Sulfur

Elemental sulfur occurs in large underground deposits along the Gulf Coast of the United States. The sulfur shown here was mined by the Frasch process and is awaiting shipment at Pennzoil's terminal at Galveston, Texas.
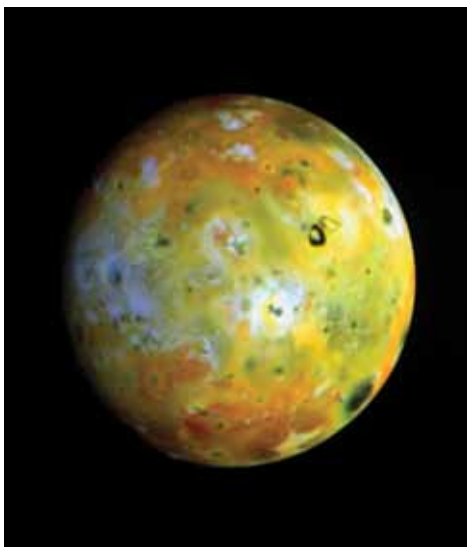
Figure J.1 Io, one of the moons of Jupiter, appears yellow because of large deposits of sulfur from volcanic activity.

Figure J.2 Sulfur is insoluble in water (left) but is soluble in carbon disulfide, CS_2, (right).

Sulfur (atomic number 16, atomic mass 32.065) is a yellow, tasteless solid that is often found in nature as the free element (Figure J.1). Sulfur is essentially insoluble in water but dissolves readily in carbon disulfide, $CS_2(l)$ (Figure J.2). It does not react with dilute acids or bases, but it does react with many metals at elevated temperatures to form metal sulfides.

Sulfur, which constitutes only 0.05% of the earth's crust, is not one of the most prevalent elements. Yet it is one of the most commercially important ones because it is the starting material for the most important industrial chemical, sulfuric acid.

J-1. Sulfur Is Recovered from Large Underground Deposits by the Frasch Process

Prior to 1900, most of the world's supply of sulfur came from Sicily, where sulfur occurs at the surfaces around hot springs and volcanoes. In the early 1900s, however, large subsurface deposits of sulfur were found along the Gulf Coast of the United States. The sulfur occurs in limestone caves, more than 300 meters (1000 feet) beneath layers of rock, clay, and quicksand. The recovery of the sulfur from these deposits posed a great technological problem, which was solved by the engineer Herman Frasch. The **Frasch process** (Figure J.3) uses an arrangement of three concentric pipes placed in a bore hole that penetrates to the base of the sulfur-bearing calcite, $CaCO_3(s)$, rock formation. Pres-

surized hot water at a temperature of 180°C is forced down the outermost pipe to melt the sulfur (melting point 119°C). The molten sulfur, which is twice as dense as water, sinks to the bottom of the deposit and then is forced up the middle pipe as a foam by the action of compressed air injected through the innermost pipe. The molten sulfur rises to the surface, where it is pumped into tank cars for shipment or into storage areas. About 40% of the U.S. annual sulfur production of around 10 million metric tons is obtained by the Frasch process from the region around the Gulf of Mexico in Louisiana and Texas (Frontispiece).

About 50% of U.S. and most Canadian sulfur is produced by the **Claus process**, in which sulfur is obtained from the hydrogen sulfide that occurs in some natural gas deposits and from the $H_2S(g)$ produced when sulfur is removed from petroleum. In the Claus process, hydrogen sulfide is burned in air to produce sulfur dioxide gas, which is then reacted with additional hydrogen sulfide to produce sulfur according to the equations

$$2\,H_2S(g) + 3\,O_2(g) \rightarrow 2\,SO_2(g) + 2\,H_2O(g) \quad (1)$$

$$SO_2(g) + 2\,H_2S(g) \rightarrow 3\,S(l) + 2\,H_2O(g) \quad (2)$$
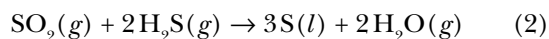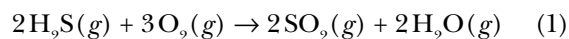
These reactions also are thought to be responsible for the surface deposits of sulfur around hot springs and volcanoes (Figure J.4).

Hot compressed air

Liquid sulfur

180°C water at
7 bar pressure

Sulfur bearing
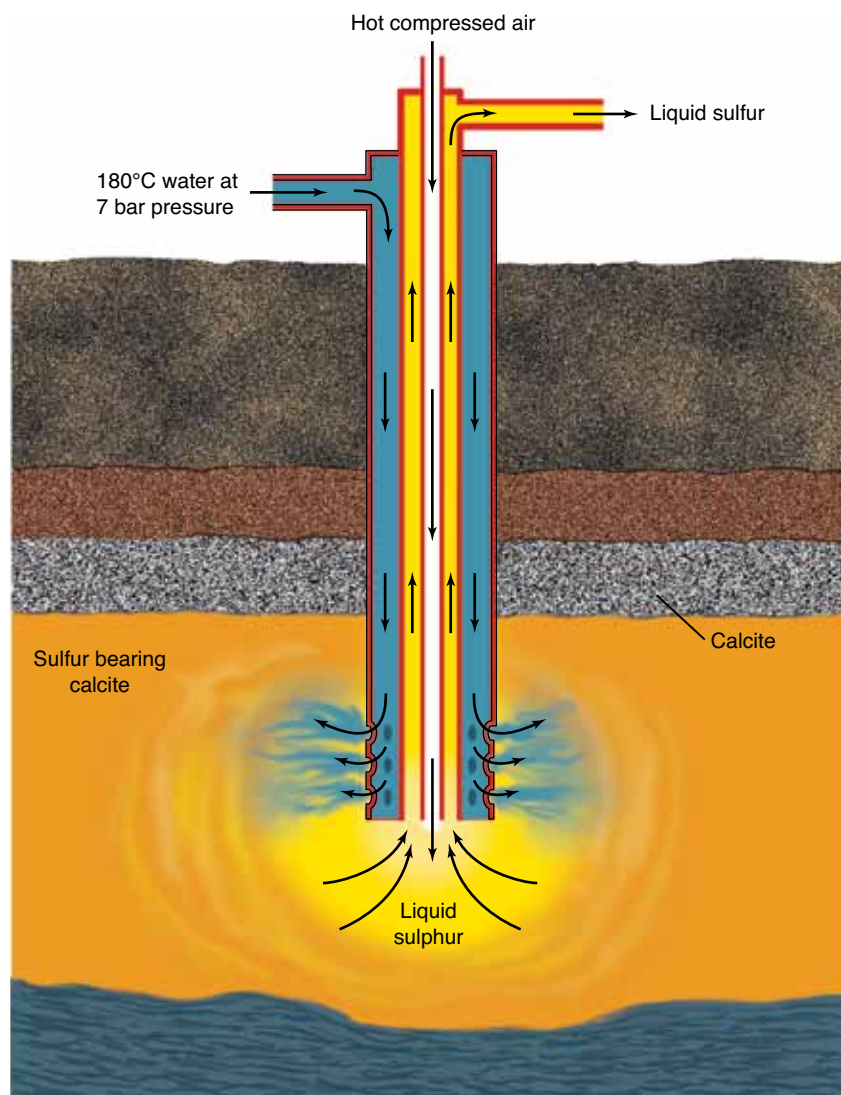calcite

Calcite

Liquid
sulphur

Figure J.3 The Frasch process for sulfur extraction. (*left*) Three concentric pipes are sunk into sulfur-bearing calcite rock. Water at 180°C and 7 bar is forced down the outermost pipe to melt the sulfur. Hot compressed air is forced down the innermost pipe and mixes with the molten sulfur to form a foam of water, air, and sulfur. The mixture rises to the surface through the middle pipe. The sulfur, when dried, has a purity of 99.5%. (*above*) Sulfur with hot water and air can be seen surfacing from Culberson Mine in West Texas.

Figure J.4 Many of the hot springs and geysers in the western United States have yellow deposits of sulfur around them.

J-2. Sulfide Ores Are Important Sources of Several Metals

Deposits of metal sulfides are found in many regions and are valuable ores of the respective metals. Galena, $PbS(s)$, cinnabar, $HgS(s)$, and iron pyrite, $FeS_2(s)$, are examples of metal sulfides that are ores (Figure J.5). In obtaining metals from sulfide ores, the ores usually are heated in an oxygen atmosphere. This process is called **roasting**. The chemical equation for the roasting of galena is

$$2\,PbS(s) + 3\,O_2(g) \rightarrow 2\,PbO(s) + 2\,SO_2(g)$$
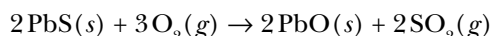
The lead oxide then is reduced by heating with carbon in the form of coke:

$$PbO(s) + C(s) \rightarrow Pb(l) + CO(g)$$
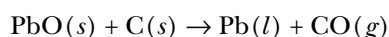
The sulfur dioxide produced by roasting is a serious atmospheric pollutant and should be recovered.

Sulfur is also found in nature in a few insoluble sulfates, such as barite, $BaSO_4(s)$ (barium sulfate), and gypsum, $CaSO_4 \cdot 2H_2O(s)$ (calcium sulfate dihydrate) (Figure J.6).

J-3. Solid Sulfur Consists of Rings of Eight Sulfur Atoms

Below 96°C sulfur exists as yellow, transparent rhombic crystals, shown in Figure J.7a. If **rhombic sulfur** is heated above 96°C, then it becomes opaque and the crystals expand into monoclinic crystals (Figure J.7b). The molecular units of the rhombic form are rings containing eight sulfur atoms, $S_8(s)$ (Figure J.8). **Monoclinic sulfur** is the stable form from 96°C to the melting point. The molecular units of monoclinic sulfur are also $S_8(s)$ rings, but the rings themselves

Figure J.6 Gypsum occurs in nature in a wide variety of crystalline forms, including some of the largest crystals found in nature (see Interchapter I Frontispiece). Shown here is desert rose, an opaque flowerlike form with embedded grains of sand found in arid regions.
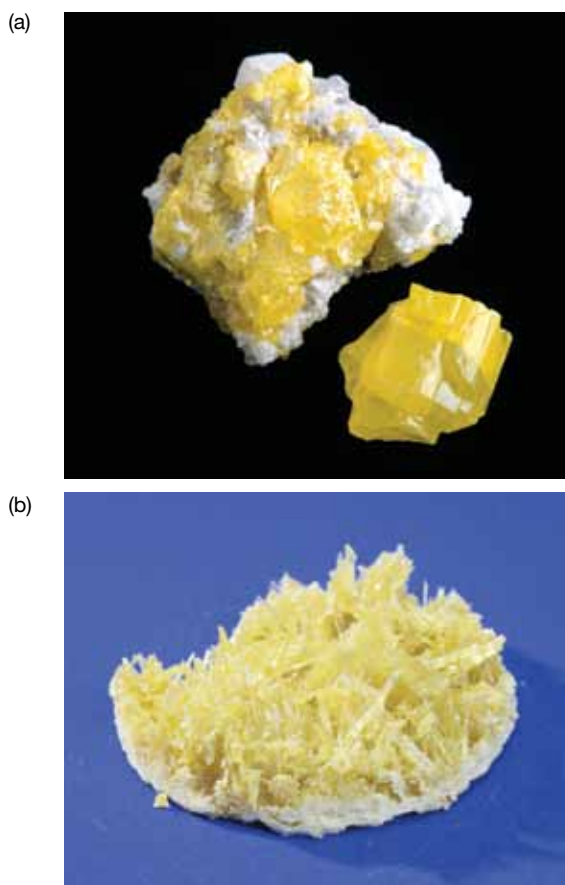
(a)

(b)

Figure J.7 Sulfur occurs as (a) rhombic and (b) monoclinic crystals. Rhombic sulfur is the stable form below 96°C. From 96°C to 119°C (the normal melting point), monoclinic sulfur is the stable form. The terms rhombic and monoclinic are derived from the shape of the crystals.

Figure J.5 Many metal sulfides are valuable ores of the respective metals. Shown here are (left to right) galena, $PbS(s)$, cinnabar, $HgS(s)$, iron pyrite, $FeS_2(s)$, and sphalerite, $ZnS(s)$.
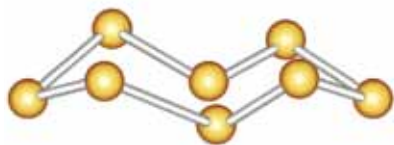
Figure J.8 Under most conditions, sulfur exists as eight-membered rings, $S_8(s)$. The ring is not flat but puckered in such a way that four of the atoms lie in one plane and four lie in another plane. Each sulfur atom forms two sulfur-sulfur bonds and also has two lone pairs of electrons.

are arranged differently in rhombic and monoclinic sulfur, which are allotropic forms of solid sulfur.

Monoclinic sulfur melts at 115.21°C to a thin, pale yellow liquid consisting of $S_8(s)$ rings. Upon heating to about 150°C there is little change; but beyond 150°C, the liquid sulfur begins to thicken and turns reddish-brown. By 200°C, the liquid is so thick it hardly pours (Figure J.9). The molecular explanation for this behavior is simple. At about 150°C, thermal agitation causes the S_8 rings to begin to break apart and form chains of sulfur atoms:
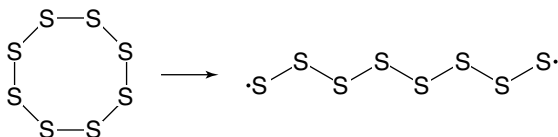
These free radical chains can then join together (polymerize) to form longer chains, which become entangled in one another and cause the liquid to thicken. Above 250°C, the liquid begins to flow more easily because the thermal agitation is sufficient to begin to break the chains of sulfur atoms. At the boiling point (444.61°C), liquid sulfur pours freely and the vapor molecules consist mostly of $S_8(g)$ rings.

If liquid sulfur at about 200°C is placed quickly in cold water (this process is called **quenching**), then a rubbery substance known as **plastic sulfur** is formed (Figure J.10). The material is rubbery because the long, coiled chains of sulfur atoms can straighten out somewhat if they are pulled. This molecular explanation of rubbery character (elasticity) is discussed in Interchapter S. As plastic sulfur cools, it slowly becomes hard again as it rearranges itself into the rhombic form.

J-4. Sulfuric Acid Is the Leading Industrial Chemical

By far the most important use of sulfur is in the manufacture of sulfuric acid. Most sulfuric acid is made by the **contact process**. Sulfur is first burned in oxygen to produce sulfur dioxide:

$$S(s) + O_2(g) \rightarrow SO_2(g)$$
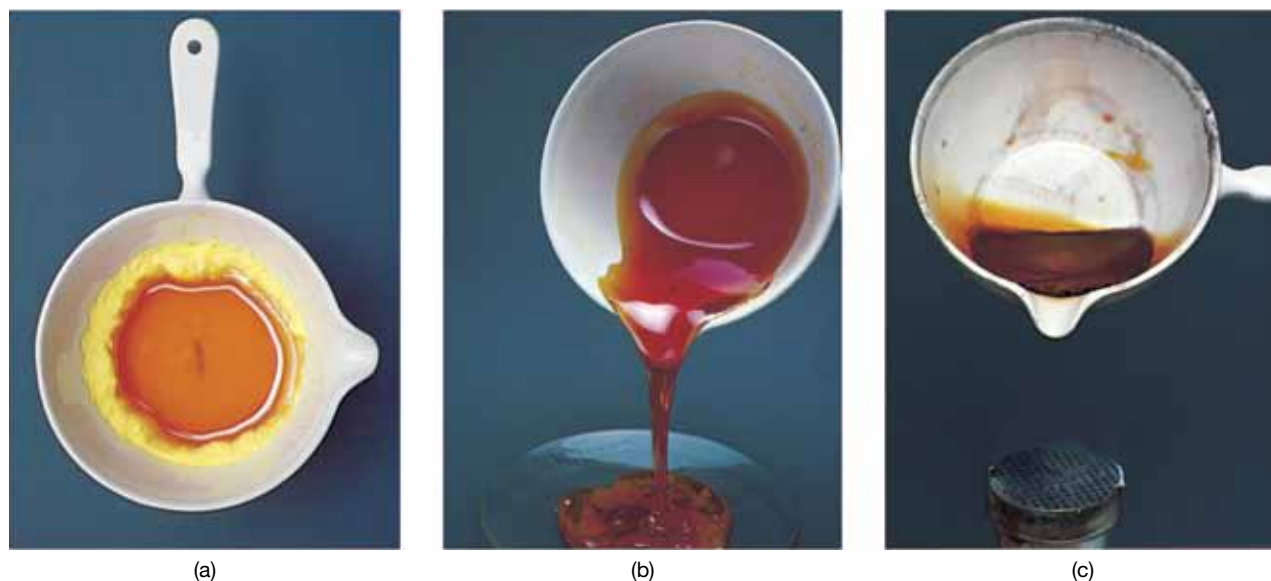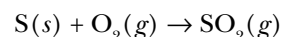

| (a) | (b) | (c) |

Figure J.9 Molten sulfur at various temperatures. (a) Sulfur melts at 119°C to a thin, yellow liquid. (b) By 200°C the liquid turns reddish-brown and is so thick that it hardly pours. (c) Upon further heating, the liquid becomes fluid once again and pours easily.
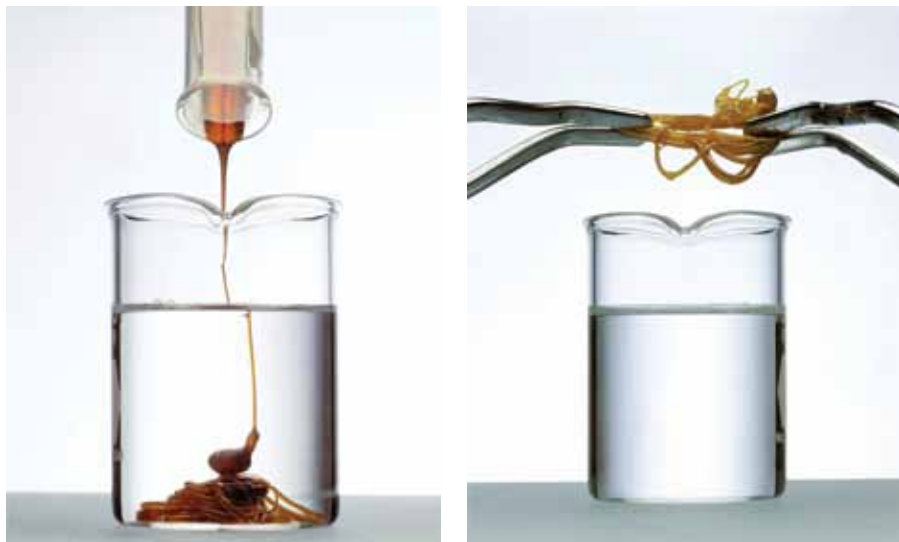
Figure J.10 If liquid sulfur at about 200°C is cooled quickly by pouring it into cold water, a rubbery substance called plastic sulfur is formed.

The sulfur dioxide is then converted to sulfur trioxide in the presence of the catalyst vanadium pentoxide (as noted in Section 18-6, although platinum is a more effective catalyst for this reaction, vanadium pentoxide is far less costly):

$$2\,SO_2(g) + O_2(g) \xrightarrow{V_2O_5(s)} 2\,SO_3(g)$$
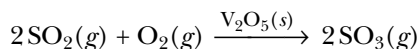
The sulfur trioxide is absorbed into nearly pure liquid sulfuric acid to form **fuming sulfuric acid (oleum)**:

$$H_2SO_4(l) + SO_3(g) \rightarrow \underset{\text{oleum}}{H_2S_2O_7} \qquad (35\%\ \text{in}\ H_2SO_4)$$
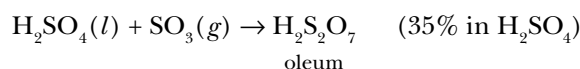
The oleum is added to water or aqueous sulfuric acid to produce the desired final concentration of aqueous sulfuric acid. Sulfur trioxide cannot be absorbed directly in water because the acid mist of $H_2SO_4(l)$ that forms is very difficult to condense.

Almost 38 million metric tons of sulfuric acid are produced annually in the United States (Appendix H.) Commercial-grade sulfuric acid is one of the least expensive chemicals, costing about 30 cents per kilogram in bulk quantities. Very large quantities of sulfuric acid are used in the production of fertilizers and numerous industrial chemicals, the petroleum industry, metallurgical processes, synthetic fiber production, and paints, pigments, and explosives manufacture.

Pure, anhydrous sulfuric acid is a colorless, syrupy liquid that freezes at 10°C and boils at 290°C. The standard laboratory acid is 97% H_2SO_4 by mass and is 18 M

in $H_2SO_4(aq)$. Concentrated sulfuric acid is a powerful dehydrating agent. Gases are sometimes bubbled through it to remove traces of water vapor—provided, of course, that the gases do not react with the acid.

Sulfuric acid is such a strong dehydrating agent it can remove water from carbohydrates, such as cellulose and sugar, even though these substances contain no free water. When concentrated sulfuric acid is poured over sucrose, $C_{12}H_{22}O_{11}(s)$, we have the reaction described by the equation

$$C_{12}H_{22}O_{11}(s) \xrightarrow{97\%\ H_2SO_4} 12\,C(s) + 11\,H_2O$$
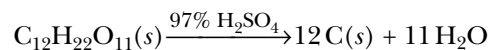
This impressive reaction is shown in Figure J.11. Similar reactions are responsible for the destructive action of concentrated sulfuric acid on wood, paper, clothing, and skin.

The high boiling point and strength of sulfuric acid are the basis of its use in the production of other acids. For example, dry hydrogen chloride gas is produced by the reaction of sodium chloride with sulfuric acid desribed by

$$2\,NaCl(s) + H_2SO_4(l) \rightarrow Na_2SO_4(s) + 2\,HCl(g)$$
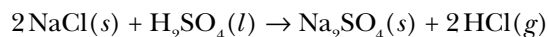
The high boiling point of the sulfuric acid allows the $HCl(g)$ to be driven off by heating. The $HCl(g)$ is then added to water to produce hydrochloric acid. This reaction is a double-replacement reaction driven by the removal of a gaseous product from the reaction mixture.

J6

Figure J.11 Concentrated sulfuric acid is a powerful dehydrating agent capable of converting sucrose to carbon.

J-5. Sulfur Reacts Directly with Most Metals and Nonmetals

Sulfur is a fairly reactive element that undergoes combination reactions with most metals and nonmetals. For example, sulfur reacts directly with lithium and mercury at room temperature:

$$2\,Li(s) + S(s) \rightarrow Li_2S(s)$$

$$Hg(l) + S(s) \rightarrow HgS(s)$$
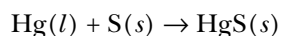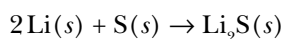
The reaction of mercury with sulfur is used in the cleanup of mercury spills in the laboratory (Figure J.12). The reaction of sulfur with most transition metals requires a high temperature. With the exception of the alkali metal sulfides, most metal sulfides are insoluble in water.

The addition of a solution of a strong acid to a metal sulfide yields hydrogen sulfide gas; for example, at 25°C,

$$FeS(s) + 2\,H^+(aq) \rightarrow Fe^{2+}(aq) + H_2S(g)$$
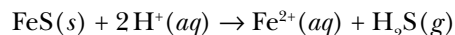
Hydrogen sulfide, $H_2S(g)$, is a colorless gas with an offensive odor suggestive of rotten eggs. It is also poisonous. Trace amounts of hydrogen sulfide occur naturally in the atmosphere as a result of volcanic activity and the decay of organic matter. The presence of hydrogen sulfide in the atmosphere is partly responsible for the tarnishing of silver. In the presence of oxygen, silver reacts with hydrogen sulfide according to

$$4\,Ag(s) + 2\,H_2S(g) + O_2(g) \rightarrow 2\,Ag_2S(s) + 2\,H_2O(l)$$
$$\text{black}$$
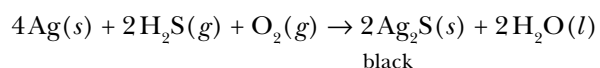
The silver sulfide formed by the reaction is a black, insoluble solid that appears as a dark tarnish (Figure J.13).

Organic compounds that contain an –SH group are called **mercaptans** and are notoriously foul smelling. The *Guinness Book of World Records* reports that ethyl mercaptan, $CH_3CH_2SH(l)$, has the worst odor
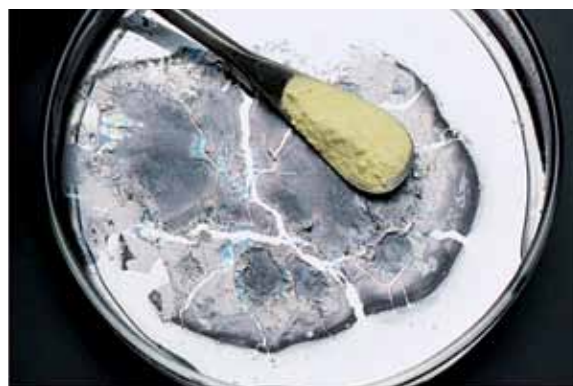

Figure J.12 Because it reacts directly with mercury at room temperature, sulfur can be used to clean up mercury spills.

Figure J.13 Silver sulfide is a black, insoluble solid that appears as a dark tarnish on the surface of silver.

of any substance, but many other mercaptans have comparably obnoxious odors. The odor of a skunk's spray is due to a mixture of mercaptans. Because pure methane, $CH_4(g)$, is odorless, trace amounts of methyl mercaptan, $CH_3SH(g)$, are added to natural gas, which is mostly methane, so that the presence of a natural gas leak can be detected by smell.

Sulfur burns in oxygen to form sulfur dioxide, a colorless gas with a characteristic choking odor. Most sulfur dioxide is used to make sulfuric acid, but some is used as a bleaching agent in the manufacture of paper products, oils, and starch and as a food additive to inhibit browning. Large quantities are used in the wine industry as a fungicide for grapevines and as a preservative for wines.

Sulfur dioxide is very soluble in water; at 25°C and one bar of $SO_2(g)$, about 200 grams of sulfur dioxide dissolve in one liter of water. Some of the sulfur dioxide reacts with the water to form the hydrogen sulfite ions according to

$$SO_2(g) + 2H_2O(l) \leftrightarrows H_3O^+(aq) + HSO_3^-(aq)$$
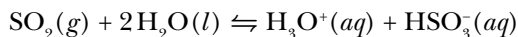
Neutralization of aqueous solutions of $SO_2(g)$ produces salts called sulfites. For example, if sodium hydroxide is added to an aqueous solution of sulfur dioxide, then sodium sulfite is formed:

$$2NaOH(aq) + SO_2(aq) \rightarrow Na_2SO_3(aq) + H_2O(l)$$
$$\text{sodium sulfite}$$
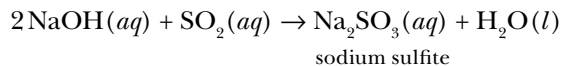
Sodium sulfite is used occasionally as a preservative, especially for dehydrated fruits. The sulfite ion acts as

a fungicide; however, it imparts a characteristic sulfur dioxide odor and taste to the food, and some people experience allergic reactions to sulfites. Many bottles of wine indicate on the label that they contain sulfites.

The thiosulfate ion is produced when an aqueous solution of a metal sulfite, such as $Na_2SO_3(aq)$, is boiled in the presence of solid sulfur:

$$S(s) + SO_3^{2-}(aq) \rightarrow S_2O_3^{2-}(aq)$$
$$\text{thiosulfate}$$
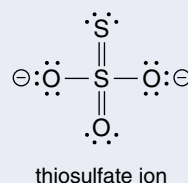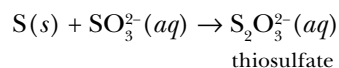
thiosulfate ion

The thiosulfate ion has a tetrahedral structure. We should point out that the two sulfur atoms in $S_2O_3^{2-}$ are not equivalent (margin). The structure is analogous to that of the sulfate ion, with one of the oxygen atoms replaced by a sulfur atom. The designation *thio-* denotes the replacement of an oxygen atom by a sulfur atom. Sodium thiosulfate pentahydrate, $Na_2S_2O_3\cdot5H_2O(s)$, is used extensively as "hypo" in black-and-white photography to dissolve silver salts via a complexation reaction described by

$$AgBr(s) + 2S_2O_3^{2-}(aq) \rightarrow Ag(S_2O_3)_2^{3-}(aq) + Br^-(aq)$$
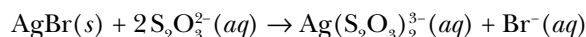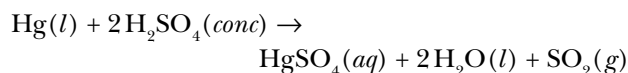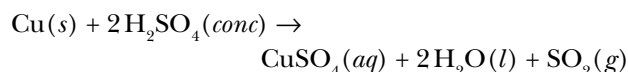
J-6. Several Sulfur-Oxygen Species Are Useful Oxidizing or Reducing Agents

At 25°C and 1 M concentration, sulfuric acid is a poor oxidizing agent. Dilute solutions of sulfuric acid show typical acidic behavior. They react with the more reactive metals to give the metal salts of the acid plus hydrogen. For example,

$$Zn(s) + H_2SO_4(aq) \rightarrow ZnSO_4(aq) + H_2(g)$$
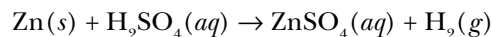
The less reactive metals such as copper and mercury are not attacked by the dilute acid. However, hot, concentrated sulfuric acid acts as an oxidizing agent even with the less reactive metals. For example,

$$Cu(s) + 2\,H_2SO_4(conc) \rightarrow$$
$$CuSO_4(aq) + 2\,H_2O(l) + SO_2(g)$$

$$Hg(l) + 2\,H_2SO_4(conc) \rightarrow$$
$$HgSO_4(aq) + 2\,H_2O(l) + SO_2(g)$$

The more reactive metals can reduce the sulfur atom in sulfuric acid further to produce free sulfur or hydrogen sulfide. For example,

$$4\,Zn(s) + 5\,H_2SO_4(conc) \rightarrow$$
$$4\,ZnSO_4(aq) + 4\,H_2O(l) + H_2S(g)$$
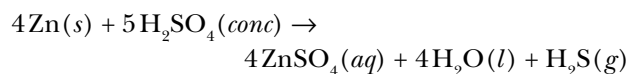
Electrochemical oxidation of aqueous sulfuric acid yields the peroxodisulfate ion, $S_2O_8^{2-}(aq)$, which has a peroxide bond (–O–O–) and consequently is a powerful oxidizing agent,

$$S_2O_8^{2-}(aq) + 2\,e^- \rightarrow 2\,SO_4^{2-}(aq)$$
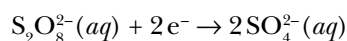
which is capable of oxidizing Ag(I) to Ag(III).

The thiosulfate ion is a mild reducing agent that is used in analytical chemistry for the determination of iodine, which is produced by the action of many mild oxidizing agents; for example,

$$2\,S_2O_3^{2-}(aq) + I_3^-(aq) \rightarrow 3\,I^-(aq) + S_4O_6^{2-}(aq)$$
tetrathionate
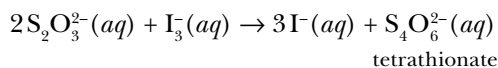
The tetrathionate ion has a sulfur-sulfur bond, with a structure similar to that of the $S_2O_8^{2-}(aq)$ ion. The thiosulfate ion is unstable in acidic solutions and decomposes to sulfur and sulfur dioxide:

$$2\,S_2O_3^{2-}(aq) + 2\,H^+(aq) \rightarrow S(s) + SO_2(aq) + H_2O(l)$$
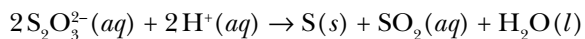
The sulfur prepared in this way is unusual in that it consists of six-membered rings, $S_6(s)$, of sulfur atoms.

Electrochemical reduction of the sulfite ion in aqueous solution yields the dithionite ion, $S_2O_4^{2-}(aq)$, which is a strong reducing agent in basic solution:

$$S_2O_4^{2-}(aq) + 4\,OH^-(aq) \rightarrow 2\,SO_3^{2-}(aq) + 2\,H_2O(l) + 2\,e^-$$
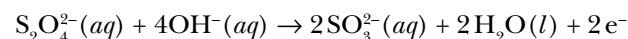
The strong reducing power of dithionite is a result of the weak sulfur-sulfur bond. Zinc dithionite is extensively used to bleach paper and textiles.

Some commercially important compounds of sulfur are given in Table J.1.

TABLE J.1 Some compounds of sulfur

Compound	Uses
sulfuric acid, $H_2SO_4(l)$	manufacture of fertilizers, dyes, explosives, steel, and other acids; petroleum industry; metallurgy; plastics
sulfur dioxide, $SO_2(g)$	disinfectant in the food and brewing industries; bleaching agent for paper, textiles, oils, etc.; fumigant, preservative
aluminum sulfate, $Al_2(SO_4)_3(s)$	leather tanning; sizing paper; fireproofing and waterproofing cloth; clarifying agent for oils and fats; water treatment; decolorizer and deodorizer; antiperspirants
ammonium sulfate, $(NH_4)_2SO_4(s)$	fertilizer; water treatment; fireproofing fabrics; tanning
sodium sulfate, $Na_2SO_4(s)$	manufacture of paper and glass; textiles; dyes; ceramic glazes; pharmaceuticals; solar energy storage (as the decahydrate, called Glauber's salt)

TERMS YOU SHOULD KNOW

Frasch process   *J1*
Claus process   *J1*
roasting of an ore   *J3*
rhombic sulfur   *J3*
monoclinic sulfur   *J3*
quenching   *J4*
plastic sulfur   *J4*
contact process   *J4*
fuming sulfuric acid (oleum)   *J5*
mercaptan   *J6*

QUESTIONS

J-1. Describe the Frasch process.

J-2. Salts of sulfuric acid are called _____. Salts of sulfurous acid are called _____.

J-3. Why would it be unwise to attempt to increase the acidity of the soil around plants by adding concentrated sulfuric acid?

J-4. Epsom salt is magnesium sulfate heptahydrate. Write the formula for Epsom salt.

J-5. Use balanced chemical equations to show how zinc can be obtained from the ore sphalerite, $ZnS(s)$.

J-6. Give the chemical formula for each of the following substances:

(a) sulfur dioxide

(b) sulfur trioxide

(c) sulfuric acid

(d) sulfurous acid

(e) hydrogen sulfide

J-7. Give the chemical formula for each of the following substances:

(a) iron pyrite

(b) gypsum

(c) cinnabar

(d) sodium thiosulfate pentahydrate

J-8. Describe what happens at various stages when sulfur (initially in the rhombic form) is heated slowly from 90°C to 200°C.

J-9. Describe, using balanced chemical equations, the contact process for the manufacture of sulfuric acid.

J-10. Write a balanced chemical equation for the formation of the fertilizer, ammonium sulfate, from ammonia and sulfuric acid.

J-11. Describe the Claus process.

J-12. Give the chemical formula for each of the following substances:

(a) calcium thiosulfate

(b) sodium dithionite

(c) potassium peroxodisulfate

(d) lithium tetrathionate

J-13. Use VSEPR theory (Chapter 8) to predict the geometries of the following oxysulfur ions:

(a) SO_3^{2-} (b) SO_4^{2-}

(c) $S_2O_3^{2-}$ (d) SO_3

J-14. In acid solution $S_2O_8^{2-}(aq)$ decomposes to yield hydrogen peroxide, $H_2O_2(aq)$. Write the balanced chemical equation describing the decomposition reaction.