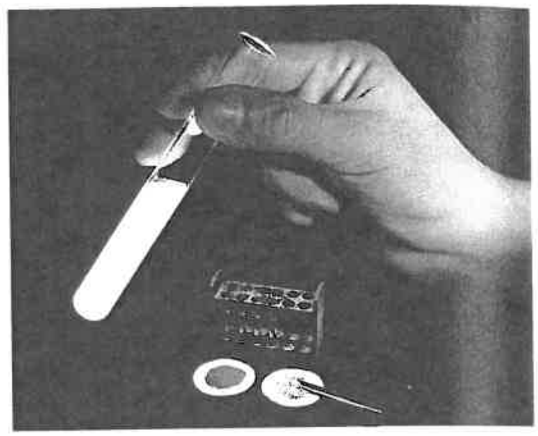
DISCUSSING THE TECHNOLOGY

1. **Applying** If a luminol test yields a positive reaction, what is the next logical step?
2. **Hypothesizing** Why can it almost never be assumed that stains are uncontaminated, although stain evidence is important in a criminal investigation?

Figure 16.14
Chemiluminescence

◀ When lightning is produced by an electrical discharge in the atmosphere, electrons in molecules of O_2 and N_2 gases are excited to higher energy levels. Energy from the electricity breaks the molecules into atoms. When the atoms recombine to form molecules and the electrons return to lower energy levels, light energy is released through chemiluminescence.

When luminol is oxidized and is observed in the dark, an eerie blue-green glow is produced through chemiluminescence. ▶



Fact of the Matter

Nitrous oxide is produced by a redox reaction between oxygen and nitrogen during lightning storms. It was discovered and studied in the late 1700s by Joseph Priestley, who found that inhaling it resulted in unusual side effects including laughing, singing, and fighting. For this reason, it was called laughing gas. Its anesthetic properties were discovered by accident in Connecticut in 1844 at a public demonstration given for amusement when a man who inhaled nitrous oxide cut his leg badly in a scuffle but felt no pain until the gas wore off.

Chemiluminescence: It's Cool

Some redox reactions can release light energy at room temperature. The production of this kind of cool light by a chemical reaction is called chemiluminescence. The light from chemiluminescent reactions can be used in emergency light sticks that work without an external energy source. You may recall learning in Chapter 6 how these light sticks work. Now you know that the reaction that takes place when the two solutions in the light sticks are mixed involves an oxidation and a reduction.

Some chemiluminescent redox reactions occur naturally in the atmosphere as a result of lightning, **Figure 16.14.** Other chemiluminescent reactions involve luminol, an organic compound that emits cool light when it is oxidized. Luminol reactions are utilized by forensic chemists to analyze evidence in crime investigations. They spray luminol onto a location where the presence of blood is suspected. If blood is present, the iron(II) ions in the blood oxidize the luminol to form a chemiluminescent compound that glows in the dark. The iron is reduced by the luminol. **Figure 16.14** shows the glow from the oxidized form of luminol.

Biochemical Redox Processes

How are bears able to stay warm enough to keep from freezing during their winter hibernation? How do marathon runners get the energy to finish a race without stopping to eat? In both cases, fats stored in the body are oxidized. Oxygen molecules from the air are reduced as they gain electrons to form water. In a series of redox reactions called respiration,

Figure 16.15
Keeping Warm
Although it is common to think that only mammals keep warm, in truth, all plants and animals maintain a temperature at which their enzymes function best. Plants keep from freezing because heat is produced as a by-product of respiration and photosynthesis. One of the first plants to poke through the snow in early spring is the heat-producing skunk cabbage. The heat it releases allows it to get a head start on other plants and also contributes to the unpleasant odor that gives it its name.

energy is released. **Figure 16.15** shows one effect of this heat in plants. Respiration will be discussed in Chapter 19. Many other redox reactions take place in living things. Electrons are transferred between molecules in redox reactions during photosynthesis and in the reactions that fireflies use to flash light signals to potential mates. You will study photosynthesis in Chapter 20.

Some organisms can use the energy released during redox reactions to convert chemical energy into light energy, a process called bioluminescence. You are probably familiar with the flashing lights given off by fireflies during courtship, but did you know that many different organisms—including some fish, at least one type of mushroom, and a caterpillar known as a glowworm—also are bioluminescent? **Figure 16.16** shows bioluminescence in fireflies.

Now that you have learned what redox reactions are and have read about some of the processes of which they are part, you can reexamine the redox reaction that makes cut fruit turn brown. The color is due to brown pigments that are formed by the oxidation of colorless compounds normally present in the cells of the fruit. Oxygen in the air is the oxidizing agent that reacts with the colorless compounds to produce the brown pigments. The oxygen is reduced when it accepts electrons from the pigments, so the pigments function as reducing agents. This combination of oxidation and reduction goes hand in hand in a redox reaction because electrons that are lost by one element must be gained by another.

WORD ORIGIN

bioluminescent:
bios (GK) life
lumen (L) light
escentis (L) beginning to be, have, or do

A bioluminescent substance undergoes a chemical reaction in living things in which potential energy in chemical bonds is converted into light energy.

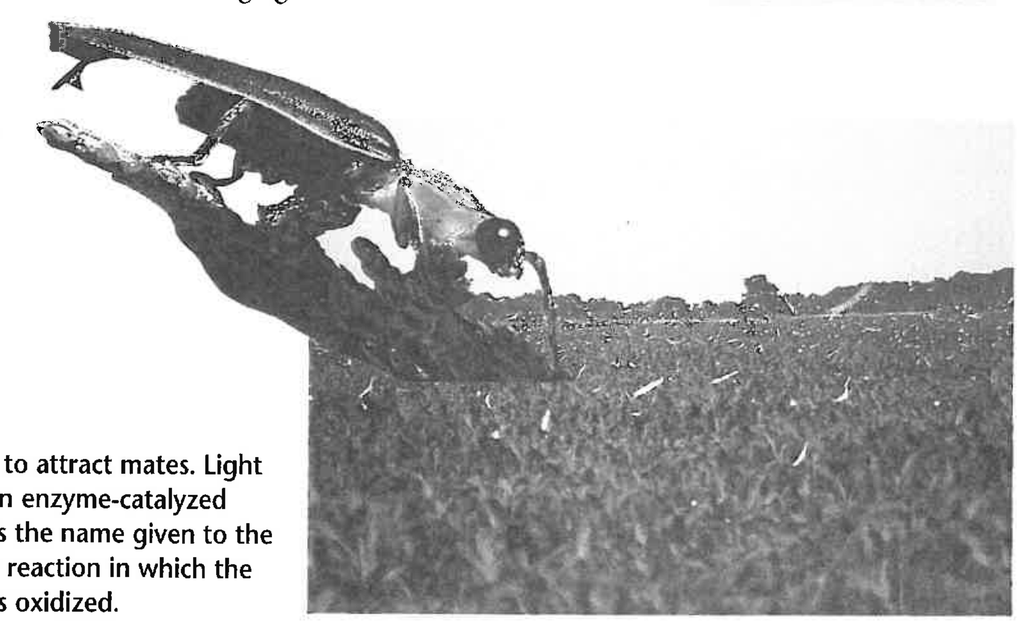


Figure 16.16
Firefly Signals
Fireflies use flashes of light to attract mates. Light energy is released during an enzyme-catalyzed redox reaction. Luciferase is the name given to the enzyme that speeds up the reaction in which the organic molecule luciferin is oxidized.

Fact of the MATTER

Myoglobin, found in muscle tissue, is an iron-containing protein that stores oxygen. Myoglobin in living muscle tissue is bound to oxygen and is a red color. It becomes pale purple after death when the oxygen is lost. Heating meat results in oxidation of the iron in myoglobin, which then has the brown color that tells you the meat is cooked.

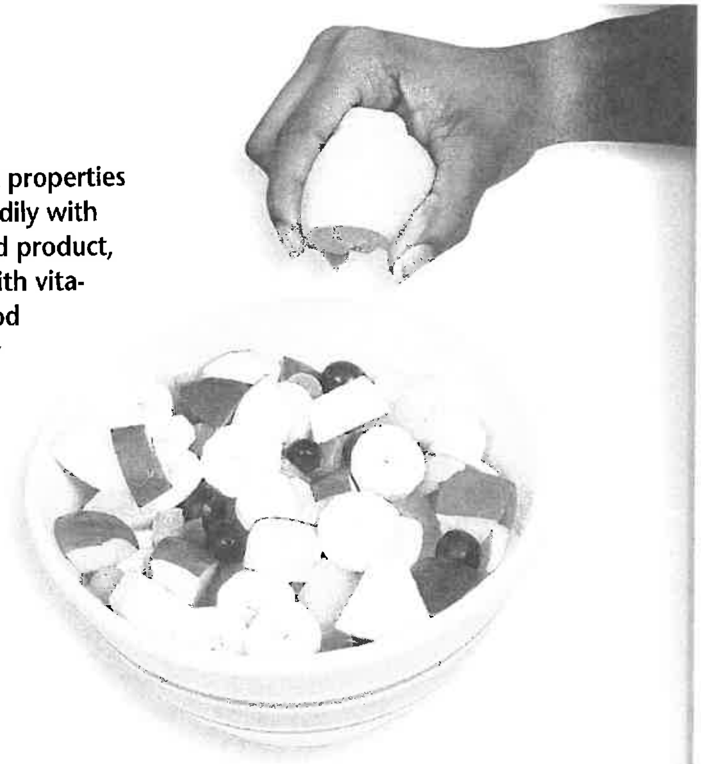


Figure 16.17
Antioxidants
Vitamin C owes its antioxidant properties to the fact that it reacts so readily with oxygen. When added to a food product, oxygen reacts preferentially with vitamin C, thereby sparing the food product from oxidation. Other anti-oxidant food additives include the synthetic compounds BHA and BHT and the natural antioxidant, vitamin E.

The skin of a fruit keeps oxygen out, which is why unbroken fruit does not turn brown. Coating cut fruit with an antioxidant can prevent browning and keep a fruit salad looking fresh longer. The vitamin C in lemons is a good antioxidant. If lemon juice is squirted onto cut banana or apple slices, they will not brown as quickly because the vitamin C reacts with oxygen more readily than do the fruit-browning compounds, **Figure 16.17.**

Supplemental Problems

For more practice with solving problems, see Supplemental Practice Problems, Appendix B.

Connecting Ideas

Most reactions involve electron transfer and thus are redox reactions. You have learned to identify which element is reduced and which is oxidized when you are given the equation for a redox reaction. You might wonder why one element accepts electrons from another and whether you can predict which element will be oxidized and which will be reduced. Learning to make those predictions is the next step in your study of electron-transfer processes in compounds and will help you understand how redox reactions in batteries produce electricity.

SECTION REVIEW

Understanding Concepts

1. What role does the reducing agent hydroquinone play in the production of a photographic negative?
2. How is most of the iron that is used for making steel purified from iron ores?
3. Why do aluminum cans degrade more slowly than cans made of iron?

Thinking Critically

4. **Applying Concepts** Oxygen is required for the production of light by fireflies. What role does the oxygen play in the reaction?

Applying Chemistry

5. **Bleaching** Why can't rust stains be removed with bleach?

CHAPTER 16 ASSESSMENT

REVIEWING MAIN IDEAS

16.1 The Nature of Oxidation-Reduction Reactions

- Oxidation occurs when an atom or ion loses one or more electrons and attains a more positive oxidation number. Reduction takes place when an atom or ion gains electrons and attains a more negative oxidation number.
- Oxidation and reduction reactions always occur together in a net process called a redox reaction.
- An oxidizing agent is the substance that gains electrons and is reduced during a redox reaction. A reducing agent is the substance that loses electrons and is oxidized during a redox reaction.

16.2 Applications of Oxidation-Reduction Reactions

- In photography, light triggers the reduction of silver ions to silver metal on photographic film.
- Bleach removes stains from clothing by oxidizing colored molecules to form colorless molecules.
- Metals such as copper and aluminum are resistant to corrosion even though they are easily oxidized because the products of their reactions with oxygen form protective coatings on the surface of the metal.
- Chemiluminescent reactions in emergency light sticks, lightning, and the luminol reaction convert the energy of chemical bonds into light energy.
- Some organisms use redox reactions to produce light, which they use in communication. This light production is called bioluminescence.
- Cut fruits turn brown because compounds in the fruit cells react with oxygen in a redox reaction to produce brown pigments. Coating the fruits with antioxidants can prevent this browning.

Key Terms

For each of the following terms, write a sentence that shows your understanding of its meaning.

oxidation	oxidizing agent
oxidation-reduction reaction	reducing agent
	reduction

UNDERSTANDING CONCEPTS

1. What is the difference between an oxidizing agent and a reducing agent?
2. Which of the changes indicated are oxidations and which are reductions?
   a) Cu becomes Cu^{2+}
   b) Sn^{4+} becomes Sn^{2+}
   c) Cr^{3+} becomes Cr^{6+}
   d) Ag becomes Ag^{+}
3. Identify the oxidizing agent in each of the following reactions.
   a) $Cu^{2+}(aq) + Mg(s) \rightarrow Cu(s) + Mg^{2+}(aq)$
   b) $Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(l) + 3CO_2(g)$
4. What is the oxidizing agent in household bleach?
5. Why does a photographic negative need to be fixed?
6. In which direction do electrons move during a redox reaction: from oxidizing agent to reducing agent or vice versa?
7. Why is aluminum metal used to remove tarnish from silver?
8. What chemical process do hibernating animals use to stay warm?
9. Write the equation for the redox reaction that occurs when a piece of iron metal is dipped in a solution of copper(II) sulfate.

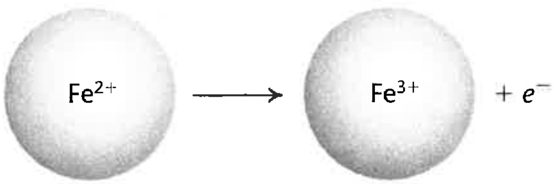
CHAPTER 16 ASSESSMENT

10. Identify the oxidizing and reducing agents in the following reaction. The equation is not balanced.

$$H_2O_2(l) + I^-(aq) + H^+ \rightarrow I_2(aq) + H_2O(l)$$

11. Identify the following as an oxidation reaction or a reduction reaction.

$$Fe^{2+} \rightarrow Fe^{3+} + e^-$$



APPLYING CONCEPTS

12. If galvanized nails, which have been coated with zinc, are placed in a brown solution containing I_2, the solution slowly turns colorless. Adding a few drops of bleach to the colorless solution results in a return of the brown color. Explain what makes these changes occur.

13. When methane in natural gas undergoes complete combustion, carbon dioxide and water are produced in an exothermic reaction.

a) Write a balanced equation that represents this reaction.
b) Is this a redox reaction? Explain.
c) Is the oxygen molecule oxidized or reduced during this reaction?

14. List several ways in which a steel chain-link fence could be treated to prevent corrosion.

15. When hydrogen peroxide is added to a colorless solution of potassium iodide, a red-brown color appears. What substance is responsible for the color?

16. Write the equation for a reaction that is not a redox reaction. Are electrons transferred in this reaction?

17. Indigo is one of the oldest known dyes. It has been detected in cloth used to wrap mummies that are more than 5000 years old. When cotton jeans are dyed with indigo, they are dipped into a yellow solution of indigo and sodium hydrosulfite, which is a good reducing agent. Within minutes after being taken out of the solution, the jeans turn blue. How can you explain this?

18. A shiny copper mirror can be formed on the inside of a test tube in which the following reaction takes place.

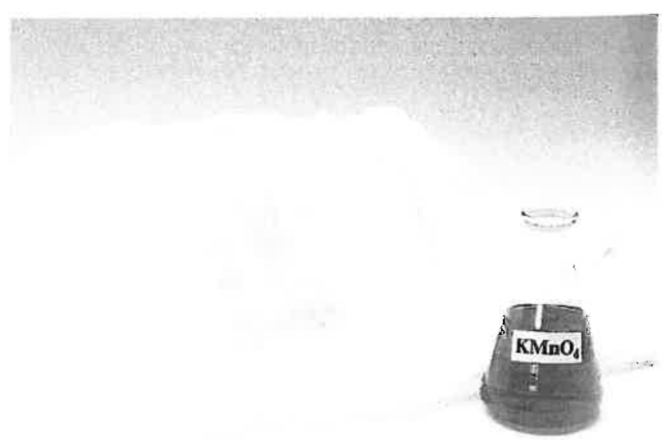
$$\underset{\text{formaldehyde}}{H_2C{=}O(aq)} + Cu^{2+}(aq) + 2OH^-(aq) \rightarrow Cu(s) + \underset{\text{formic acid}}{HCOOH(aq)} + H_2O(l)$$

a) Identify the substance that is reduced during this reaction.
b) Identify the substance that is oxidized during this reaction.
c) What is the oxidizing agent in this reaction?
d) What is the reducing agent in this reaction?

19. Potassium permanganate ($KMnO_4$) is a stain remover that can be used to clean most white fabrics. However, there is one problem with using it; it is a deep purple color that leaves behind its own stain. Fortunately, the purple stain can then be removed by treating the fabric with oxalic acid. The reaction is as follows.

$$\underset{\text{(oxalic acid)}}{5H_2C_2O_4} + \underset{\text{(purple)}}{2MnO_4^-} + 6H^+ \rightarrow 10CO_2 + \underset{\text{(colorless)}}{2Mn^{2+}} + 8H_2O$$

a) What is the oxidizing agent in this reaction?
b) What is the reducing agent in this reaction?



CHAPTER 16 ASSESSMENT

20. Is oxygen a necessary reactant for an oxidation reaction? Explain.

21. Sodium nitrite is often added to meat to inhibit the growth of microorganisms and to keep the meat from spoiling. Under the acidic conditions in our stomachs, nitrites can be converted into potentially cancer-causing substances. Vitamin C can convert nitrite ions into nitrogen monoxide gas and may help protect us from the effects of these ions.

$$NO_2^-(aq) \rightarrow NO(g)$$

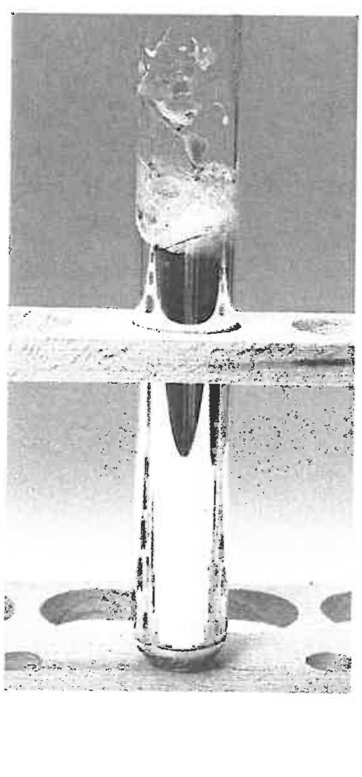
a) Is the nitrite ion oxidized or reduced in this reaction?

b) Does vitamin C act as an oxidizing agent or a reducing agent?

22. A redox reaction involving silver is used in a chemical test to determine whether an unknown organic compound is an aldehyde. This test is called a Tollen's test. It is also sometimes called the silver mirror test because a spectacular shiny layer of elemental silver plates out on the inside of a test tube if an aldehyde is present. In this test, a silver nitrate solution is mixed with a solution of the unknown substance, and the mixture is observed to see whether the mirror forms.

a) Is silver reduced or oxidized when the mirror forms?

b) Does the aldehyde function as an oxidizing agent or a reducing agent?



23. Why is gold rather than copper used to coat electrical connections in expensive electronic equipment?

Everyday Chemistry

24. Just before World War I, a German chemist named Fritz Haber developed a process for fixing atmospheric nitrogen into ammonia. The ammonia produced this way can be converted into ammonium nitrate, an important fertilizer and explosive.

$$3H_2 + N_2 \rightarrow 2NH_3$$

a) What element is oxidized during this reaction? What is reduced?

b) What is the oxidizing agent? What is the reducing agent?

Physics Connection

25. By passing an electric current through water, the water can be separated into its component elements in the reverse of the reaction used to power the main stage of the space shuttle.

$$2H_2O(l) + \text{energy} \rightarrow 2H_2(g) + O_2(g)$$

a) Is this a redox reaction? If so, what element is oxidized?

b) Where does the energy for this endothermic reaction come from?

How It Works

26. If ethanol were less volatile, how might the usefulness of a Breathalyzer test be affected? Explain.

Chemistry and Technology

27. Why should a positive result from the luminol test not be taken as proof of the presence of blood?

CHAPTER 16 ASSESSMENT

THINKING CRITICALLY

Using a Table

28. The table below lists some of the most common compounds that are used as oxidizing agents.

Common Oxidizing Agents	
O_2	$K_2Cr_2O_7$
H_2O_2	HNO_3
$KMnO_4$	$NaClO$
Cl_2	$KClO_3$

a) Name each of the compounds in the table.
b) List at least one practical application, mentioned in this chapter or from a reference book, of each of these oxidizing agents.
c) Make a similar table for common reducing agents. Should any compounds be listed in both tables?

Making Predictions

29. Hydrogen peroxide (H_2O_2) can be used to restore white areas of paintings that have darkened from the reaction of lead paint pigments with polluted air containing hydrogen sulfide gas.

$$\underset{\text{(black)}}{PbS} + 4H_2O_2 \rightarrow \underset{\text{(white)}}{PbSO_4} + 4H_2O$$

Could hydrogen peroxide be used to remove tarnish from silver objects? Would the reaction have any undesirable effects?

Interpreting Data

30. **ChemLab** Write the balanced equation for the reaction that caused the limewater to become cloudy. Is this a redox reaction? Explain.

31. **MiniLab 1** Why do you think corrosion seems to occur mostly at the head and point of a nail?

Making Inferences

32. **MiniLab 2** When a pile of orange ammonium dichromate is ignited, it decomposes in an exothermic reaction in which the green product and flames shoot upward like an erupting volcano. (**CAUTION:** *Do **NOT** perform this reaction.*)

$$(NH_4)_2Cr_2O_7(s) \rightarrow Cr_2O_3(s) + N_2(g) + 4H_2O(g)$$

a) What is the reducing agent in this reaction? The oxidizing agent?
b) How is this reaction similar to the Breathalyzer reaction?

CUMULATIVE REVIEW

33. Identify each of the following as a pure substance or a mixture. (Chapter 1)

a) petroleum	d) diamond
b) fruit juice	e) milk
c) smog	f) iron ore

34. List some characteristic properties of metals. (Chapter 3)

35. Name each of the following ionic compounds. (Chapter 5)

a) NaF	d) $Na_2Cr_2O_7$
b) CaS	e) KCN
c) $Al(OH)_3$	f) NH_4Cl

36. How many grams of nitrogen are needed to react completely with 346 g of hydrogen to form ammonia by the Haber process? (Chapter 12)

$$N_2 + 3H_2 \rightarrow 2NH_3$$

37. Draw Lewis electron dot diagrams for each of the following covalent molecules. (Chapter 9)

a) $CHCl_3$	c) CH_3CH_3
b) CH_3CH_2OH	

CHAPTER 16 ASSESSMENT

SKILL REVIEW

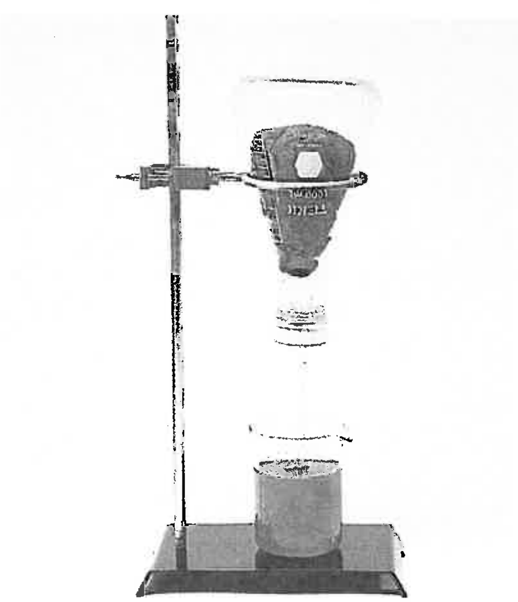
38. **Designing an Experiment** Do you think silver will tarnish more quickly in clean air or in polluted air? Design an experiment to test your hypothesis.

WRITING IN CHEMISTRY

39. Research the evidence that suggests that the antioxidant properties of vitamin C may help prevent cancer in people who take large doses of this vitamin. Write a summary of your findings in which you propose how you would do more tests to determine whether or not vitamin C has anticarcinogenic properties.

PROBLEM SOLVING

40. A flask filled with acid-washed steel wool is fitted with a long, thin glass tube in a rubber stopper. When the flask is inverted so the tube opening is in a beaker of colored water, the water slowly begins to rise in the tube. Write a summary of this experiment, as if you had performed it. Explain what makes the water rise. Predict what portion of the flask will be filled with water at the end of the experiment.



41. The patina coating on the Statue of Liberty has preserved most of the copper metal in the statue. Some damage does occur wherever steel rivets are in contact with copper and exposed to water. Do library research to determine why those sites are more susceptible to corrosion than the rest of the statue. Write up your findings in a short report. Include a diagram or make a poster showing the movement of electrons in the process.

42. Metallic lithium reacts vigorously with fluorine gas to form lithium fluoride.
    a) Write an equation for this process.
    b) Is this an oxidation-reduction reaction?
    c) If it is an oxidation-reduction, which element is oxidized? Which is reduced?
    d) If 2.0 g of lithium are reacted with 0.1 L fluorine at STP, which reactant is limiting?
    e) If 0.04 g of lithium fluoride is formed in reaction in part **d.**, what is the percent yield?

43. Identify the oxidizing reagent in each of the following reactions.
    a) $C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$
    b) $CuO(s) + H_2(g) \rightarrow Cu(s) + H_2O(l)$
    c) $2FeO(s) + C(s) \rightarrow 2Fe(s) + CO_2(g)$
    d) $2Fe^{2+}(aq) + Br_2(l) \rightarrow 2Fe^{3+}(aq) + 2\ Br^-(aq)$

44. When coal and other fossil fuels containing sulfur are burned, sulfur is converted to sulfur dioxide: $S(s) + O_2(g) \rightarrow SO_2(g)$
    a) Is this an oxidation-reduction reaction?
    b) If it is an oxidation-reduction, which element is oxidized? Which is reduced?
    c) If 7.0×10^3 kg of fuels containing 3.5 percent sulfur are burned in a city on a given day, how much SO_2 will be emitted? Assume that the sulfur reacts completely.

45. Sodium nitrite is formed when sodium nitrate reacts with lead:
    $NaNO_3(s) + Pb(s) \rightarrow NaNO_2(s) + PbO(s)$
    a) What is the oxidizing reagent in this reaction? What is the reducing reagent?
    b) If 5.00 g of sodium nitrate is reacted with an excess of lead, what mass of sodium nitrite will form if the yield is 100 percent?