

## WHAT'S AHEAD

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# 22

## CHEMISTRY OF THE NONMETALS

### 22.1 | Periodic Trends and Chemical Reactions



A great number of chemical elements go into making up living spaces with all their paraphernalia. One of the first questions we might ask is:

What is the relative importance of metallic and nonmetallic elements? Some carpets or mats may be made of organic fibers derived from bamboo. Walls may be made of cellulosic material that is essentially nonmetallic. Objects such as chair coverings, chairs, and ceramic plant pots are all constructed from mainly nonmetallic elements as well. Metals are certainly important too, as they are necessary to manufacture the electrical wiring in the walls, perhaps steel girders in the building's frame, perhaps plumbing fixtures. Overall, however, the stuff of which such a living space is constructed is largely nonmetallic in origin.

Chemical innovation has resulted in a host of materials that form the stuff of modern life. We've learned in earlier chapters about a variety of chemical reaction types that allows chemists to purify materials and polymerize small molecules into much larger ones. We've also learned how the properties of pure substances and mixtures depend on underlying molecular properties. But what are the chemical and physical properties of the elements that make up all these materials? In this chapter and the next, we look at the properties of many elements and at how these properties determine the possibilities for useful applications.

In this chapter, we start by taking a panoramic view of the descriptive chemistry of the nonmetallic elements, starting with hydrogen and then progressing, group by group, from right to left across the periodic table. We emphasize hydrogen, oxygen, nitrogen, and carbon. These four nonmetals form many commercially important compounds and account for 99% of the atoms required by living cells.

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

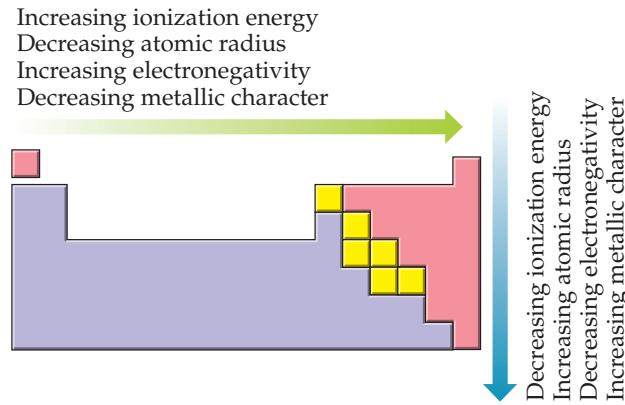
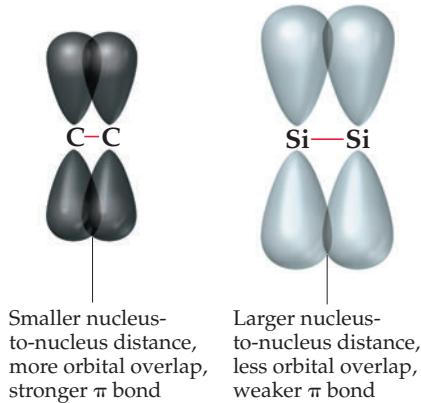
- Explain two ways in which the first element of the group differs from subsequent elements in the group

Recall that we can classify elements as metals, metalloids, and nonmetals. Except for hydrogen, which is a special case, the nonmetals occupy the upper right portion of the periodic table. This division of elements relates nicely to trends in their properties as summarized in [Figure 22.1](#). Electronegativity, for example, increases as we move left to right across a period and decreases as we move down a group. The nonmetals thus have higher electronegativities than the metals. This difference leads to the formation of ionic solids in reactions between metals and nonmetals. In contrast, compounds formed between two or more nonmetals are usually molecular substances.

The chemistry exhibited by the first member of a nonmetal group can differ from that of subsequent members in important ways. Two differences are particularly notable:

- The first member is able to accommodate fewer bonded neighbors. For example, nitrogen is able to bond to a maximum of three Cl atoms,  $\text{NCl}_3$ , whereas phosphorus can bond to five,  $\text{PCl}_5$ . The small size of nitrogen is largely responsible for this difference.
- The first member can more readily form  $\pi$  bonds and hence double and triple bonds. This trend is also due, in part, to size because small atoms are able to approach each other more closely. As a result, the overlap of  $p$  orbitals, which results in the formation of  $\pi$  bonds, is more effective for the first element in each group ([Figure 22.2](#)). More effective overlap means stronger  $\pi$  bonds, reflected in bond enthalpies. For example, the difference between the enthalpies of the C—C bond and the C=C bond is about 270 kJ/mol ([Table 8.3](#)); this large value reflects the “strength” of a carbon–carbon  $\pi$  bond. On the other hand, the difference between Si—Si and Si=Si bonds is only about 100 kJ/mol, significantly lower than that for carbon, reflecting much weaker  $\pi$  bonding.

As we shall see,  $\pi$  bonds are particularly important in the chemistry of carbon, nitrogen, and oxygen, each the first member in its group. The heavier elements in these groups have a tendency to form only single bonds.

**▲ Figure 22.1** Trends in elemental properties.**▲ Figure 22.2**  $\pi$  Bonds in Period 2 and Period 3 elements.

The ready ability of Period 2 elements to form  $\pi$  bonds is an important factor in determining the elemental forms of these elements. Compare, for example, carbon and silicon. Carbon has five major crystalline *allotropes*: diamond, graphite, buckminsterfullerene, graphene, and carbon nanotubes. Diamond is a covalent-network solid that has C—C  $\sigma$  bonds but no  $\pi$  bonds. Other allotropes of carbon have  $\pi$  bonds that result from the sideways overlap of  $p$  orbitals. Elemental silicon, however, exists only as a diamond-like covalent-network solid with  $\sigma$  bonds; it has no forms analogous to graphite, buckminsterfullerene, graphene, or carbon nanotubes, apparently because Si—Si  $\pi$  bonds are too weak.

We likewise see significant differences in the dioxides of carbon and silicon as a result of their relative abilities to form  $\pi$  bonds (Figure 22.3).  $\text{CO}_2$  is a molecular substance containing C=O double bonds, whereas  $\text{SiO}_2$  is a covalent-network solid in which four oxygen atoms are bonded to each silicon atom by single bonds, forming an extended structure that has the empirical formula  $\text{SiO}_2$ .

## Sample Exercise 22.1

### Identifying Elemental Properties

Of the elements Li, K, N, P, and Ne, which (a) is the most electronegative, (b) has the greatest metallic character, (c) can bond to more than four atoms in a molecule, and (d) forms  $\pi$  bonds most readily?

### SOLUTION

**Analyze** We are given a list of elements and asked to predict several properties that can be related to periodic trends.

**Plan** We can use Figures 22.1 and 22.2 to guide us to the answers.

### Solve

- (a) Electronegativity increases as we proceed toward the upper right portion of the periodic table, excluding the noble gases. Thus, N is the most electronegative element of our choices.
- (b) Metallic character correlates inversely with electronegativity—the less electronegative an element, the greater its metallic character. The element with the greatest metallic character is therefore K, which is closest to the lower left corner of the periodic table.
- (c) Nonmetals tend to form molecular compounds, so we can narrow our choice to the three nonmetals on the list: N, P,

and Ne. To form more than four bonds, an element must be able to expand its valence shell to allow more than an octet of electrons around it. Valence-shell expansion occurs for Period 3 elements and below; N and Ne are both in Period 2 and do not undergo valence-shell expansion. Thus, the answer is P.

- (d) Period 2 nonmetals form  $\pi$  bonds more readily than elements in Period 3 and below. There are no compounds known that contain covalent bonds to Ne. Thus, N is the element from the list that forms  $\pi$  bonds most readily.

### ► Practice Exercise

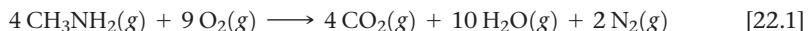
Which description correctly describes a difference between the chemistry of oxygen and sulfur?

- (a) Oxygen is a nonmetal and sulfur is a metalloid.
- (b) Oxygen can form more than four bonds, whereas sulfur cannot.
- (c) Sulfur has a higher electronegativity than oxygen.
- (d) Oxygen is better able to form  $\pi$  bonds than sulfur.

## Chemical Reactions

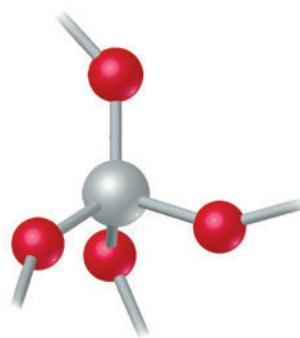
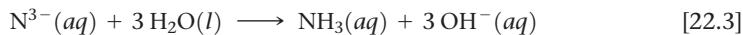
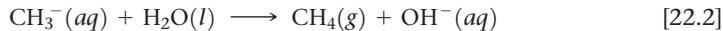
Because O<sub>2</sub> and H<sub>2</sub>O are abundant in our environment, it is particularly important to consider how these substances react with other compounds. About one-third of the reactions discussed in this chapter involve either O<sub>2</sub> (oxidation or combustion reactions) or H<sub>2</sub>O (especially proton-transfer reactions).

In combustion reactions, hydrogen-containing compounds produce H<sub>2</sub>O. Carbon-containing ones produce CO<sub>2</sub> (unless the amount of O<sub>2</sub> is insufficient, in which case CO or even C can form). Nitrogen-containing compounds tend to form N<sub>2</sub>, although NO can form in special cases or in small amounts. A reaction illustrating these points is:



The formation of H<sub>2</sub>O, CO<sub>2</sub>, and N<sub>2</sub> reflects the high thermodynamic stability of these substances, indicated by the large bond energies for the O—H, C=O, and N≡N bonds (463, 799, and 941 kJ/mol, respectively).

When dealing with proton-transfer reactions, remember that the weaker a Brønsted-Lowry acid, the stronger its conjugate base. For example, H<sub>2</sub>, OH<sup>-</sup>, NH<sub>3</sub>, and CH<sub>4</sub> are exceedingly weak proton donors that have *no* tendency to act as acids in water. Thus, the species formed by removing one or more protons from them are extremely strong bases. All of them react readily with water, removing protons from H<sub>2</sub>O to form OH<sup>-</sup>. Two representative reactions are:



Fragment of extended SiO<sub>2</sub> lattice; Si forms only single bonds



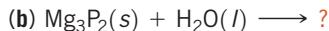
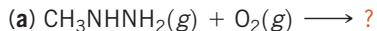
CO<sub>2</sub>; C forms double bonds

▲ Figure 22.3 Comparison of the bonds in SiO<sub>2</sub> and CO<sub>2</sub>.

### Sample Exercise 22.2

#### Predicting the Products of Chemical Reactions

Predict the products formed in each of the following reactions, and write a balanced equation:



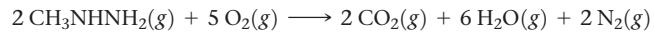
#### SOLUTION

**Analyze** We are given the reactants for two chemical equations and asked to predict the products and then balance the equations.

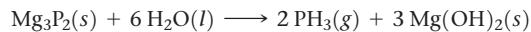
**Plan** We need to examine the reactants to see if we might recognize a reaction type. In (a) the carbon compound is reacting with O<sub>2</sub>, which suggests a combustion reaction. In (b) water reacts with an ionic compound. The anion P<sup>3-</sup> is a strong base and H<sub>2</sub>O is able to act as an acid, so the reactants suggest an acid-base (proton-transfer) reaction.

#### Solve

(a) Based on the elemental composition of the carbon compound, this combustion reaction should produce CO<sub>2</sub>, H<sub>2</sub>O, and N<sub>2</sub>:



(b) Mg<sub>3</sub>P<sub>2</sub> is ionic, consisting of Mg<sup>2+</sup> and P<sup>3-</sup> ions. The P<sup>3-</sup> ion, like N<sup>3-</sup>, has a strong affinity for protons and reacts with H<sub>2</sub>O to form OH<sup>-</sup> and PH<sub>3</sub> (PH<sup>2-</sup>, PH<sub>2</sub>, and PH<sub>3</sub> are all exceedingly weak proton donors).



Mg(OH)<sub>2</sub> has low solubility in water and will precipitate.

#### ► Practice Exercise

When CaC<sub>2</sub> reacts with water, what carbon-containing compound forms?

- (a) CO   (b) CO<sub>2</sub>   (c) CH<sub>4</sub>   (d) C<sub>2</sub>H<sub>2</sub>   (e) H<sub>2</sub>CO<sub>3</sub>

## Self-Assessment Exercise

**22.1** Carbon dioxide is found in nature as CO<sub>2</sub>(g). Would you expect silicon dioxide to be found in nature as SiO<sub>2</sub>(g)?

(a) Yes

(b) No

## Exercises

- 22.2** Identify each of the following elements as a metal, nonmetal, or metalloid: (a) germanium, (b) bismuth, (c) sulphur, (d) calcium, (e) rhenium, (f) tin.
- 22.3** Consider the elements Ba, Na, O, B, P, and Kr. From this list, select the element that (a) is most electronegative, (b) has the greatest metallic character, (c) most readily forms a positive ion, (d) exhibits a maximum oxidation state of +5, (e) exists as monoatomic gas at room temperature, (f) has multiple allotropes.
- 22.4** Which of the following statements are true?
- (a) Si can form an ion with six fluorine atoms,  $\text{SiF}_6^{2-}$ , whereas carbon cannot.
- 22.5** Complete and balance the following equations:
- (a)  $\text{Mg}_3\text{N}_2(s) + \text{H}_2\text{O}(l) \longrightarrow$
- (b)  $\text{C}_3\text{H}_7\text{OH}(l) + \text{O}_2(g) \longrightarrow$
- (c)  $\text{MnO}_2(s) + \text{C}(s) \xrightarrow{\Delta} \longrightarrow$
- (d)  $\text{AlP}(s) + \text{H}_2\text{O}(l) \longrightarrow$
- (e)  $\text{Na}_2\text{S}(s) + \text{HCl}(aq) \longrightarrow$

22.1 (b)

Answers to Self-Assessment Exercise



## 22.2 | Hydrogen



The mass percent of hydrogen in water changes from 11% to 20% as the isotope of hydrogen is changed from  $^1\text{H}$  to  $^2\text{H}$ . This dramatic change effects both the physical and chemical properties of the material; for example, the density of ice made from  $^2\text{H}_2\text{O}$  is greater than water made from  $^1\text{H}_2\text{O}$ , and so ice cubes sink, unlike ice made from  $^1\text{H}_2\text{O}$ , which floats, as pictured here.

In this section, we review some of the properties and chemistry of hydrogen. By the end of the section, you should be able to

- Appreciate the unique nature of hydrogen.

Because hydrogen produces water when burned in air, the French chemist Antoine Lavoisier gave it the name *hydrogen*, which means “water producer” (Greek: *hydro*, water; *genmao*, to produce).

Hydrogen is the most abundant element in the universe. It is the nuclear fuel consumed by our Sun and other stars to produce energy. Although about 75% of the known mass of the universe is hydrogen, it constitutes only 0.87% of Earth's mass. Most of the hydrogen on our planet is found associated with oxygen. Water, which is 11% hydrogen by mass, is the most abundant hydrogen compound.

## Isotopes of Hydrogen

The most common isotope of hydrogen,  ${}^1\text{H}$ , has a nucleus consisting of a single proton. This isotope, sometimes referred to as **protium**,\* makes up 99.9844% of naturally occurring hydrogen.

Two other isotopes are known:  ${}^2\text{H}$ , whose nucleus contains a proton and a neutron, and  ${}^3\text{H}$ , whose nucleus contains a proton and two neutrons. The  ${}^2\text{H}$  isotope, **deuterium**, makes up 0.0156% of naturally occurring hydrogen. It is not radioactive, and it is often given the symbol D in chemical formulas, as in  $\text{D}_2\text{O}$  (deuterium oxide), which is known as *heavy water*.

Because an atom of deuterium is about twice as massive as an atom of protium, the properties of deuterium-containing substances vary somewhat from those of the protium-containing analogs. For example, the normal melting and boiling points of  $\text{D}_2\text{O}$  are 3.81 °C and 101.42 °C, respectively, versus 0.00 °C and 100.00 °C for  $\text{H}_2\text{O}$ . Not surprisingly, the density of  $\text{D}_2\text{O}$  at 25 °C (1.104 g/mL) is greater than that of  $\text{H}_2\text{O}$  (0.997 g/mL). Replacing protium with deuterium (a process called *deuteration*) can also have a profound effect on reaction rates, a phenomenon called a *kinetic-isotope effect*. For example, heavy water can be obtained from the electrolysis  $[2 \text{H}_2\text{O}(l) \longrightarrow 2 \text{H}_2(g) + \text{O}_2(g)]$  of ordinary water because the small amount of naturally occurring  $\text{D}_2\text{O}$  in the sample undergoes electrolysis more slowly than  $\text{H}_2\text{O}$  and, therefore, becomes concentrated during the reaction.

The third isotope,  ${}^3\text{H}$ , **tritium**, is radioactive, with a half-life of 12.3 yr:



Because of its short half-life, only trace quantities of tritium exist naturally. The isotope can be synthesized in nuclear reactors by neutron bombardment of lithium-6:



Deuterium and tritium are useful in studying reactions of compounds containing hydrogen. A compound is “labeled” by replacing one or more ordinary hydrogen atoms with deuterium or tritium at specific locations in a molecule. By comparing the locations of the label atoms in reactants and products, the reaction mechanism can often be inferred. When methanol ( $\text{CH}_3\text{OH}$ ) is placed in  $\text{D}_2\text{O}$ , for example, the H atom of the O—H bond exchanges rapidly with the D atoms, forming  $\text{CH}_3\text{OD}$ . The H atoms of the  $\text{CH}_3$  group do not exchange. This experiment demonstrates the kinetic stability of C—H bonds and reveals the speed at which the O—H bond in the molecule breaks and re-forms.

## Properties of Hydrogen

Hydrogen is the only element that is not a member of any family in the periodic table. Because of its  $1s^1$  electron configuration, it is generally placed above lithium in the table. However, it is definitely *not* an alkali metal. It forms a positive ion much less readily than any alkali metal. The ionization energy of the hydrogen atom is 1312 kJ/mol, whereas that of lithium is 520 kJ/mol.

Hydrogen is sometimes placed above the halogens in the periodic table because the hydrogen atom can pick up one electron to form the *hydride ion*,  $\text{H}^-$ , which has the same electron configuration as helium. However, the electron affinity of hydrogen,  $EA = -73 \text{ kJ/mol}$ , is not as large as that of any halogen. In general, hydrogen shows no closer resemblance to the halogens than it does to the alkali metals.

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\*Giving unique names to isotopes is limited to hydrogen. Because of the proportionally large differences in their masses, the isotopes of H show appreciably more differences in their properties than isotopes of heavier elements.

Elemental hydrogen exists at room temperature as a colorless, odorless, tasteless gas composed of diatomic molecules. We can call  $\text{H}_2$  *dihydrogen*, but it is more commonly referred to as either *molecular hydrogen* or simply hydrogen. Because  $\text{H}_2$  is nonpolar and has only two electrons, attractive forces between molecules are extremely weak. As a result, its melting point ( $-259^\circ\text{C}$ ) and boiling point ( $-253^\circ\text{C}$ ) are very low.

The H—H bond enthalpy (436 kJ/mol) is high for a single bond. (Table 8.3) By comparison, the Cl—Cl bond enthalpy is only 242 kJ/mol. Because  $\text{H}_2$  has a strong bond, most reactions involving  $\text{H}_2$  are slow at room temperature. However, the molecule is readily activated by heat, irradiation, or catalysis. The activation generally produces hydrogen atoms, which are very reactive. Once  $\text{H}_2$  is activated, it reacts rapidly and exothermically with a wide variety of substances.

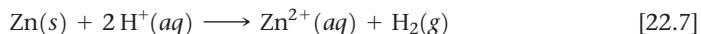
Hydrogen forms strong covalent bonds with many other elements, including oxygen; the O—H bond enthalpy is 463 kJ/mol. The formation of the strong O—H bond makes hydrogen an effective reducing agent for many metal oxides. When  $\text{H}_2$  is passed over heated CuO, for example, copper is produced:



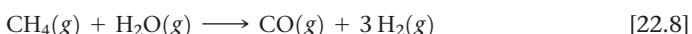
When  $\text{H}_2$  is ignited in air, a vigorous reaction occurs, forming  $\text{H}_2\text{O}$ . Air containing as little as 4%  $\text{H}_2$  by volume is potentially explosive. Combustion of hydrogen–oxygen mixtures is used in liquid-fuel rocket engines such as those of the Space Shuttle. The hydrogen and oxygen are stored at low temperatures in liquid form.

## Production of Hydrogen

When a small quantity of  $\text{H}_2$  is needed in the laboratory, it is usually obtained by the reaction between an active metal such as zinc and a dilute strong acid such as HCl or  $\text{H}_2\text{SO}_4$ :



Large quantities of  $\text{H}_2$  are produced by reacting methane with steam at  $1100^\circ\text{C}$ . We can view this process as involving two reactions:



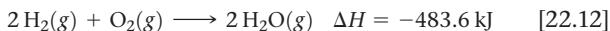
Carbon heated with water to about  $1000^\circ\text{C}$  is another source of  $\text{H}_2$ :



This mixture, known as *water gas*, is used as an industrial fuel.

## A CLOSER LOOK The Hydrogen Economy

The reaction of hydrogen with oxygen is highly exothermic:



Because  $\text{H}_2$  has a low molar mass and a high enthalpy of combustion, it has a high energy density by mass. (That is, its combustion produces high energy per gram.) The only product of the reaction is water vapor, which means that hydrogen is environmentally cleaner than fossil fuels. Thus, the prospect of using hydrogen widely as a fuel is attractive. Furthermore, the hydrogen can be utilized as a fuel in hydrogen fuel cells, enhancing the efficiency of its use.

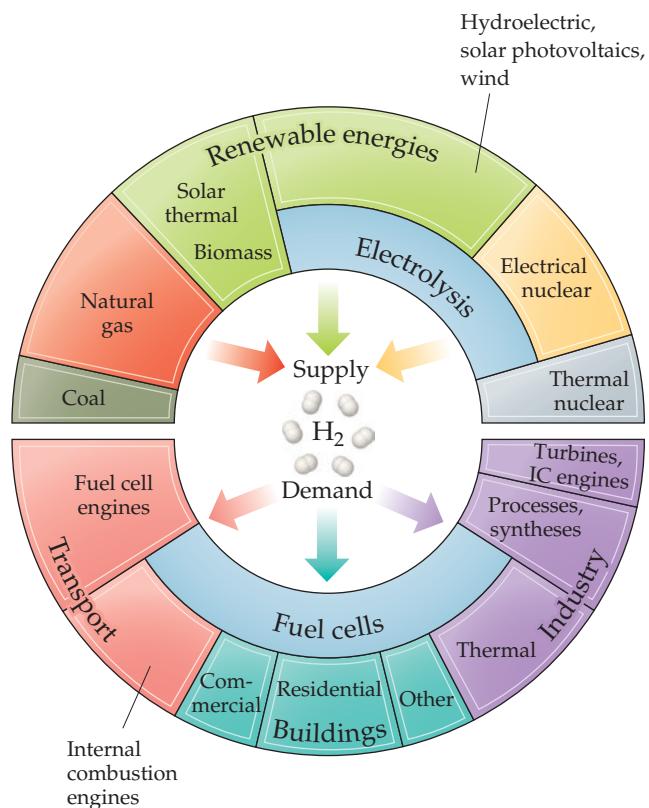
The term *hydrogen economy* is used to describe the concept of delivering and using hydrogen as a fuel in place of fossil fuels. In order to develop a hydrogen economy, it would be necessary to generate elemental hydrogen on a large scale and arrange for its transport and storage. These matters provide significant technical challenges.

**Figure 22.4** illustrates various sources and uses of  $\text{H}_2$  fuel. The generation of  $\text{H}_2$  through electrolysis of water is in principle the cleanest route, because this process produces only hydrogen and oxygen.

(Figure 1.7) However, the energy required to electrolyze water must come from somewhere. If we burn fossil fuels to generate this energy, we have not advanced very far toward a true hydrogen economy. If the energy for electrolysis came instead from a hydroelectric or nuclear power plant, solar cells, or wind generators, consumption of nonrenewable energy sources and undesired production of  $\text{CO}_2$  could be avoided.

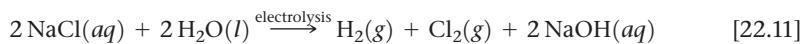
The storage of hydrogen is another technical obstacle that must be overcome in developing a hydrogen economy. Although  $\text{H}_2(g)$  has a high energy density by mass, it has a low energy density by volume. Thus, storing hydrogen as a gas requires a large volume compared to the energy it delivers. There are also safety issues associated with handling and storing the gas because its combustion can be explosive. Storing hydrogen in the form of various hydride compounds such as  $\text{LiAlH}_4$  is being investigated as a means of reducing the volume and increasing the safety. One problem with this approach, however, is that such compounds have high energy density by volume but low energy density by mass.

**Related Exercises:** 22.11, 22.64, 22.104



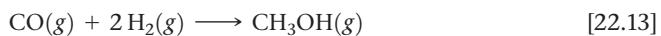
▲ Figure 22.4 The hydrogen economy would require hydrogen to be produced from various sources and would use hydrogen in energy-related applications.

Electrolysis of water consumes too much energy and is consequently too costly to be used commercially to produce H<sub>2</sub>. However, H<sub>2</sub> is produced as a by-product in the electrolysis of brine (NaCl) solutions in the course of commercial Cl<sub>2</sub> and NaOH manufacture:



## Uses of Hydrogen

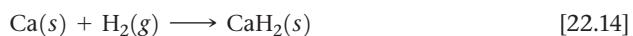
Hydrogen is commercially important. About half of the H<sub>2</sub> produced is used to synthesize ammonia by the Haber process. Much of the remaining hydrogen is used to convert high-molecular-weight hydrocarbons from petroleum into lower-molecular-weight hydrocarbons suitable for fuel (petrol, diesel, and others) in a process known as *cracking*. Hydrogen is also used to manufacture methanol via the catalytic reaction of CO and H<sub>2</sub> at high pressure and temperature:



## Binary Hydrogen Compounds

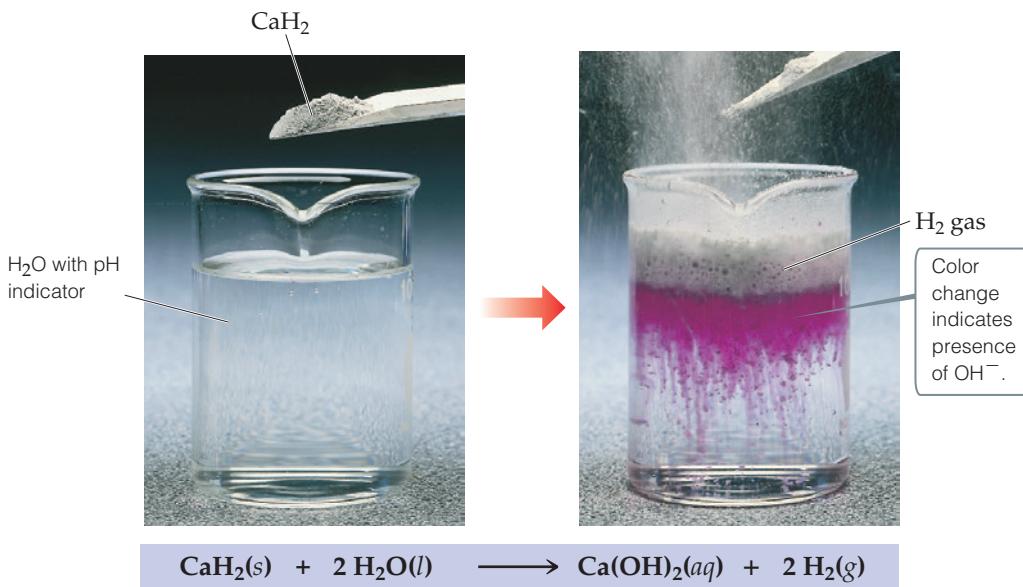
Hydrogen reacts with other elements to form three types of compounds: (1) ionic hydrides, (2) metallic hydrides, and (3) molecular hydrides.

The **ionic hydrides** are formed by the alkali metals and by the heavier alkaline earths (Ca, Sr, and Ba). These active metals are much less electronegative than hydrogen. (Figure 8.8) Consequently, hydrogen acquires electrons from them to form hydride ions (H<sup>-</sup>):



 Go Figure

This reaction is exothermic. Is the beaker on the right warmer or colder than the beaker on the left?



▲ Figure 22.5 The reaction of CaH<sub>2</sub> with water.

 Go Figure

Which is the most thermodynamically stable hydride? Which is the least thermodynamically stable?

14	15	16	17
CH <sub>4</sub> (g) −50.8	NH <sub>3</sub> (g) −16.7	H <sub>2</sub> O(l) −237	HF(g) −271
SiH <sub>4</sub> (g) +56.9	PH <sub>3</sub> (g) +18.2	H <sub>2</sub> S(g) −33.0	HCl(g) −95.3
GeH <sub>4</sub> (g) +117	AsH <sub>3</sub> (g) +111	H <sub>2</sub> Se(g) +71	HBr(g) −53.2
	SbH <sub>3</sub> (g) +187	H <sub>2</sub> Te(g) +138	HI(g) +1.30

▲ Figure 22.6 Standard free energies of formation of molecular hydrides. All values are kilojoules per mole of hydride.

The hydride ion is very basic and reacts readily with compounds having even weakly acidic protons to form H<sub>2</sub> as shown in Figure 22.5 and summarized by the following equation:



Ionic hydrides can therefore be used as convenient (although expensive) sources of H<sub>2</sub>.

Calcium hydride (CaH<sub>2</sub>) is used to inflate life rafts, weather balloons, and the like where a simple, compact means of generating H<sub>2</sub> is desired (Figure 22.5).

**Metallic hydrides** are formed when hydrogen reacts with transition metals. These compounds are so named because they retain their metallic properties. In many metallic hydrides, the ratio of metal atoms to hydrogen atoms is not fixed or in small whole numbers. The composition can vary within a range, depending on reaction conditions. TiH<sub>2</sub> can be produced, for example, but preparations usually yield TiH<sub>1.8</sub>. These nonstoichiometric metallic hydrides are sometimes called *interstitial hydrides*. Because hydrogen atoms are small enough to fit between the sites occupied by the metal atoms, many metal hydrides behave like interstitial alloys.

The **molecular hydrides**, formed by nonmetals and metalloids, are either gases or liquids under standard conditions. The simple molecular hydrides are listed in Figure 22.6, together with their standard free energies of formation,  $\Delta G_f^\circ$ . In each family, the thermal stability (measured as  $\Delta G_f^\circ$ ) decreases as we move down the family. (Recall that the more stable a compound is with respect to its elements under standard conditions, the more negative  $\Delta G_f^\circ$  is.)

## Self-Assessment Exercise

22.6 What is the oxidation state of H in LiAlH<sub>4</sub>?

- (a) −1  
(b) 0  
(c) +1

## Exercises

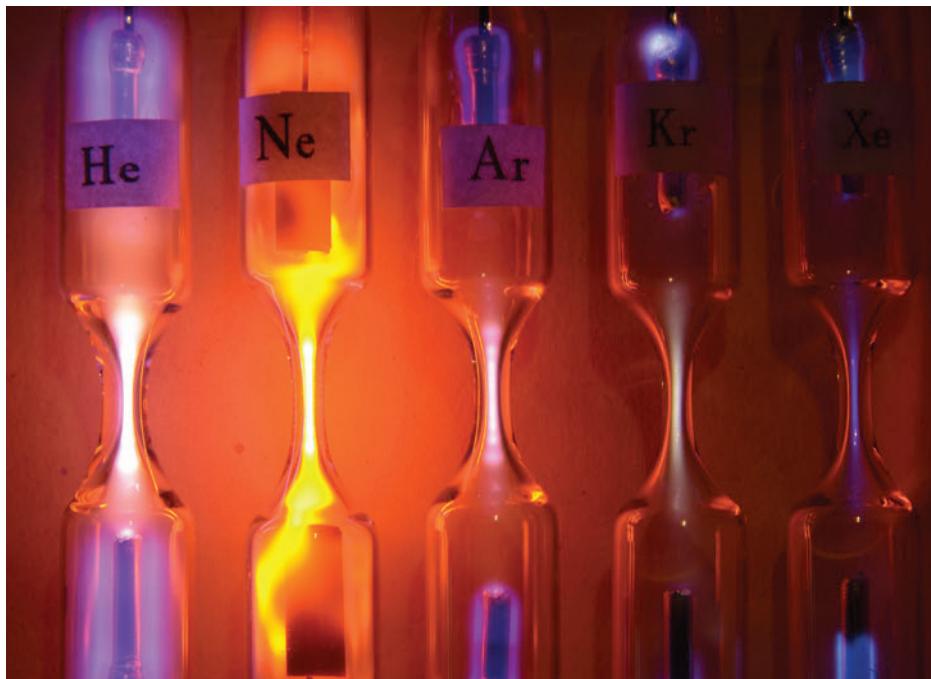
- 22.7** (a) Give the names and chemical symbols for the three isotopes of hydrogen. (b) List the isotopes in order of decreasing natural abundance. (c) Which hydrogen isotope is radioactive? (d) Write the nuclear equation for the radioactive decay of this isotope.
- 22.8** What does hydrogen have in common with the halogens? Explain.
- 22.9** Write balanced equations for each of the following reactions (some of these are analogous to reactions shown in the chapter). (a) Aluminum metal reacts with acids to form hydrogen gas. (b) Steam reacts with magnesium metal to give magnesium oxide and hydrogen. (c) Manganese(IV) oxide is reduced to manganese(II) oxide by hydrogen gas. (d) Calcium hydride reacts with water to generate hydrogen gas.
- 22.10** Identify the following hydrides as ionic, metallic, or molecular: (a)  $\text{MgH}_2$ , (b)  $\text{HI}$ , (c)  $\text{LaNi}_{4.7}\text{Al}_{0.3}\text{H}_6$ .
- 22.11** The  $\text{H}_2/\text{O}_2$  fuel cell converts elemental hydrogen and oxygen into water, producing, theoretically, 1.23 V. What is the most sustainable way to obtain hydrogen to run a large number of fuel cells? Explain.

22.6 (a)

Answers to Self-Assessment Exercise



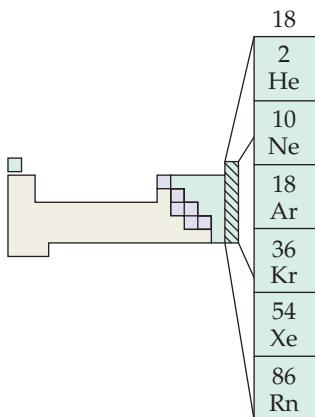
## 22.3 | Group 18: The Noble Gases



In this section, we review some of the properties of the noble gasses. By the end of this section, you should be able to

- Understand that some Group 18 elements form compounds

The elements of Group 18 are chemically unreactive. Indeed, most of our references to these elements have been in relation to their physical properties, as when we discussed intermolecular forces. The relative inertness of these elements is due to the presence of



a completed octet of valence-shell electrons (except He, which only has a filled 1s shell). The stability of such an arrangement is reflected in the high ionization energies of the Group 18 elements.

The Group 18 elements are all gases at room temperature. They are components of Earth's atmosphere, except for radon, which exists only as a short-lived radioisotope. Only argon is relatively abundant. (Table 18.1)

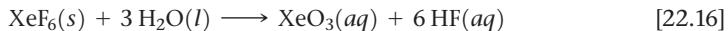
Neon, argon, krypton, and xenon are used in lighting, display, and laser applications in which the atoms are excited electrically and electrons that are in a higher energy state emit light as they return to the ground state. Argon is also used as a protective atmosphere to prevent oxidation in welding and certain high-temperature metallurgical processes.

Helium is in many ways the most important noble gas. Liquid helium is used as a coolant to conduct experiments at very low temperatures. Helium boils at 4.2 K and 101.3 kPa, the lowest boiling point of any substance. It is found in relatively high concentrations in many natural-gas wells from which it is isolated.

## Noble Gas Compounds

Because the noble gases are exceedingly stable, they react only under rigorous conditions. We expect the heavier ones to be most likely to form compounds because their ionization energies are lower. (Figure 7.10) A lower ionization energy suggests the possibility of sharing an electron with another atom, leading to a chemical bond. In addition, because the Group 18 elements (except helium) already contain eight electrons in their valence shell, formation of covalent bonds will require an expanded valence shell. Valence-shell expansion occurs most readily with larger atoms.

The first noble gas compound was reported in 1962. This discovery caused a sensation because it undercut the belief that the noble gas elements were inert. The initial study involved xenon in combination with fluorine, the element we would expect to be most reactive in pulling electron density from another atom. Since that time chemists have prepared several xenon compounds of fluorine and oxygen (Table 22.1). The fluorides  $\text{XeF}_2$ ,  $\text{XeF}_4$ , and  $\text{XeF}_6$  are made by direct reaction of the elements. By varying the ratio of reactants and altering reaction conditions, each of the three compounds can be obtained. The oxygen containing compounds are formed when the fluorides react with water as, for example,



**TABLE 22.1 Properties of Xenon Compounds**

Compound	Oxidation State of Xe	Melting Point (°C)	$\Delta H_f^\circ$ (kJ/mol) <sup>a</sup>
$\text{XeF}_2$	+2	129	-109(g)
$\text{XeF}_4$	+4	117	-218(g)
$\text{XeF}_6$	+6	49	-298(g)
$\text{XeOF}_4$	+6	-41 to -28	+146(l)
$\text{XeO}_3$	+6	- <sup>b</sup>	+402(s)
$\text{XeO}_2\text{F}_2$	+6	31	+145(s)
$\text{XeO}_4$	+8	- <sup>c</sup>	-

<sup>a</sup>At 25 °C, for the compound in the state indicated.

<sup>b</sup>A solid; decomposes at 40 °C.

<sup>c</sup>A solid; decomposes at -40 °C.



### Sample Exercise 22.3

#### Predicting a Molecular Structure

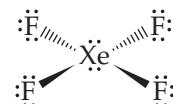
Use the VSEPR model to predict the structure of  $\text{XeF}_4$ .

#### SOLUTION

**Analyze** We must predict the geometrical structure given only the molecular formula.

**Plan** We must first write the Lewis structure for the molecule. We then count the number of electron pairs (domains) around the Xe atom and use that number and the number of bonds to predict the geometry.

**Solve** There are 36 valence-shell electrons (8 from xenon and 7 from each fluorine). If we make four single Xe—F bonds, each fluorine has its octet satisfied. Xe then has 12 electrons in its valence shell, so we expect an octahedral arrangement of six electron pairs. Two of these are nonbonded pairs. Because nonbonded pairs require more volume than bonded pairs, it is reasonable to expect these nonbonded pairs to be opposite each other. The expected structure is square planar, as shown in **Figure 22.7**.



▲ **Figure 22.7** Xenon tetrafluoride.

**Comment** The experimentally determined structure agrees with this prediction.

#### ► Practice Exercise

Compounds containing the  $\text{XeF}_3^+$  ion have been characterized. Describe the electron-domain geometry and molecular geometry of this ion.

- (a) trigonal planar, trigonal planar (b) tetrahedral, trigonal pyramidal (c) trigonal bipyramidal, T shaped (d) tetrahedral, tetrahedral (e) octahedral, square planar

The other noble gas elements form compounds much less readily than xenon. For many years, only one binary krypton compound,  $\text{KrF}_2$ , was known with certainty, and it decomposes to its elements at  $-10^\circ\text{C}$ . Other compounds of krypton have been isolated at very low temperatures (40 K). In 2000, a compound of argon,  $\text{HArF}$ , was discovered, but it can exist only in argon matrices at very low temperatures.

## Self-Assessment Exercise

**22.12** Predict the molecular geometry of  $\text{XeO}_3$ .

- (a) Trigonal planar  
(b) Trigonal pyramidal  
(c) T-shaped

## Exercises

**22.13** A friend tells you that the “neon” in neon signs is a compound of neon and aluminum. Can your friend be correct? Explain.

**22.14** Write the chemical formula for each of the following, and indicate the oxidation state of the halogen or noble-gas

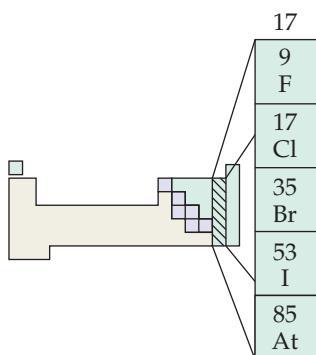
atom in each: (a) krypton tetrafluoride, (b) hexafluoroantimonate ion, (c) sodium hypoiodite, (d) perbromic acid, (e) aluminum perchlorate, (f) iron(II) iodite.

22.12 (b)

Answers to Self-Assessment Exercise



## 22.4 | Group 17: The Halogens



Fluorite is a mineral composed of calcium fluoride and is found in colors ranging from yellow to green to purple. It is a commercial source of fluorine in the form of hydrogen fluoride. In contrast chlorine, bromine and iodine may all be obtained from sea water.

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

- Understand the trends in selected physical and chemical properties of the halogens

The elements of Group 17, the halogens, have the outer-electron configuration  $ns^2np^5$ , where  $n$  ranges from 2 through 6. The halogens have large negative electron affinities, and they most often achieve a noble-gas configuration by gaining an electron, which results in a  $-1$  oxidation state. Fluorine, being the most electronegative element, exists in compounds only in the  $-1$  state. The other halogens exhibit positive oxidation states up to  $+7$  in combination with more electronegative atoms such as O. In the positive oxidation states, the halogens tend to be good oxidizing agents, readily accepting electrons.

Chlorine, bromine, and iodine are found as the halides in seawater and in salt deposits. Fluorine occurs in the minerals fluorspar ( $\text{CaF}_2$ ), cryolite ( $\text{Na}_3\text{AlF}_6$ ), and fluorapatite [ $\text{Ca}_5(\text{PO}_4)_3\text{F}$ .]\* Only fluorspar is an important commercial source of fluorine.

All isotopes of astatine are radioactive. The longest-lived isotope is astatine-210, which has a half-life of 8.1 h and decays mainly by electron capture. Because astatine is so unstable, very little is known about its chemistry.

### Properties and Production of the Halogens

Most properties of the halogens vary in a regular fashion as we go from fluorine to iodine (**Table 22.2**).

Under ordinary conditions the halogens exist as diatomic molecules. The molecules are held together in the solid and liquid states by dispersion forces. Because  $\text{I}_2$  is the largest and most polarizable halogen molecule, the intermolecular forces between  $\text{I}_2$  molecules

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\*Minerals are solid substances that occur in nature. They are usually known by their common names rather than by their chemical names. What we know as rock is merely an aggregate of different minerals.

**TABLE 22.2 Some Properties of the Halogens**

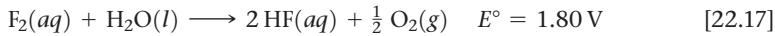
Property	F	Cl	Br	I
Atomic radius (pm)	57	102	120	139
Ionic radius, $X^-$ (pm)	133	181	196	220
First ionization energy (kJ/mol)	1681	1251	1140	1008
Electron affinity (kJ/mol)	-328	-349	-325	-295
Electronegativity	4.0	3.0	2.8	2.5
X-X single-bond enthalpy (kJ/mol)	155	242	193	151
Reduction potential (V):				
$\frac{1}{2}X_2(aq) + e^- \longrightarrow X^-(aq)$	2.87	1.36	1.07	0.54

are the strongest. Thus, I<sub>2</sub> has the highest melting point and boiling point. At room temperature and 101.3 kPa, I<sub>2</sub> is a purple solid, Br<sub>2</sub> is a red-brown liquid, and Cl<sub>2</sub> and F<sub>2</sub> are gases. (Figure 7.28) Chlorine readily liquefies upon compression at room temperature and is normally stored and handled in liquid form under pressure in steel containers.

The comparatively low bond enthalpy of F<sub>2</sub> (155 kJ/mol) accounts in part for the extreme reactivity of elemental fluorine. Because of its high reactivity, F<sub>2</sub> is difficult to work with. Certain metals, such as copper and nickel, can be used to contain F<sub>2</sub> because their surfaces form a protective coating of metal fluoride. Chlorine and the heavier halogens are also reactive, though less so than fluorine.

Because of their high electronegativities, the halogens tend to gain electrons from other substances and thereby serve as oxidizing agents. The oxidizing ability of the halogens, indicated by their standard reduction potentials, decreases going down the group. As a result, a given halogen is able to oxidize the halide anions below it. For example, Cl<sub>2</sub> oxidizes Br<sup>-</sup> and I<sup>-</sup> but not F<sup>-</sup>, as seen in Figure 22.8.

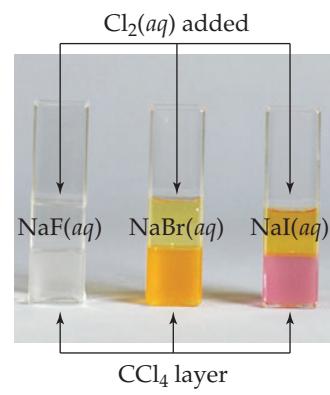
Notice in Table 22.2 that the standard reduction potential of F<sub>2</sub> is exceptionally high. As a result, fluorine gas readily oxidizes water:



Fluorine cannot be prepared by electrolytic oxidation of aqueous solutions of fluoride salts because water is oxidized more readily than F<sup>-</sup>. In practice, the element is formed by electrolytic oxidation of a solution of KF in anhydrous HF.

### Go Figure

Do Br<sub>2</sub> and I<sub>2</sub> appear to be more or less soluble in CCl<sub>4</sub> than in H<sub>2</sub>O?



No reaction      Br<sup>-</sup> oxidized to Br<sub>2</sub>      I<sup>-</sup> oxidized to I<sub>2</sub>

▲ **Figure 22.8** Reaction of Cl<sub>2</sub> with aqueous solutions of NaF, NaBr, and NaI in the presence of tetrachloromethane. The top liquid layer in each vial is water; the bottom liquid layer is tetrachloromethane. The Cl<sub>2</sub>(aq), which has been added to each vial, is colorless. The brown color in the carbon tetrachloride layer indicates the presence of Br<sub>2</sub>, whereas purple indicates the presence of I<sub>2</sub>.

### Sample Exercise 22.4

#### Predicting Chemical Reactions among the Halogens

Write the balanced equation for the reaction, if any, between (a) I<sup>-</sup>(aq) and Br<sub>2</sub>(l), (b) Cl<sup>-</sup>(aq) and I<sub>2</sub>(s).

#### SOLUTION

**Analyze** We are asked to determine whether a reaction occurs when a particular halide and halogen are combined.

**Plan** A given halogen is able to oxidize anions of the halogens below it in the periodic table. Thus, in each pair the halogen having the smaller atomic number ends up as the halide ion. If the halogen with the smaller atomic number is already the halide ion, there is no reaction. Thus, the key to determining whether a reaction occurs is locating the elements in the periodic table.

#### Solve

- (a) Br<sub>2</sub> can oxidize (remove electrons from) the anions of the halogens below it in the periodic table. Thus, it oxidizes I<sup>-</sup>:



- (b) Cl<sup>-</sup> is the anion of a halogen above iodine in the periodic table. Thus, I<sub>2</sub> cannot oxidize Cl<sup>-</sup>; there is no reaction.

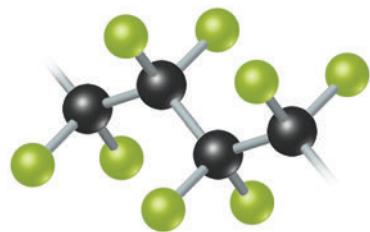
#### ► Practice Exercise

Which is (are) able to oxidize Cl<sup>-</sup>?

- (a) F<sub>2</sub>
- (b) F<sup>-</sup>
- (c) Both Br<sub>2</sub> and I<sub>2</sub>
- (d) Both Br<sup>-</sup> and I<sup>-</sup>


**Go Figure**

What is the repeating unit in this polymer?



▲ Figure 22.9 Structure of Teflon®, a fluorocarbon polymer.

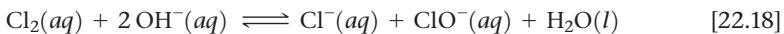
Chlorine is produced mainly by electrolysis of either molten or aqueous sodium chloride. Both bromine and iodine are obtained commercially from brines containing the halide ions; the reaction used is oxidation with Cl<sub>2</sub>.

### Uses of the Halogens

Fluorine is used to prepare fluorocarbons—very stable carbon–fluorine compounds used as refrigerants, lubricants, and plastics. Teflon® (Figure 22.9) is a polymeric fluorocarbon noted for its high thermal stability and lack of chemical reactivity.

Chlorine is by far the most commercially important halogen. About half of the chlorine is used to manufacture chlorine-containing organic compounds, such as the vinyl chloride (C<sub>2</sub>H<sub>3</sub>Cl) used in making polyvinyl chloride (PVC) plastics. Much of the remainder is used as a bleaching agent in the paper and textile industries.

When Cl<sub>2</sub> dissolves in cold dilute base, it converts into Cl<sup>−</sup> and hypochlorite, ClO<sup>−</sup>:



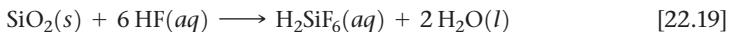
Sodium hypochlorite (NaClO) is the active ingredient in many liquid bleaches. Chlorine is also used in water treatment to oxidize and thereby destroy bacteria.

A common use of iodine is as KI in table salt. Iodized salt provides the small amount of iodine necessary in our diets; it is essential for the formation of thyroxin, a hormone secreted by the thyroid gland. Lack of iodine in the diet results in an enlarged thyroid gland, a condition called *goiter*.

### The Hydrogen Halides

All the halogens form stable diatomic molecules with hydrogen. The hydrogen halides can be formed by direct reaction of the elements.

The hydrogen halides form hydrohalic acid solutions when dissolved in water. These solutions have the characteristic properties of acids, such as reactions with active metals to produce hydrogen gas. Hydrofluoric acid also reacts readily with **silica** (SiO<sub>2</sub>) and with silicates to form hexafluorosilicic acid (H<sub>2</sub>SiF<sub>6</sub>):



### Interhalogen Compounds

Because the halogens exist as diatomic molecules, diatomic molecules made up of two different halogen atoms exist. These compounds are the simplest examples of **interhalogens**, compounds, such as ClF and IF<sub>5</sub>, formed between two halogen elements.

The vast majority of the higher interhalogen compounds have a central Cl, Br, or I atom surrounded by fluorine atoms. The large size of the iodine atom allows the formation of IF<sub>3</sub>, IF<sub>5</sub>, and IF<sub>7</sub>, in which the oxidation state of I is +3, +5, and +7, respectively. With the smaller bromine and chlorine atoms, only compounds with three or five fluorines form. The only higher interhalogen compounds that do not have outer F atoms are ICl<sub>3</sub> and ICl<sub>5</sub>; the large size of the I atom can accommodate five Cl atoms, whereas Br is not large enough to allow even BrCl<sub>3</sub> to form. All of the interhalogen compounds are powerful oxidizing agents.

### Oxyacids and Oxyanions

**Table 22.3** summarizes the formulas of the known oxyacids of the halogens and the way they are named.\* The acid strengths of the oxyacids increase with the increasing oxidation state of the central halogen atom. All the oxyacids are strong oxidizing agents. The

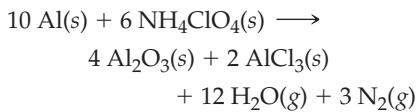
\*Fluorine forms one oxyacid, HOF. Because the electronegativity of fluorine is greater than that of oxygen, we must consider fluorine to be in a −1 oxidation state and oxygen to be in the 0 oxidation state in this compound.

**TABLE 22.3** The Stable Oxyacids of the Halogens

Oxidation State of Halogen	Formula of Acid			Acid Name
	Cl	Br	I	
+1	HClO	HBrO	HIO	Hypohalous acid
+3	HClO <sub>2</sub>	—	—	Halous acid
+5	HClO <sub>3</sub>	HBrO <sub>3</sub>	HIO <sub>3</sub>	Halic acid
+7	HClO <sub>4</sub>	HBrO <sub>4</sub>	HIO <sub>4</sub>	Perhalic acid

oxyanions, formed on removal of H<sup>+</sup> from the oxyacids, are generally more stable than the oxyacids. Hypochlorite salts are used as bleaches and disinfectants because of the powerful oxidizing capabilities of the ClO<sup>-</sup> ion. Chlorate salts are similarly very reactive. For example, potassium chlorate is used to make matches and fireworks.

Perchloric acid and its salts are the most stable oxyacids and oxyanions. Dilute solutions of perchloric acid are quite safe, and many perchlorate salts are stable except when heated with organic materials. When heated, however, perchlorates can become vigorous, even violent, oxidizers. Considerable caution should be exercised, therefore, when handling these substances, and it is crucial to avoid contact between perchlorates and readily oxidized material. The use of ammonium perchlorate (NH<sub>4</sub>ClO<sub>4</sub>) as the oxidizer in the solid booster rockets for the Space Shuttle demonstrates the oxidizing power of perchlorates. The solid propellant contains a mixture of NH<sub>4</sub>ClO<sub>4</sub> and powdered aluminum, the reducing agent. Each shuttle launch requires about 6 × 10<sup>5</sup> kg of NH<sub>4</sub>ClO<sub>4</sub> (Figure 22.10).



The large volume of gases produced provides thrust for the booster rockets.

▲ **Figure 22.10** Launch of the Space Shuttle *Columbia* from the Kennedy Space Center.

## Self-Assessment Exercise

- 22.15** What is the oxidation state of Cl in each Cl species in Equation 22.18?

- (a) Cl<sub>2</sub> 0; Cl<sup>-</sup> -1; ClO<sup>-</sup> -1  
 (b) Cl<sub>2</sub> 0; Cl<sup>-</sup> -1; ClO<sup>-</sup> +1  
 (c) Cl<sub>2</sub> 0; Cl<sup>-</sup> +1; ClO<sup>-</sup> +1

## Exercises

- 22.16** Name the following compounds and assign oxidation states to the halogens in them: (a) BCl<sub>3</sub>, (b) Sr(IO<sub>4</sub>)<sub>2</sub>, (c) LiOCl, (d) HClO, (e) CuClO, (f) Mg(IO<sub>2</sub>)<sub>2</sub>.  
**22.17** Explain the following observations: (a) For a given oxidation state, the acid strength of the oxyacid in aqueous solution

decreases in the order chlorine > bromine > iodine.  
 (b) Hydrofluoric acid cannot be stored in glass bottles.  
 (c) HI cannot be prepared by treating NaI with sulfuric acid. (d) The interhalogen ICl<sub>3</sub> is known, but BrCl<sub>3</sub> is not.

22.15 (b)

Answers to Self-Assessment Exercise



## 22.5 | Oxygen



Oxygen is one of the most reactive nonmetals, and as a consequence of this, and its abundant supply, we live in a world dominated by oxidation products. Considerable effort is put into extracting metals from their oxides and preventing oxidation of food stuffs or the rusting of iron used in construction. On the other side it is essential to the respiration of all aerobic organisms. In this overview, we look at the different forms (oxidation states) that oxygen can adopt. By the end of this section, you should be able to

- Identify the different oxides that occur and their reactions with water

Oxygen is found in combination with other elements in a great variety of compounds—water ( $\text{H}_2\text{O}$ ), silica ( $\text{SiO}_2$ ), alumina ( $\text{Al}_2\text{O}_3$ ), and the iron oxides ( $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ ) are obvious examples. Indeed, oxygen is the most abundant element by mass both in Earth's crust and in the human body. It is the oxidizing agent for the metabolism of our foods and is crucial to human life.

### Properties of Oxygen

Oxygen has two allotropes,  $\text{O}_2$  and  $\text{O}_3$ . When we speak of molecular oxygen or simply oxygen, it is usually understood that we are speaking of *dioxygen* ( $\text{O}_2$ ), the normal form of the element;  $\text{O}_3$  is ozone.

At room temperature, dioxygen is a colorless and odorless gas. Dioxygen is only slightly soluble in water (0.04 g/L, or 0.001 M at 25 °C), but its presence in water is essential to marine life.

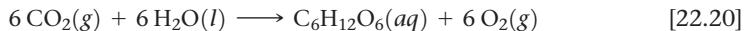
The electron configuration of the oxygen atom is  $[\text{He}]2s^22p^4$ . Thus, oxygen can complete its octet of valence electrons either by picking up two electrons to form the oxide ion ( $\text{O}^{2-}$ ) or by sharing two electrons. In its covalent compounds, it tends to form either two single bonds, as in  $\text{H}_2\text{O}$ , or a double bond, as in formaldehyde ( $\text{H}_2\text{C=O}$ ). The  $\text{O}_2$  molecule contains a double bond. The bond in  $\text{O}_2$  is very strong (bond enthalpy 495 kJ/mol). Oxygen also forms strong bonds with many other elements. Consequently, many oxygen-containing compounds are thermodynamically more stable than  $\text{O}_2$ . In the absence of a catalyst, however, most reactions of  $\text{O}_2$  have high activation energies and thus require

high temperatures to proceed at a suitable rate. Once a sufficiently exothermic reaction begins, it may accelerate rapidly, producing a reaction of explosive violence.

## Production of Oxygen

Nearly all commercial oxygen is obtained from air. The normal boiling point of O<sub>2</sub> is –183 °C, whereas that of N<sub>2</sub>, the other principal component of air, is –196 °C. Thus, when air is liquefied and then allowed to warm, the N<sub>2</sub> boils off, leaving liquid O<sub>2</sub> contaminated mainly by small amounts of N<sub>2</sub> and Ar.

Much of the O<sub>2</sub> in the atmosphere is replenished through photosynthesis, in which green plants use the energy of sunlight to generate O<sub>2</sub> (along with glucose, C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>) from atmospheric CO<sub>2</sub>:



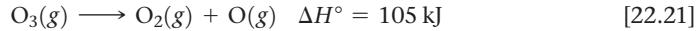
## Uses of Oxygen

In industrial use, oxygen ranks behind only sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) and nitrogen (N<sub>2</sub>). Oxygen is by far the most widely used oxidizing agent in industry. Over half of the O<sub>2</sub> produced is used in the steel industry, mainly to remove impurities from steel. It is also used to bleach pulp and paper. (Oxidation of colored compounds often gives colorless products.) Oxygen is used together with acetylene (C<sub>2</sub>H<sub>2</sub>) in oxyacetylene welding (**Figure 22.11**). The reaction between C<sub>2</sub>H<sub>2</sub> and O<sub>2</sub> is highly exothermic, producing temperatures in excess of 3000 °C.

## Ozone

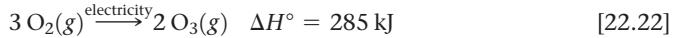
Ozone is a pale blue, poisonous gas with a sharp, irritating odor. Many people can detect as little as 0.01 ppm in air. Exposure to 0.1 to 1 ppm produces headaches, burning eyes, and irritation to the respiratory passages.

The O<sub>3</sub> molecule possesses  $\pi$  electrons that are delocalized over the three oxygen atoms. The molecule dissociates readily, forming reactive oxygen atoms:



Ozone is a stronger oxidizing agent than dioxygen. Ozone forms oxides with many elements under conditions where O<sub>2</sub> will not react; indeed, it oxidizes all the common metals except gold and platinum.

Ozone can be prepared by passing electricity through dry O<sub>2</sub>. During thunderstorms, ozone is generated (and can be smelled, if you are too close) from lightning strikes:

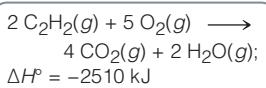


Ozone is sometimes used to treat drinking water. Like Cl<sub>2</sub>, ozone kills bacteria and oxidizes organic compounds. The largest use of ozone, however, is in the preparation of pharmaceuticals, synthetic lubricants, and other commercially useful organic compounds, where O<sub>3</sub> is used to sever carbon–carbon double bonds.

Ozone is an important component of the upper atmosphere, where it screens out ultraviolet radiation and so protects us from the effects of these high-energy rays. For this reason, depletion of stratospheric ozone is a major scientific concern. In the lower atmosphere, ozone is considered an air pollutant and is a major constituent of smog. Because of its oxidizing power, ozone damages living systems and structural materials, especially rubber.

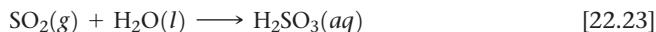
## Oxides

The electronegativity of oxygen is second only to that of fluorine. As a result, oxygen has negative oxidation states in all compounds except OF<sub>2</sub> and O<sub>2</sub>F<sub>2</sub>. The –2 oxidation state is by far the most common. Compounds that contain oxygen in this oxidation state are called *oxides*.



**▲ Figure 22.11** Welding with an oxyacetylene torch.

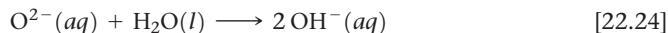
Nonmetals form covalent oxides, most of which are simple molecules with low melting and boiling points. Both  $\text{SiO}_2$  and  $\text{B}_2\text{O}_3$ , however, have extended structures. Most nonmetal oxides combine with water to give oxyacids. Sulfur dioxide ( $\text{SO}_2$ ), for example, dissolves in water to give sulfurous acid ( $\text{H}_2\text{SO}_3$ ):



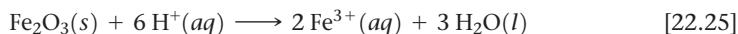
This reaction and that of  $\text{SO}_3$  with  $\text{H}_2\text{O}$  to form  $\text{H}_2\text{SO}_4$  are largely responsible for acid rain. The analogous reaction of  $\text{CO}_2$  with  $\text{H}_2\text{O}$  to form carbonic acid ( $\text{H}_2\text{CO}_3$ ) causes the acidity of carbonated water.

Oxides that form acids when they react with water are called either **acidic anhydrides** (anhydride means “without water”) or **acidic oxides**. A few nonmetal oxides, especially ones with the nonmetal in a low oxidation state—such as  $\text{N}_2\text{O}$ ,  $\text{NO}$ , and  $\text{CO}$ —do not react with water and are not acidic anhydrides.

Most metal oxides are ionic compounds. The ionic oxides that dissolve in water form hydroxides and, consequently, are called either **basic anhydrides** or **basic oxides**. Barium oxide, for example, reacts with water to form barium hydroxide (Figure 22.12). These kinds of reactions are due to the high basicity of the  $\text{O}^{2-}$  ion and its virtually complete hydrolysis in water:



Even those ionic oxides that are insoluble in water tend to dissolve in strong acids. Iron(III) oxide, for example, dissolves in acids:

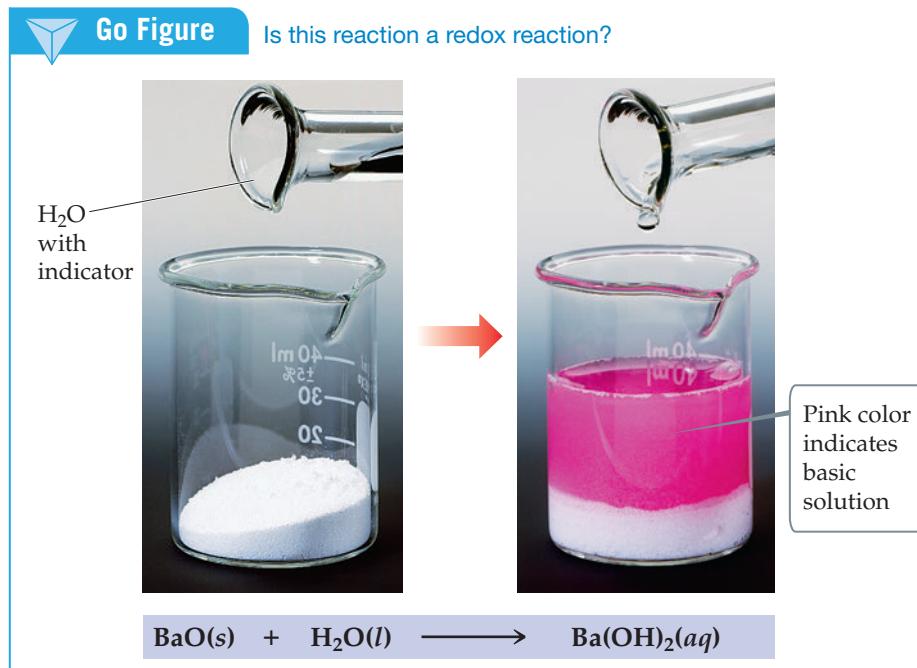


This reaction is used to remove rust ( $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ ) from iron or steel before a protective coat of zinc or tin is applied.

Oxides that can exhibit both acidic and basic characters are said to be *amphoteric*. If a metal forms more than one oxide, the basic character of the oxide decreases as the oxidation state of the metal increases (Table 22.4).

## Peroxides and Superoxides

Compounds containing O—O bonds and oxygen in the  $-1$  oxidation state are *peroxides*. Oxygen has an oxidation state of  $-\frac{1}{2}$  in  $\text{O}_2^-$ , which is called the *superoxide* ion. The



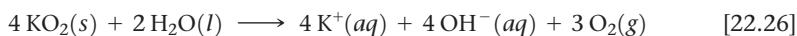
▲ Figure 22.12 Reaction of a basic oxide with water.

**TABLE 22.4 Acid–Base Character of Chromium Oxides**

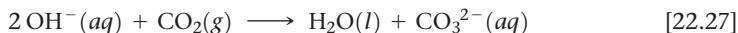
Oxide	Oxidation State of Cr	Nature of Oxide
CrO	+2	Basic
Cr <sub>2</sub> O <sub>3</sub>	+3	Amphoteric
CrO <sub>3</sub>	+6	Acidic

most active (easily oxidized) metals (K, Rb, and Cs) react with O<sub>2</sub> to give superoxides (KO<sub>2</sub>, RbO<sub>2</sub>, and CsO<sub>2</sub>). Their active neighbors in the periodic table (Na, Ca, Sr, and Ba) react with O<sub>2</sub>, producing peroxides (Na<sub>2</sub>O<sub>2</sub>, CaO<sub>2</sub>, SrO<sub>2</sub>, and BaO<sub>2</sub>). Less active metals and nonmetals produce normal oxides.

When superoxides dissolve in water, O<sub>2</sub> is produced:



Because of this reaction, potassium superoxide is used as an oxygen source in masks worn by rescue workers (**Figure 22.13**). For proper breathing in toxic environments, oxygen must be generated in the mask and exhaled carbon dioxide in the mask must be eliminated. Moisture in the breath causes the KO<sub>2</sub> to decompose to O<sub>2</sub> and KOH, and the KOH removes CO<sub>2</sub> from the exhaled breath:



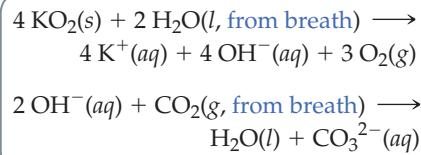
Hydrogen peroxide (**Figure 22.14**) is the most familiar and commercially important peroxide. Pure hydrogen peroxide is a clear, syrupy liquid that melts at -0.4 °C. Concentrated hydrogen peroxide is dangerously reactive because the decomposition to water and oxygen is very exothermic:



This is an example of a **disproportionation** reaction, in which an element is simultaneously oxidized and reduced. The oxidation number of oxygen changes from -1 to -2 and 0.

Hydrogen peroxide is marketed as a chemical reagent in aqueous solutions of up to about 30% by mass. A solution containing about 3% H<sub>2</sub>O<sub>2</sub> by mass is sold in drugstores and used as a mild antiseptic. Somewhat more concentrated solutions are used to bleach fabrics.

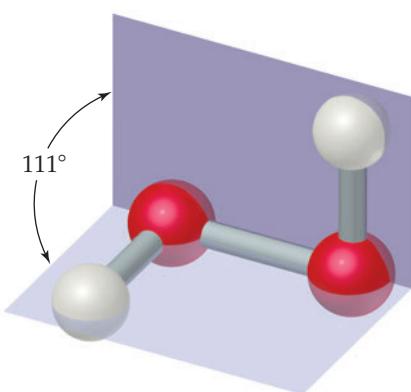
The peroxide ion is a by-product of metabolism that results from the reduction of O<sub>2</sub>. The body disposes of this reactive ion with enzymes such as peroxidase and catalase.



▲ **Figure 22.13** A self-contained breathing apparatus.

### Go Figure

Does H<sub>2</sub>O<sub>2</sub> have a dipole moment?



◀ **Figure 22.14** Molecular structure of hydrogen peroxide in the gas phase. The repulsive interaction of the O—H bonds with the lone pairs of electrons on each O atom restricts the free rotation around the O—O single bond.

## Self-Assessment Exercise

**22.18** What acid is produced by the reaction of  $\text{N}_2\text{O}_5$  with water?

- (a)  $\text{HNO}$
- (b)  $\text{HNO}_2$
- (c)  $\text{HNO}_3$

## Exercises

**22.19** Complete and balance the following equations:

- (a)  $\text{CaO}(s) + \text{H}_2\text{O}(l) \longrightarrow$
- (b)  $\text{Al}_2\text{O}_3(s) + \text{H}^+(aq) \longrightarrow$
- (c)  $\text{Na}_2\text{O}_2(s) + \text{H}_2\text{O}(l) \longrightarrow$
- (d)  $\text{N}_2\text{O}_3(g) + \text{H}_2\text{O}(l) \longrightarrow$

- (e)  $\text{KO}_2(s) + \text{H}_2\text{O}(l) \longrightarrow$
- (f)  $\text{NO}(g) + \text{O}_3(g) \longrightarrow$

**22.20** Select the more acidic member of each of the following pairs: (a)  $\text{V}_2\text{O}_5$  and  $\text{VO}$ , (b)  $\text{PbO}$  and  $\text{PbO}_2$ , (c)  $\text{N}_2\text{O}_3$  and  $\text{N}_2\text{O}_2$ , (d)  $\text{SO}_2$  and  $\text{SeO}_2$ , (e)  $\text{Al}_2\text{O}_3$  and  $\text{SeO}_2$ , (f)  $\text{CO}_2$  and  $\text{B}_2\text{O}_3$ .

22.18 (c)

Answers to Self-Assessment Exercise

## 22.6 | The Other Group 16 Elements: S, Se, Te, and Po



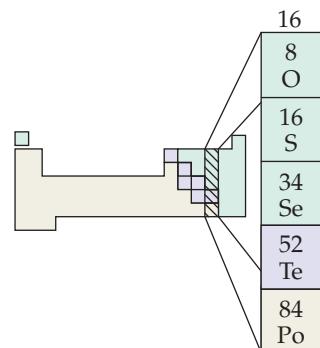
Deep in the ocean, there is no light and little food. Nevertheless, there can be thriving ecosystems centered around hydrothermal vents associated with tectonic activity. Here, bacteria have evolved to convert the heat and sulfur compounds (usually  $\text{H}_2\text{S}$ ) emitted by the vent into food and energy. They are the bottom of a small, but important, food chain! In this section, we review the other elements of Group 16, the most important of which is sulfur. By the end of this section, you should be able to

- Name the most important types of sulfur compound

**TABLE 22.5 Some Properties of the Group 16 Elements**

Property	O	S	Se	Te
Atomic radius (pm)	66	105	121	138
$X^{2-}$ ionic radius (pm)	140	184	198	221
First ionization energy (kJ/mol)	1314	1000	941	869
Electron affinity (kJ/mol)	-141	-200	-195	-190
Electronegativity	3.5	2.5	2.4	2.1
X—X single-bond enthalpy (kJ/mol)	146*	266	172	126
Reduction potential to $H_2X$ in acidic solution (V)	1.23	0.14	-0.40	-0.72

\*Based on O—O bond enthalpy in  $H_2O_2$ .



The other Group 16 elements are sulfur, selenium, tellurium, and polonium. Of these, sulfur is the most important, and polonium, which has no stable isotopes and is found only in minute quantities in radium-containing minerals, is least important.

The Group 16 elements possess the general outer-electron configuration  $ns^2np^4$  with  $n$  ranging from 2 to 6. Thus, these elements attain a noble-gas electron configuration by adding two electrons, which results in a -2 oxidation state. Except for oxygen, the Group 16 elements are also commonly found in positive oxidation states up to +6, and they can have expanded valence shells. Thus, we have such compounds as  $SF_6$ ,  $SeF_6$ , and  $TeF_6$  with the central atom in the +6 oxidation state.

**Table 22.5** summarizes some properties of the Group 16 elements.

### Occurrence and Production of S, Se, and Te

Sulfur, selenium, and tellurium can all be mined from the earth. Large underground deposits are the principal source of elemental sulfur (**Figure 22.15**). Sulfur also occurs widely as sulfide ( $S^{2-}$ ) and sulfate ( $SO_4^{2-}$ ) minerals. Its presence as a minor component of coal and petroleum poses a major problem. Combustion of these “unclean” fuels leads to serious pollution by sulfur oxides. Much effort has been directed at removing this sulfur, and these efforts have increased the availability of sulfur.

Selenium and tellurium occur in rare minerals, such as  $Cu_2Se$ ,  $PbSe$ ,  $Cu_2Te$ , and  $PbTe$ , and as minor constituents in sulfide ores of copper, iron, nickel, and lead.

### Properties and Uses of Sulfur, Selenium, and Tellurium

Elemental sulfur is yellow, tasteless, and nearly odorless. It is insoluble in water and exists in several allotropic forms. The thermodynamically stable form at room temperature is rhombic sulfur, which consists of puckered  $S_8$  rings with each sulfur atom forming two bonds (Figure 7.26).

Most of the sulfur produced world wide each year is used to manufacture sulfuric acid. Sulfur is also used to vulcanize rubber, a process that toughens rubber by introducing cross-linking between polymer chains.

Selenium is used in photoelectric cells and light meters because its electrical conductivity increases greatly upon exposure to light. Photocopiers also depend on the photoconductivity of selenium. Photocopy machines contain a belt or drum coated with a film of selenium. This drum is electrostatically charged and then exposed to light reflected from the image being photocopied. The charge drains from the regions where the selenium film has been made conductive by exposure to light. A black powder (the toner) sticks only to the areas that remain charged. The photocopy is made when the toner is transferred to a sheet of plain paper.



▲ **Figure 22.15** Massive amounts of sulfur are extracted every year from the earth.



▲ Figure 22.16 Iron pyrite ( $\text{FeS}_2$ , on the right) with gold for comparison.

## Sulfides

When an element is less electronegative than sulfur, *sulfides* that contain  $\text{S}^{2-}$  form. Many metallic elements are found in the form of sulfide ores, such as  $\text{PbS}$  (galena) and  $\text{HgS}$  (cinnabar). A series of related ores containing the disulfide ion,  $\text{S}_2^{2-}$  (analogous to the peroxide ion), are known as *pyrites*. Iron pyrite,  $\text{FeS}_2$ , occurs as golden yellow cubic crystals (Figure 22.16). Because it has been occasionally mistaken for gold by miners, iron pyrite is often called fool's gold.

One of the most important sulfides is hydrogen sulfide ( $\text{H}_2\text{S}$ ). One of hydrogen sulfide's most readily recognized properties is its odor, which is most frequently encountered as the offensive odor of rotten eggs. Hydrogen sulfide is toxic, but our noses can detect  $\text{H}_2\text{S}$  in extremely low, nontoxic concentrations. A sulfur-containing organic molecule, such as dimethyl sulfide,  $(\text{CH}_3)_2\text{S}$ , which is similarly odoriferous and can be detected by smell at a level of one part per trillion, is added to natural gas as a safety factor to give it a detectable odor.

## Oxides, Oxyacids, and Oxyanions of Sulfur

Sulfur dioxide, formed when sulfur burns in air, has a choking odor and is poisonous. The gas is particularly toxic to lower organisms, such as fungi, so it is used to sterilize dried fruit and wine. At 101.3 kPa and room temperature,  $\text{SO}_2$  dissolves in water to produce a 1.6 M solution. The  $\text{SO}_2$  solution is acidic, and we describe it as sulfurous acid ( $\text{H}_2\text{SO}_3$ ).

Salts of  $\text{SO}_3^{2-}$  (sulfites) and  $\text{HSO}_3^-$  (hydrogen sulfites or bisulfites) are well known. Small quantities of  $\text{Na}_2\text{SO}_3$  or  $\text{NaHSO}_3$  are used as food additives to prevent bacterial spoilage. However, they are known to increase asthma symptoms in approximately 5% of asthmatics. Thus, all food products with sulfites must now carry a warning label disclosing their presence (Figure 22.17).

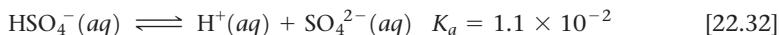
Although combustion of sulfur in air produces mainly  $\text{SO}_2$ , small amounts of  $\text{SO}_3$  are also formed. The reaction produces chiefly  $\text{SO}_2$  because the activation-energy barrier for oxidation to  $\text{SO}_3$  is very high unless the reaction is catalyzed. Interestingly, the  $\text{SO}_3$  by-product is used industrially to make  $\text{H}_2\text{SO}_4$ , which is the ultimate product of the reaction between  $\text{SO}_3$  and water. In the manufacture of sulfuric acid,  $\text{SO}_2$  is obtained by burning sulfur and then is oxidized to  $\text{SO}_3$ , using a catalyst such as  $\text{V}_2\text{O}_5$  or platinum. The  $\text{SO}_3$  is dissolved in  $\text{H}_2\text{SO}_4$  because it does not dissolve quickly in water, and then the  $\text{H}_2\text{S}_2\text{O}_7$  formed in this reaction, called pyrosulfuric acid, is added to water to form  $\text{H}_2\text{SO}_4$ :



Commercial sulfuric acid is 98%  $\text{H}_2\text{SO}_4$ . It is a dense, colorless, oily liquid. It is a strong acid, a good dehydrating agent (Figure 22.18), and a moderately good oxidizing agent.

Year after year, the production of sulfuric acid is the largest of any chemical produced in the world. It is employed in some way in almost all manufacturing.

Sulfuric acid is a strong acid, but only the first hydrogen is completely ionized in aqueous solution:



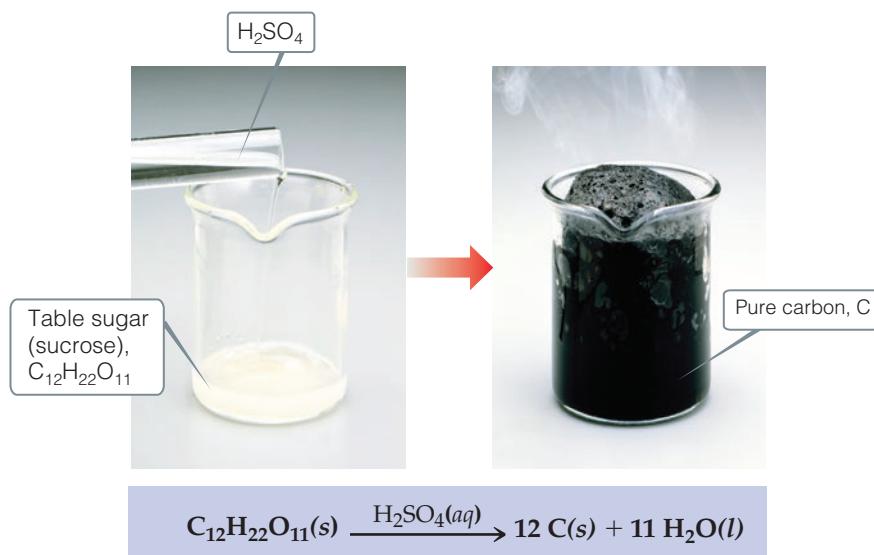
Consequently, sulfuric acid forms both sulfates ( $\text{SO}_4^{2-}$  salts) and bisulfates (or hydrogen sulfates,  $\text{HSO}_4^-$  salts). Hydrogen sulfate salts are common components of the “dry acids” used for adjusting the pH of swimming pools and hot tubs; they are also components of many toilet bowl cleaners.

Another important sulfur-containing ion is thiosulfate ion ( $\text{S}_2\text{O}_3^{2-}$ ). The term *thio* indicates substitution of sulfur for oxygen. The structures of the sulfate and thiosulfate ions are compared in Figure 22.19.

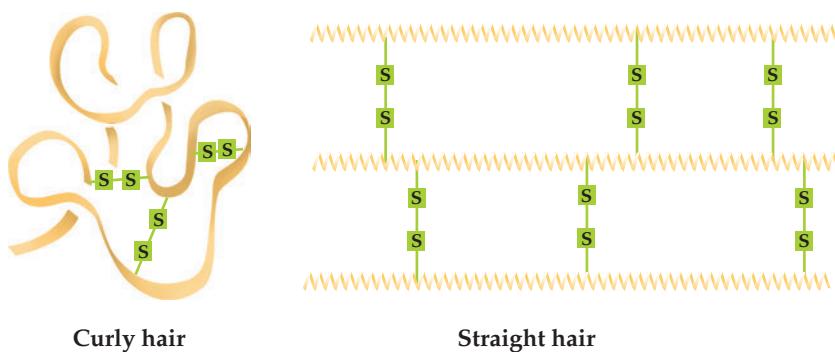
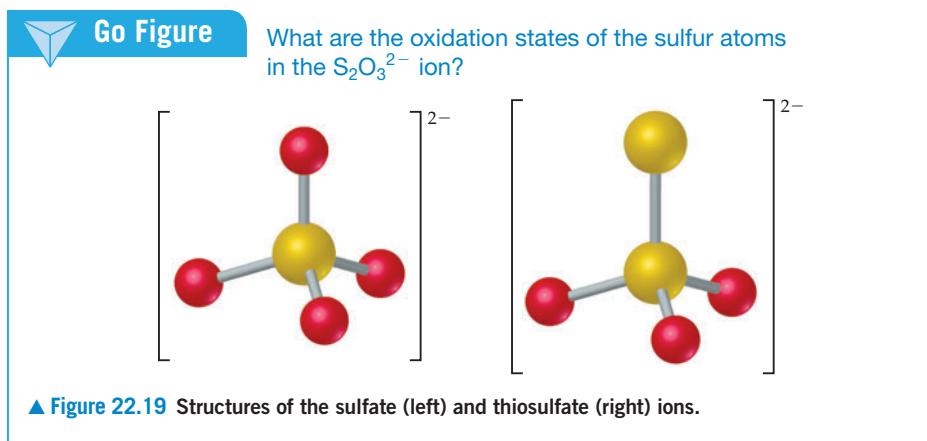
Thiols, organic compounds with a  $-\text{SH}$  group bonded to carbon, play important roles in biology. When thiols are oxidized under mild conditions, they form disulfides, organic compounds with  $\text{S}-\text{S}$  bonds between carbon atoms. In the



▲ Figure 22.17 Food label warning of sulfites.



▲ Figure 22.18 Sulfuric acid dehydrates table sugar to produce elemental carbon.



▲ Figure 22.20 Hair straightening and curling. People can alter the shape of their hair by first applying a reducing agent that breaks the disulfide bonds between protein strands. The hair is given its desired shape, and then an oxidizing agent is added to form new disulfide bonds to maintain the shape.

opposite fashion, disulfide bonds can be broken by reducing them to thiols. The shape and function of proteins can be modified by forming or breaking disulfide bonds between protein strands. Hair-straightening and curling technologies rely on the breaking and re-forming of disulfide bonds between the protein molecules of hair (Figure 22.20).

## Self-Assessment Exercise

**22.21** The structure of the thiosulfate ion is shown in figure 22.19. The oxidation state of one sulfur atom is  $-2$ , what is the oxidation state of the other sulfur atom?

- (a)  $-2$   
(b)  $0$

(c)  $+4$

(d)  $+6$

## Exercises

**22.22** Write the chemical formula for each of the following compounds, and indicate the oxidation state of the Group 16 elements in each: (a) selenious acid, (b) sulphur trioxide, (c) selenium dichloride, (d) aluminium selenide, (e) iron(II) sulfate, (f) tellurium trioxide.

**22.23** An aqueous solution of  $\text{SO}_2$  reduces (a) aqueous  $\text{KMnO}_4$  to  $\text{MnSO}_4(aq)$ , (b) acidic aqueous  $\text{K}_2\text{Cr}_2\text{O}_7$  to aqueous  $\text{Cr}^{3+}$ , (c) aqueous  $\text{Hg}_2(\text{NO}_3)_2$  to mercury metal. Write balanced equations for these reactions.

**22.24** The  $\text{SF}_5^-$  ion is formed when  $\text{SF}_4(g)$  reacts with fluoride salts containing large cations, such as  $\text{CsF}(s)$ . Draw the

Lewis structures for  $\text{SF}_4$  and  $\text{SF}_5^-$ , and predict the molecular structure of each.

**22.25** Write a balanced equation for each of the following reactions. (You may have to guess at one or more of the reaction products, but you should be able to make a reasonable guess, based on your study of this chapter.) (a) Hydrogen selenide can be prepared by reaction of an aqueous acid solution on aluminum selenide. (b) Sodium thiosulfate is used to remove excess  $\text{Cl}_2$  from chlorine-bleached fabrics. The thiosulfate ion forms  $\text{SO}_4^{2-}$  and elemental sulfur, while  $\text{Cl}_2$  is reduced to  $\text{Cl}^-$ .

22.21 (d)

Answers to Self-Assessment Exercise

## 22.7 | Nitrogen



On 4 August 2020, a massive explosion of almost 3000 tons of ammonium nitrate devastated the port of Beirut, killing at least 220 people, injuring more than 5000, and making an estimated 300,000 homeless. The blast was so powerful that it could be heard in Cyprus, some 200 km away. Ammonium nitrate is a commonly used fertilizer.

It is usually manufactured as small pellets that are reasonably safe to handle but, when stored, can absorb moisture and form a solid, rock like mass. Heat, such as from a fire, can cause the mass to ignite and explode.

Nitrogen and its compounds display a staggering nine different oxidation states, and we revise some of its chemistry in this section. By the end, you should be able to

- Appreciate the wide variety of bonding arrangements that nitrogen can adopt

Nitrogen constitutes 78% by volume of Earth's atmosphere, where it occurs as  $\text{N}_2$  molecules. Although nitrogen is a key element in living organisms, compounds of nitrogen are not abundant in Earth's crust. The major natural deposits of nitrogen compounds are those of  $\text{KNO}_3$  (salt peter) in India and  $\text{NaNO}_3$  (Chile salt peter) in Chile and other desert regions of South America.

## Properties of Nitrogen

Nitrogen is a colorless, odorless, tasteless gas composed of  $\text{N}_2$  molecules. The  $\text{N}_2$  molecule is very unreactive because of the strong triple bond between nitrogen atoms (the  $\text{N}\equiv\text{N}$  bond enthalpy is 941 kJ/mol, nearly twice that for the bond in  $\text{O}_2$ . (Table 8.3)) When substances burn in air, they normally react with  $\text{O}_2$  but not with  $\text{N}_2$ .

The electron configuration of the nitrogen atom is  $[\text{He}]2s^22p^3$ . The element exhibits all formal oxidation states from +5 to -3 (Table 22.6). The +5, 0, and -3 oxidation states are the most common and generally the most stable of these. Because nitrogen is more electronegative than all other elements except fluorine, oxygen, and chlorine, it exhibits positive oxidation states only in combination with these three elements.

## Production and Uses of Nitrogen

Elemental nitrogen is obtained in commercial quantities by fractional distillation of liquid air. Because of its low reactivity, large quantities of  $\text{N}_2$  are used as an inert gaseous blanket to exclude  $\text{O}_2$  in food processing, manufacture of chemicals, metal fabrication, and production of electronic devices. Liquid  $\text{N}_2$  is employed as a coolant to freeze foods rapidly.

The largest use of  $\text{N}_2$  is in the manufacture of nitrogen-containing fertilizers. These fertilizers provide a source of *fixed* nitrogen—nitrogen that has been incorporated into compounds. We have previously discussed nitrogen fixation in the “Chemistry Put to Work” box in Section 14.7 and in the “Chemistry Put to Work” box in Section 15.2. Our starting point in fixing nitrogen is the manufacture of ammonia via the Haber process. The ammonia can then be converted into a variety of useful, simple nitrogen-containing species (Figure 22.21).

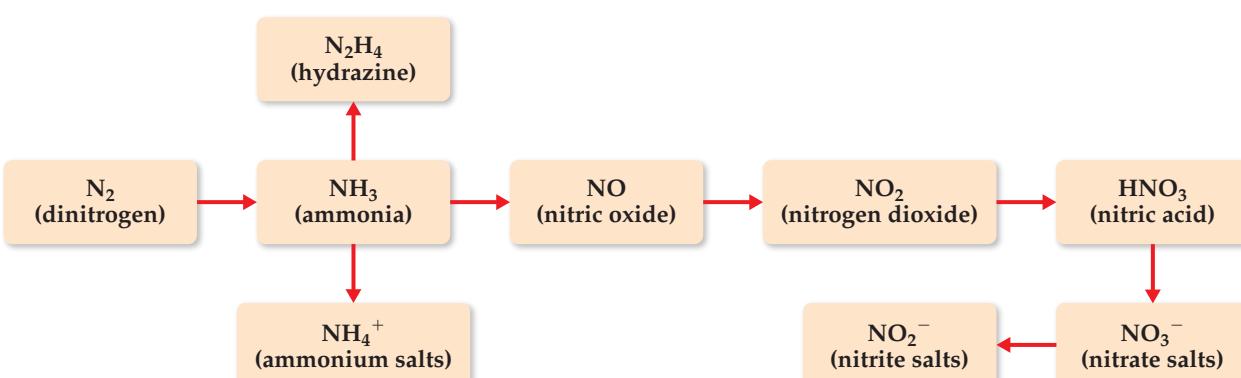
**TABLE 22.6 Oxidation States of Nitrogen**

Oxidation State	Examples
+5	$\text{N}_2\text{O}_5$ , $\text{HNO}_3$ , $\text{NO}_3^-$
+4	$\text{NO}_2$ , $\text{N}_2\text{O}_4$
+3	$\text{HNO}_2$ , $\text{NO}_2^-$ , $\text{NF}_3$
+2	$\text{NO}$
+1	$\text{N}_2\text{O}$ , $\text{H}_2\text{N}_2\text{O}_2$ , $\text{N}_2\text{O}_2^{2-}$ , $\text{HNF}_2$
0	$\text{N}_2$
-1	$\text{NH}_2\text{OH}$ , $\text{NH}_2\text{F}$
-2	$\text{N}_2\text{H}_4$
-3	$\text{NH}_3$ , $\text{NH}_4^+$ , $\text{NH}_2^-$



### Go Figure

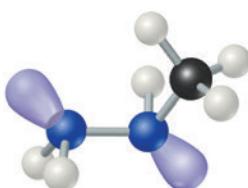
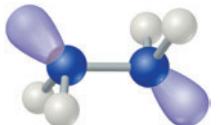
In which of these species is the oxidation number of nitrogen +3?



▲ Figure 22.21 Sequence of conversion of  $\text{N}_2$  into common nitrogen compounds.


**Go Figure**

Is the N—N bond length in these molecules shorter or longer than the N—N bond length in  $\text{N}_2$ ?

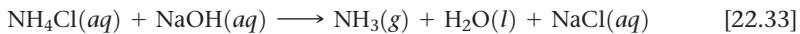


▲ Figure 22.22 Hydrazine (top,  $\text{N}_2\text{H}_4$ ) and methylhydrazine (bottom,  $\text{CH}_3\text{NHNH}_2$ ).

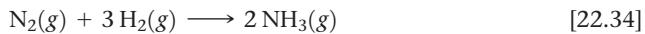
## Hydrogen Compounds of Nitrogen

*Ammonia* is one of the most important compounds of nitrogen. It is a colorless, toxic gas that has a characteristic irritating odor. As noted in previous discussions, the  $\text{NH}_3$  molecule is basic ( $K_b = 1.8 \times 10^{-5}$ ).

In the laboratory,  $\text{NH}_3$  can be prepared by the action of  $\text{NaOH}$  on an ammonium salt. The  $\text{NH}_4^+$  ion, which is the conjugate acid of  $\text{NH}_3$ , transfers a proton to  $\text{OH}^-$ . The resultant  $\text{NH}_3$  is volatile and is driven from the solution by mild heating:

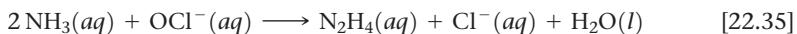


Commercial production of  $\text{NH}_3$  is achieved by the Haber process:



About 75% is used for fertilizer.

*Hydrazine* ( $\text{N}_2\text{H}_4$ ) is another important hydride of nitrogen. The hydrazine molecule contains an N—N single bond (Figure 22.22). It can be prepared by the reaction of ammonia with hypochlorite ion ( $\text{OCl}^-$ ) in aqueous solution:



The reaction involves several intermediates, including chloramine ( $\text{NH}_2\text{Cl}$ ). The poisonous  $\text{NH}_2\text{Cl}$  bubbles out of solution when household ammonia and chlorine bleach (which contains  $\text{OCl}^-$ ) are mixed. This reaction is one reason for the frequently cited warning not to mix bleach and household ammonia.

Pure hydrazine is a strong and versatile reducing agent. The major use of hydrazine and compounds related to it, such as methylhydrazine (Figure 22.22), is as rocket fuel.

## Sample Exercise 22.5

### Writing a Balanced Equation

Hydroxylamine ( $\text{NH}_2\text{OH}$ ) reduces copper(II) to the free metal in acid solutions. Write a balanced equation for the reaction, assuming that  $\text{N}_2$  is the oxidation product.

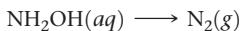
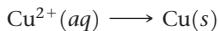
#### SOLUTION

**Analyze** We are asked to write a balanced oxidation-reduction equation in which  $\text{NH}_2\text{OH}$  is converted to  $\text{N}_2$  and  $\text{Cu}^{2+}$  is converted to Cu.

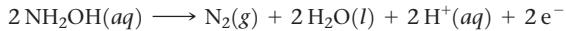
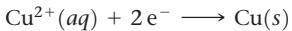
**Plan** Because this is a redox reaction, the equation can be balanced by the method of half-reactions discussed in Section 20.2. Thus, we begin with two half-reactions, one involving the  $\text{NH}_2\text{OH}$  and  $\text{N}_2$  and the other involving  $\text{Cu}^{2+}$  and Cu.

#### Solve

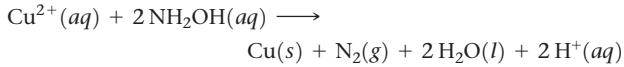
The unbalanced and incomplete half-reactions are



Balancing these equations as described in Section 20.2 gives



Adding these half-reactions gives the balanced equation:

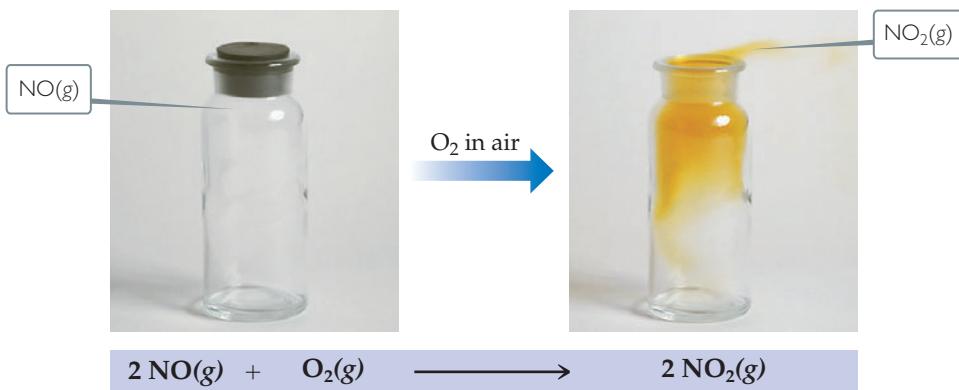


#### ► Practice Exercise

In power plants, hydrazine is used to prevent corrosion of the metal parts of steam boilers by the  $\text{O}_2$  dissolved in the water. The hydrazine reacts with  $\text{O}_2$  in water to give  $\text{N}_2$  and  $\text{H}_2\text{O}$ . Write a balanced equation for this reaction.

## Oxides and Oxyacids of Nitrogen

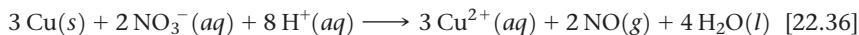
Nitrogen forms three common oxides:  $\text{N}_2\text{O}$  (nitrous oxide),  $\text{NO}$  (nitric oxide), and  $\text{NO}_2$  (nitrogen dioxide). It also forms two unstable oxides that we will not discuss,  $\text{N}_2\text{O}_3$  (dinitrogen trioxide) and  $\text{N}_2\text{O}_5$  (dinitrogen pentoxide).



▲ Figure 22.23 Formation of  $\text{NO}_2(g)$  as  $\text{NO}(g)$  combines with  $\text{O}_2(g)$  in the air.

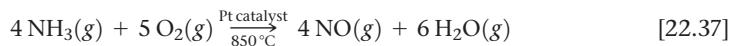
*Nitrous oxide* ( $\text{N}_2\text{O}$ ) is also known as laughing gas because a person becomes giddy after inhaling a small amount. This colorless gas was the first substance used as a general anesthetic. It is used as the compressed gas propellant in several aerosols and foams, such as in whipped cream.

*Nitric oxide* ( $\text{NO}$ ) is also a colorless gas but, unlike  $\text{N}_2\text{O}$ , it is slightly toxic. It can be prepared in the laboratory by reduction of dilute nitric acid, using copper or iron as a reducing agent:



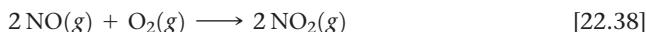
Nitric oxide is also produced by direct reaction of  $\text{N}_2$  and  $\text{O}_2$  at high temperatures. This reaction is a significant source of nitrogen oxide air pollutants. The direct combination of  $\text{N}_2$  and  $\text{O}_2$  is not used for commercial production of  $\text{NO}$ , however, because the yield is low, the equilibrium constant  $K_p$  at 2400 K being only 0.05. (“Chemistry Put to Work: Controlling Nitric Oxide Emissions”)

The commercial route to  $\text{NO}$  (and hence to other oxygen-containing compounds of nitrogen) is via the catalytic oxidation of  $\text{NH}_3$ :

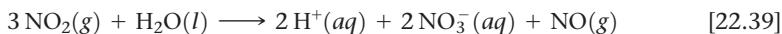


This reaction is the first step in the **Ostwald process**, by which  $\text{NH}_3$  is converted commercially into nitric acid ( $\text{HNO}_3$ ).

When exposed to air, nitric oxide reacts readily with  $\text{O}_2$  (Figure 22.23):



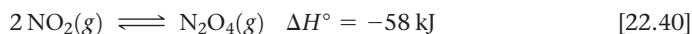
When dissolved in water,  $\text{NO}_2$  forms nitric acid:



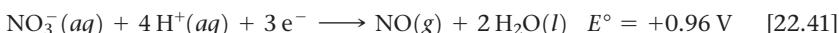
Nitrogen is both oxidized and reduced in this reaction, which means it disproportionates. The  $\text{NO}$  can be converted back into  $\text{NO}_2$  by exposure to air (Equation 22.38) and thereafter dissolved in water to prepare more  $\text{HNO}_3$ .

$\text{NO}$  is an important neurotransmitter in the human body. It causes the muscles that line blood vessels to relax, thus allowing an increased passage of blood (see “Chemistry and Life: Nitroglycerin, Nitric Oxide, and Heart Disease”).

*Nitrogen dioxide* ( $\text{NO}_2$ ) is a yellow-brown gas (Figure 22.23). Like  $\text{NO}$ , it is a major constituent of smog. It is poisonous and has a choking odor. As discussed in Section 15.1,  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  exist in equilibrium:



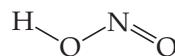
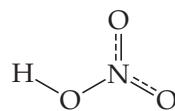
The two common oxyacids of nitrogen are nitric acid ( $\text{HNO}_3$ ) and nitrous acid ( $\text{HNO}_2$ ) (Figure 22.24). *Nitric acid* is a strong acid. It is also a powerful oxidizing agent, as indicated by the standard reduction potential in the reaction



Concentrated nitric acid attacks and oxidizes most metals except Au, Pt, Rh, and Ir.

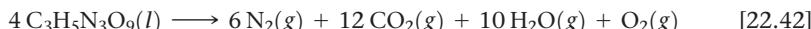
### Go Figure

Which is the shortest  $\text{NO}$  bond in these two molecules?



▲ Figure 22.24 Structures of nitric acid (top) and nitrous acid (bottom).

Its largest use is in the manufacture of  $\text{NH}_4\text{NO}_3$  for fertilizers. It is also used in the production of plastics, drugs, and explosives. Among the explosives made from nitric acid are nitroglycerin, trinitrotoluene (TNT), and nitrocellulose. The following reaction occurs when nitroglycerin explodes:



All the products of this reaction contain very strong bonds and are gases. As a result, the reaction is very exothermic, and the volume of the products is far larger than the volume occupied by the reactant. Thus, the expansion resulting from the heat generated by the reaction produces the explosion.

### CHEMISTRY AND LIFE Nitroglycerin, Nitric Oxide, and Heart Disease

During the 1870s, an interesting observation was made in Alfred Nobel's dynamite factories. Workers who suffered from heart disease that caused chest pains when they exerted themselves found relief from the pains during the workweek. It quickly became apparent that nitroglycerin, present in the air of the factory, acted to enlarge blood vessels. Thus, this powerfully explosive chemical became a standard treatment for angina pectoris, the chest pains accompanying heart failure. It took more than 100 years to discover that nitroglycerin was converted in the vascular smooth muscle into NO, which is the chemical agent actually causing dilation of the blood vessels. In 1998, the Nobel Prize in Physiology or Medicine was

awarded to Robert F. Furchtgott, Louis J. Ignarro, and Ferid Murad for their discoveries of the detailed pathways by which NO acts in the cardiovascular system. It was a sensation that this simple, common air pollutant could exert important functions in mammals, including humans.

As useful as nitroglycerin is to this day in treating angina pectoris, it has a limitation in that prolonged administration results in development of tolerance, or desensitization, of the vascular muscle to further vasorelaxation by nitroglycerin. The bioactivation of nitroglycerin is the subject of active research in the hope that a means of circumventing desensitization can be found.

### Self-Assessment Exercise

- 22.26** Which of the following reactions is a disproportionation reaction?

- (a)  $2\text{NO}_2(g) + \text{H}_2\text{O}(l) \rightarrow \text{HNO}_3(aq) + \text{HNO}_2(aq)$   
 (b)  $2\text{NH}_3(aq) + \text{OCl}^-(aq) \rightarrow \text{N}_2\text{H}_4(aq) + \text{Cl}^-(aq) + \text{H}_2\text{O}(l)$   
 (c)  $2\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4(g)$

### Exercises

- 22.27** Write the chemical formula for each of the following compounds, and indicate the oxidation state of nitrogen in each: (a) dinitrogen trioxide, (b) dinitrogen pentoxide, (c) hydrogen cyanide, (d) ammonium nitrate, (e) iron(III) nitrite, (f) nitrogen trichloride.
- 22.28** Write the Lewis structure for each of the following species, describe its geometry, and indicate the oxidation state of the nitrogen: (a)  $\text{N}_2\text{O}_3$ , (b)  $\text{NOCl}$ , (c)  $\text{NO}_2\text{Cl}$ , (d)  $\text{N}_2\text{O}_4$ .
- 22.29** Write a balanced net ionic equation for each of the following reactions: (a) Dilute nitric acid reacts with zinc metal with formation of nitrous oxide. (b) Concentrated nitric

acid reacts with sulfur with formation of nitrogen dioxide. (c) Concentrated nitric acid oxidizes sulfur dioxide with formation of nitric oxide. (d) Hydrazine is burned in excess fluorine gas, forming  $\text{NF}_3$ . (e) Hydrazine reduces  $\text{CrO}_4^{2-}$  to  $\text{Cr(OH)}_4^-$  in base (hydrazine is oxidized to  $\text{N}_2$ ).

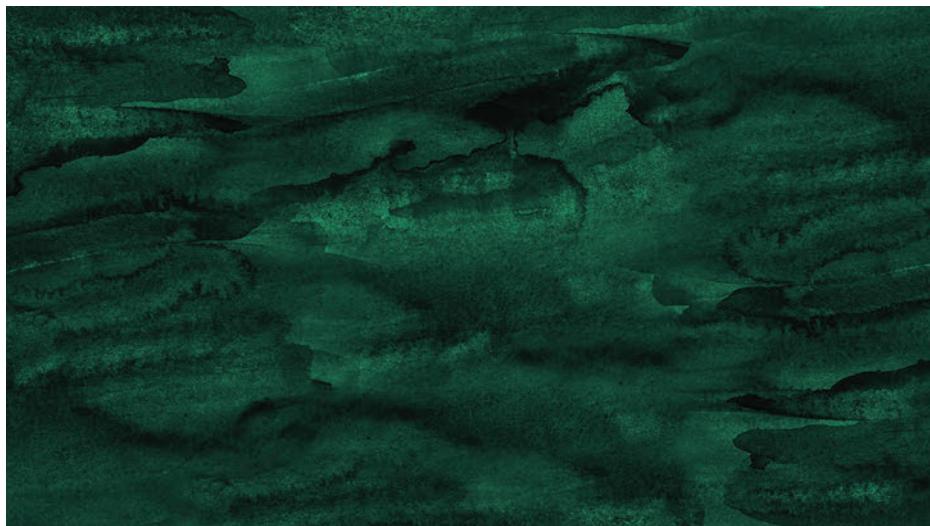
- 22.30** Write complete balanced half-reactions for (a) reduction of nitrate ion to NO in acidic solution, (b) oxidation of  $\text{HNO}_2$  to  $\text{NO}_2$  in acidic solution.

22.26 (a)

Answers to Self-Assessment Exercise



## 22.8 | The Other Group 15 Elements: P, As, Sb, and Bi



Paris green is an arsenic compound that shows a pale blue green color when finely ground and darker emerald green if the particle size is larger. While its toxicity was realized from the start, it was a popular pigment with artists such as Turner, Monet, Gauguin, and van Gogh.

In this section, we review the other Group 15 elements focusing our attention on phosphorus—one that is essential to life. By the end of this section, you should be able to

- Understand the structure and properties of phosphorus compounds

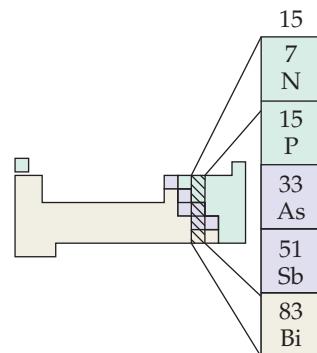
Of the other Group 15 elements—phosphorus, arsenic, antimony, and bismuth—phosphorus has a central role in several aspects of biochemistry and environmental chemistry.

The Group 15 elements have the outer-shell electron configuration  $ns^2np^3$ , with  $n$  ranging from 2 to 6. A noble-gas configuration is achieved by adding three electrons to form the  $-3$  oxidation state. Ionic compounds containing  $X^{3-}$  ions are not common, however. More commonly, the Group 15 element acquires an octet of electrons via covalent bonding and oxidation numbers ranging from  $-3$  to  $+5$ .

Because of its lower electronegativity, phosphorus is found more frequently in positive oxidation states than is nitrogen. Furthermore, compounds in which phosphorus has the  $+5$  oxidation state are not as strongly oxidizing as the corresponding compounds of nitrogen. Compounds in which phosphorus has a  $-3$  oxidation state are much stronger reducing agents than are the corresponding nitrogen compounds.

Some properties of the Group 15 elements are listed in **Table 22.7**. The variation in properties among Group 15 elements is more striking than that seen in Groups 16 and 17. Nitrogen at the one extreme exists as a gaseous diatomic molecule, clearly nonmetallic. At the other extreme, bismuth is a reddish white, metallic-looking substance that has most of the characteristics of a metal.

The values listed for  $X-X$  single-bond enthalpies are not reliable because it is difficult to obtain such data from thermochemical experiments. However, there is no doubt



**TABLE 22.7 Properties of the Group 15 Elements**

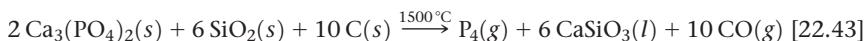
Property	N	P	As	Sb	Bi
Atomic radius (pm)	71	107	119	139	148
First ionization energy (kJ/mol)	1402	1012	947	834	703
Electron affinity (kJ/mol)	> 0	-72	-78	-103	-91
Electronegativity	3.0	2.1	2.0	1.9	1.9
X—X single-bond enthalpy (kJ/mol)*	163	200	150	120	—
X≡X triple-bond enthalpy (kJ/mol)	941	490	380	295	192

\*Approximate values only.

about the general trend: a low value for the N—N single bond, an increase at phosphorus, and then a gradual decline to arsenic and antimony. From observations of the elements in the gas phase, it is possible to estimate the X≡X triple-bond enthalpies. Here, we see a trend that is different from that for the X—X single bond. Nitrogen forms a much stronger triple bond than the other elements, and there is a steady decline in the triple-bond enthalpy down through the group. These data help us to appreciate why nitrogen alone of the Group 15 elements exists as a diatomic molecule in its stable state at 25 °C. All the other elements exist in structural forms with single bonds between the atoms.

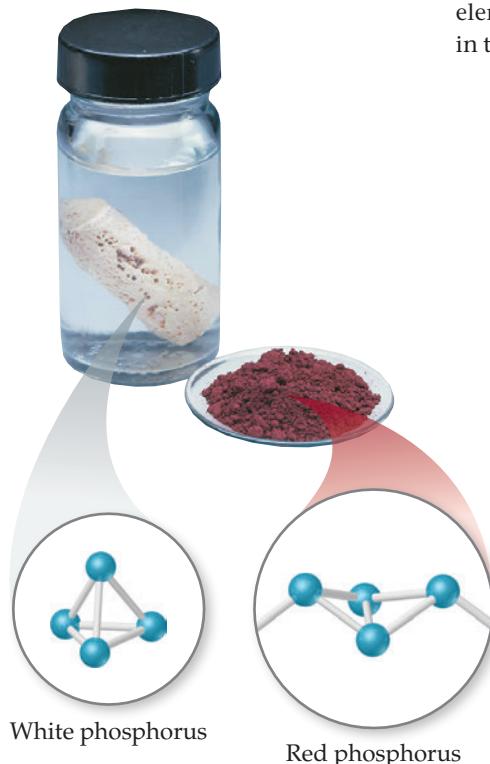
### Occurrence, Isolation, and Properties of Phosphorus

Phosphorus occurs mainly in the form of phosphate minerals. The principal source of phosphorus is phosphate rock, which contains phosphate principally as  $\text{Ca}_3(\text{PO}_4)_2$ . The element is produced commercially by the reduction of calcium phosphate with carbon in the presence of  $\text{SiO}_2$ :



The phosphorus produced in this fashion is the allotrope known as white phosphorus. This form distills from the reaction mixture as the reaction proceeds.

Phosphorus exists in several allotropic forms. White phosphorus consists of  $\text{P}_4$  tetrahedra (Figure 22.25). The bond angles in this molecule, 60°, are unusually small, so there is much strain in the bonding, which is consistent with the high reactivity of white phosphorus. This allotrope bursts spontaneously into flames if exposed to air. When heated in the absence of air to about 400 °C, white phosphorus is converted to a more stable allotrope known as red phosphorus, which does not ignite on contact with air. Red phosphorus is also considerably less poisonous than the white form. We will denote elemental phosphorus as simply  $\text{P}(s)$ .

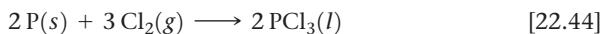


▲ **Figure 22.25 White and red phosphorus.** Despite the fact that both contain only phosphorus atoms, these two forms of phosphorus differ greatly in reactivity. The white allotrope, which reacts violently with oxygen, must be stored under water so that it is not exposed to air. The much less reactive red form does not need to be stored this way.

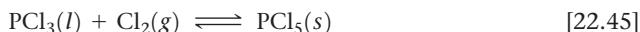
### Phosphorus Halides

Phosphorus forms a wide range of compounds with the halogens, the most important of which are the trihalides and pentahalides. Phosphorus trichloride ( $\text{PCl}_3$ ) is commercially the most significant of these compounds and is used to prepare a wide variety of products, including soaps, detergents, plastics, and insecticides.

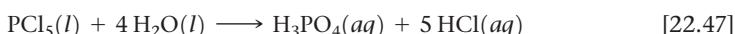
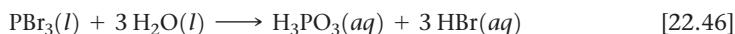
Phosphorus chlorides, bromides, and iodides can be made by direct oxidation of elemental phosphorus with the elemental halogen.  $\text{PCl}_3$ , for example, which is a liquid at room temperature, is made by passing a stream of dry chlorine gas over white or red phosphorus:



If excess chlorine gas is present, an equilibrium is established between  $\text{PCl}_3$  and  $\text{PCl}_5$ .



The phosphorus halides react readily with water, and most fume in air because of reaction with water vapor. In the presence of excess water, the products are the corresponding phosphorus oxyacid and hydrogen halide:

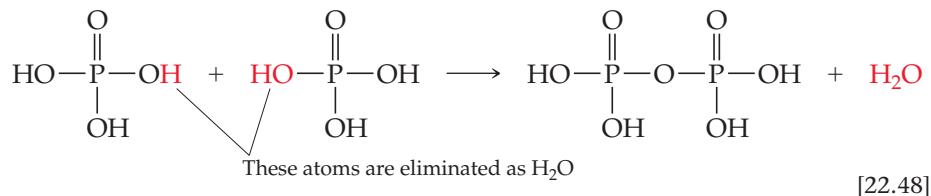


## Oxy Compounds of Phosphorus

Probably the most significant phosphorus compounds are those in which the element is combined with oxygen. Phosphorus(III) oxide ( $\text{P}_4\text{O}_6$ ) is obtained by allowing white phosphorus to oxidize in a limited supply of oxygen. When oxidation takes place in the presence of excess oxygen, phosphorus(V) oxide ( $\text{P}_4\text{O}_{10}$ ) forms. This compound is also readily formed by oxidation of  $\text{P}_4\text{O}_6$ . These two oxides represent the two most common oxidation states for phosphorus, +3 and +5. The structural relationship between  $\text{P}_4\text{O}_6$  and  $\text{P}_4\text{O}_{10}$  is shown in **Figure 22.26**. Notice the resemblance these molecules have to the  $\text{P}_4$  molecule (Figure 22.26); all three substances have a  $\text{P}_4$  core.

Phosphorus(V) oxide is the anhydride of phosphoric acid ( $\text{H}_3\text{PO}_4$ ), a weak triprotic acid. In fact,  $\text{P}_4\text{O}_{10}$  has a very high affinity for water and is consequently used as a drying agent. Phosphorus(III) oxide is the anhydride of phosphorous acid ( $\text{H}_3\text{PO}_3$ ), a weak diprotic acid (**Figure 22.27**).\*

One characteristic of phosphoric and phosphorous acids is their tendency to undergo *condensation reactions* when heated. For example, two  $\text{H}_3\text{PO}_4$  molecules are joined by the elimination of one  $\text{H}_2\text{O}$  molecule to form  $\text{H}_4\text{P}_2\text{O}_7$ :



Phosphoric acid and its salts find their most important uses in detergents and fertilizers. The phosphates in detergents are often in the form of sodium tripolyphosphate ( $\text{Na}_5\text{P}_3\text{O}_{10}$ ). The phosphate ions “soften” water by binding their oxygen groups to the metal ions that contribute to the hardness of water. This keeps the metal ions from interfering with the action of the detergent. The phosphates also keep the pH above 7 and thus prevent the detergent molecules from becoming protonated.

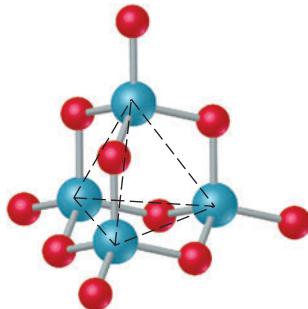
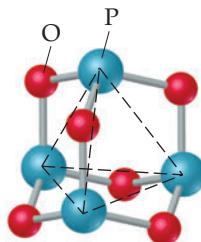
Most mined phosphate rock is converted to fertilizers. The  $\text{Ca}_3(\text{PO}_4)_2$  in phosphate rock is insoluble ( $K_{sp} = 2.0 \times 10^{-29}$ ). It is converted to a soluble form for use in fertilizers by treatment with sulfuric or phosphoric acid. The reaction with phosphoric acid yields  $\text{Ca}(\text{H}_2\text{PO}_4)_2$ :



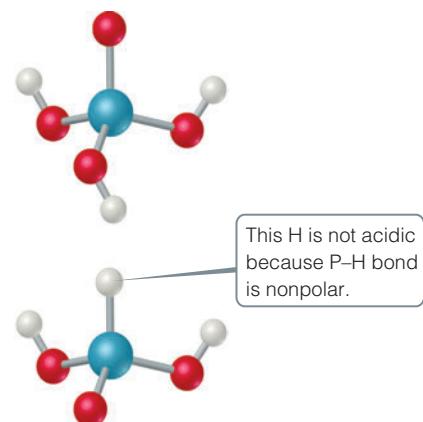
Although the solubility of  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  allows it to be assimilated by plants, it also allows it to be washed from the soil and into bodies of water, thereby contributing to water pollution.

## Go Figure

How do the electron domains about P in  $\text{P}_4\text{O}_6$  differ from those about P in  $\text{P}_4\text{O}_{10}$ ?



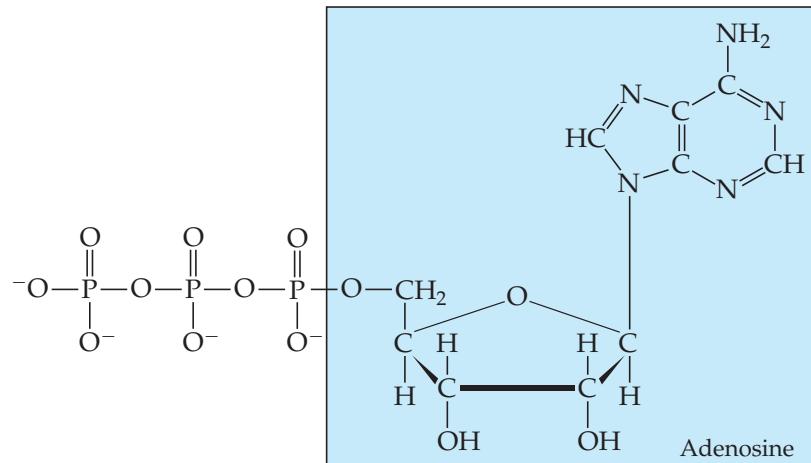
▲ **Figure 22.26** Structures of  $\text{P}_4\text{O}_6$  (top) and  $\text{P}_4\text{O}_{10}$  (bottom).



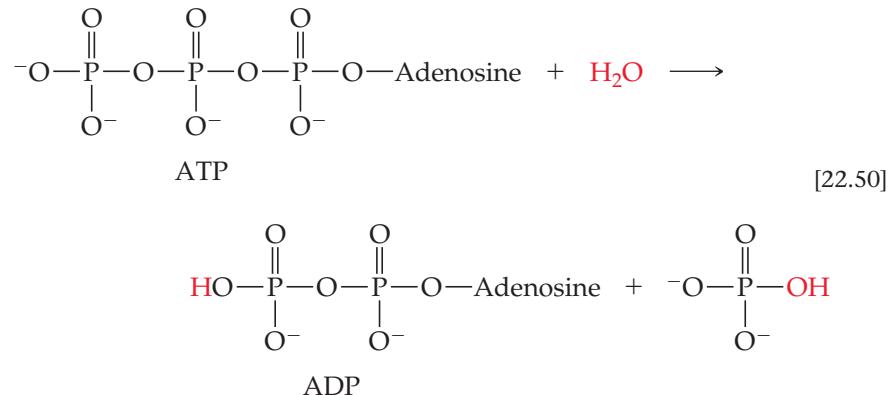
▲ **Figure 22.27** Structures of  $\text{H}_3\text{PO}_4$  (top) and  $\text{H}_3\text{PO}_3$  (bottom).

\*Note that the element phosphorus (*FOS·for·us*) has a *-us* suffix, whereas the first word in the name phosphorous (*fos·FOR·us*) acid has an *-ous* suffix.

Phosphorus compounds are important in biological systems. The element occurs in phosphate groups in RNA and DNA, the molecules responsible for the control of protein biosynthesis and transmission of genetic information. It also occurs in adenosine triphosphate (ATP), which stores energy in biological cells and has the following structure:



The  $\text{P}-\text{O}-\text{P}$  bond of the end phosphate group is broken by hydrolysis with water, forming adenosine diphosphate (ADP):



This reaction releases 33 kJ of energy under standard conditions, but in the living cell, the Gibbs free energy change for the reaction is closer to  $-57 \text{ kJ/mol}$ . The concentration of ATP inside a living cell is in the range of 1–10 mM, and a typical human metabolizes her or his body mass of ATP in one day! ATP is continually made from ADP and continually converted back to ADP, releasing energy that can be harnessed by other cellular reactions.

## CHEMISTRY AND LIFE Arsenic in Drinking Water

Arsenic, in the form of its oxides, has been known as a poison for centuries.

When it contaminates drinking water, this can cause widespread poisoning, as has occurred in Bangladesh. Historically, surface water sources in that country have been contaminated with microorganisms, causing significant health problems. During the 1970s, international agencies, headed by the United Nations Children's Fund (UNICEF), began investing millions of dollars of aid money in Bangladesh for wells to provide "clean" drinking water. Unfortunately, no one tested the well water for the presence of arsenic; the problem was not discovered until the 1980s. The result has

been the biggest outbreak of mass poisoning in history. Up to half of the country's estimated 10 million wells have arsenic concentrations above 50 ppb.

In water, the most common forms of arsenic are the arsenate ion and its protonated hydrogen anions ( $\text{AsO}_4^{3-}$ ,  $\text{HAsO}_4^{2-}$ , and  $\text{H}_2\text{AsO}_4^-$ ) and the arsenite ion and its protonated forms ( $\text{AsO}_3^{3-}$ ,  $\text{HAsO}_3^{2-}$ ,  $\text{H}_2\text{AsO}_3^-$ , and  $\text{H}_3\text{AsO}_3$ ). These species are collectively referred to by the oxidation number of the arsenic as arsenic(V) and arsenic(III), respectively. Arsenic(V) is more prevalent in oxygen-rich (aerobic) surface waters, whereas arsenic(III) is more likely to occur in oxygen-poor (anaerobic) groundwaters.

One of the challenges in determining the health effects of arsenic in drinking waters is the different chemistry of arsenic(V) and arsenic(III), as well as the different concentrations required for physiological responses in different individuals. In Bangladesh, skin lesions were the first sign of the arsenic problem. Statistical studies correlating arsenic levels with the occurrence of disease indicate a lung and bladder cancer risk arising from even low levels of arsenic.

The current technologies for removing arsenic perform most effectively when treating arsenic in the form of arsenic(V), so water treatment strategies require preoxidation of the drinking water. Once in the form of arsenic(V), there are a number of possible removal strategies. For example,  $\text{Fe}^{3+}$  can be added to precipitate  $\text{FeAsO}_4$ , which is then removed by filtration.

## Self-Assessment Exercise

**22.31** Which oxyacid is produced when  $\text{PF}_3$  reacts with water?

- (a)  $\text{H}_3\text{PO}_3$
- (b)  $\text{H}_3\text{PO}_4$
- (c)  $\text{H}_4\text{P}_2\text{O}_7$

## Exercises

- 22.32** Write a chemical formula for each compound or ion, and indicate the oxidation state of the Group 15 element in each formula: (a) diarsenic trisulfide, (b) arsenic pentoxide, (c) phosphorus trichloride, (d) phosphonium ion, (e) indium antimonide, (f) sodium arsenite.
- 22.33** Account for the following observations: (a)  $\text{H}_3\text{PO}_3$  is a diprotic acid. (b) Nitric acid is a strong acid, whereas phosphoric acid is weak. (c) Phosphate rock is ineffective as a

phosphate fertilizer. (d) Phosphorus does not exist at room temperature as diatomic molecules, but nitrogen does. (e) Solutions of  $\text{Na}_3\text{PO}_4$  are quite basic.

- 22.34** Write a balanced equation for each of the following reactions: (a) hydrolysis of  $\text{PCl}_5$ , (b) dehydration of phosphoric acid (also called orthophosphoric acid) to form pyrophosphoric acid, (c) reaction of  $\text{P}_4\text{O}_{10}$  with water.

22.32 (a)

Answers to Self-Assessment Exercise

## 22.9 | Carbon



Carbon constitutes only 0.027% of Earth's crust. Although some carbon occurs in elemental form as graphite and diamond, most is found in combined form. Over half occurs in carbonate compounds. Carbon is also found in coal, petroleum, and natural gas. The importance of the element stems in large part from its occurrence in all living organisms: Life as we know it is based on carbon compounds. In this section, we focus on inorganic carbon, and by the end, you should be able to

- Recognize the main reactions involving oxides of carbon, carbonates, and carbides

### Elemental Forms of Carbon

We have seen that carbon exists in several allotropic crystalline forms: graphite, diamond, fullerenes, carbon nanotubes, and graphene. Fullerenes, nanotubes, and graphene are discussed in Chapter 12; here we focus on graphite and diamond.

*Graphite* is a soft, black, slippery solid that has a metallic luster and conducts electricity. It consists of parallel sheets of  $sp^2$  hybridized carbon atoms held together by dispersion forces. *Diamond* is a clear, hard solid in which the carbon atoms form an  $sp^3$  hybridized covalent network. Diamond is denser than graphite ( $d = 2.25 \text{ g/cm}^3$  for graphite;  $d = 3.51 \text{ g/cm}^3$  for diamond). At approximately 10 GPa at 3000 °C, graphite converts to diamond. In fact, almost any carbon-containing substance, if put under sufficiently high pressure, forms diamonds; scientists at General Electric in the 1950s used peanut butter to make diamonds. About  $3 \times 10^4 \text{ kg}$  of industrial grade diamonds are synthesized each year, mainly for use in cutting, grinding, and polishing tools.

Graphite has a well-defined crystalline structure, but it also exists in two common amorphous forms: **carbon black** and **charcoal**. Carbon black is formed when hydrocarbons are heated in a very limited supply of oxygen, such as in this methane reaction:

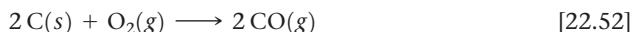


Carbon black is used as a pigment in black inks; large amounts are also used in making vehicle tires.

Charcoal is formed when wood is heated strongly in the absence of air. Charcoal has an open structure, giving it an enormous surface area per unit mass. "Activated charcoal," a pulverized form of charcoal whose surface is cleaned by heating with steam, is widely used to adsorb molecules. It is used in filters to remove offensive odors from air and colored or bad-tasting impurities from water.

### Oxides of Carbon

Carbon forms two principal oxides: carbon monoxide (CO) and carbon dioxide (CO<sub>2</sub>). *Carbon monoxide* is formed when carbon or hydrocarbons are burned in a limited supply of oxygen:



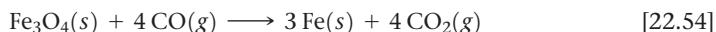
CO is a colorless, odorless, tasteless gas that is toxic because it binds to hemoglobin in the blood and thus interferes with oxygen transport. Low-level poisoning results in headaches and drowsiness; high-level poisoning can cause death.

Carbon monoxide is unusual in that it has a nonbonding pair of electrons on carbon: :C≡O:. It is isoelectronic with N<sub>2</sub>, so you might expect CO to be equally unreactive. Moreover, both substances have high bond energies (1072 kJ/mol for C≡O and 941 kJ/mol for N≡N). Because of the lower nuclear charge on carbon (compared with either N or O), however, the carbon nonbonding pair is not held as strongly as that on N or O. Consequently, CO is better able to function as a Lewis base than is N<sub>2</sub>; for example, CO can coordinate its nonbonding pair to the iron of hemoglobin, displacing O<sub>2</sub>, but N<sub>2</sub> cannot.

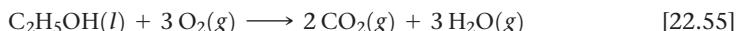
Carbon monoxide has several commercial uses. Because it burns readily, forming CO<sub>2</sub>, it is employed as a fuel:



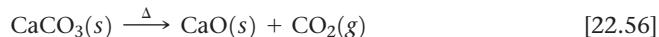
Carbon monoxide is an important reducing agent, widely used in metallurgical operations to reduce metal oxides, such as the iron oxides:



*Carbon dioxide* is produced when carbon-containing substances are burned in excess oxygen, such as in this reaction involving ethanol:



It is also produced when many carbonates are heated:



## CHEMISTRY PUT TO WORK | Carbon Fibers and Composites

The properties of graphite are anisotropic; that is, they differ in different directions through the solid. Along the carbon planes, graphite possesses great strength because of the number and strength of the carbon–carbon bonds in this direction. The bonds between planes are relatively weak, however, making graphite weak in that direction.

Fibers of graphite can be prepared in which the carbon planes are aligned to varying extents parallel to the fiber axis. These fibers are lightweight (density of about  $2 \text{ g/cm}^3$ ) and chemically quite unreactive. The oriented fibers are made by first slowly pyrolyzing (decomposing by action of heat) organic fibers at about  $150$  to  $300^\circ\text{C}$ . These fibers are then heated to about  $2500^\circ\text{C}$  to graphitize them (convert amorphous carbon to graphite). Stretching the fiber during pyrolysis helps orient the graphite planes parallel to the fiber axis. More amorphous carbon fibers are formed by pyrolysis of organic fibers at lower temperatures ( $1200$  to  $400^\circ\text{C}$ ). These amorphous materials, commonly called *carbon fibers*, are the type most often used in commercial materials.

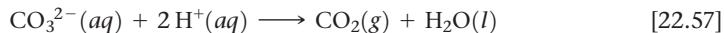
Composite materials that take advantage of the strength, stability, and low density of carbon fibers are widely used. Composites are combinations of two or more materials. These materials are present as separate phases and are combined to form structures that take advantage of certain desirable properties of each component. In carbon composites, the graphite fibers are often woven into a fabric that is embedded in a matrix that binds them into a solid structure. The fibers transmit loads evenly throughout the matrix. The finished composite is thus stronger than any one of its components.

Carbon composite materials are used widely in a number of applications, including high-performance graphite sports equipment such as tennis racquets, golf clubs, and bicycle wheels (Figure 22.28). Heat-resistant composites are required for many aerospace applications, where carbon composites now find wide use.

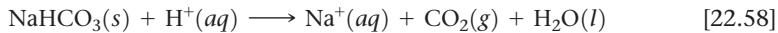


▲ Figure 22.28 Carbon composites in commercial products.

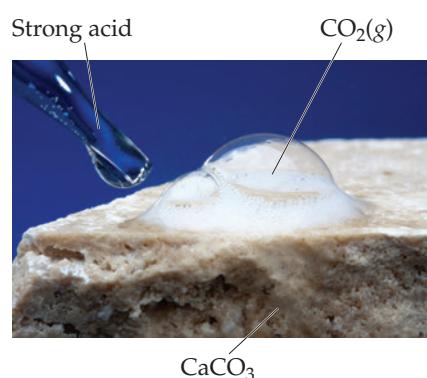
In the laboratory,  $\text{CO}_2$  can be produced by the action of acids on carbonates (Figure 22.29):



Carbon dioxide is a colorless, odorless gas. It is a minor component of Earth's atmosphere but a major contributor to the greenhouse effect. Although it is not toxic, high concentrations of  $\text{CO}_2$  increase respiration rate and can cause suffocation. It is readily liquefied by compression. When cooled at atmospheric pressure, however,  $\text{CO}_2$  forms a solid rather than liquefying. The solid sublimes at atmospheric pressure at  $-78^\circ\text{C}$ . This property makes solid  $\text{CO}_2$ , known as *dry ice*, valuable as a refrigerant. About half of the  $\text{CO}_2$  consumed annually is used for refrigeration. The other major use of  $\text{CO}_2$  is in the production of carbonated beverages. Large quantities are also used to manufacture *washing soda* ( $\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$ ), used to precipitate metal ions that interfere with the cleansing action of soap, and *baking soda* ( $\text{NaHCO}_3$ ). Baking soda is so named because this reaction occurs during baking:



The  $\text{H}^+(aq)$  is provided by vinegar, sour milk, or the hydrolysis of certain salts. The bubbles of  $\text{CO}_2$  that form are trapped in the baking dough, causing it to rise.



▲ Figure 22.29  $\text{CO}_2$  formation from the reaction between an acid and calcium carbonate in rock.

## Carbonic Acid and Carbonates

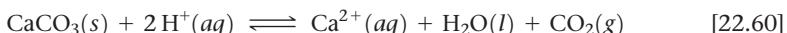
Carbon dioxide is moderately soluble in H<sub>2</sub>O at atmospheric pressure. The resulting solution is moderately acidic because of the formation of carbonic acid (H<sub>2</sub>CO<sub>3</sub>):



Carbonic acid is a weak diprotic acid. Its acidic character causes carbonated beverages to have a sharp, slightly acidic taste.

Although carbonic acid cannot be isolated, hydrogen carbonates (bicarbonates) and carbonates can be obtained by neutralizing carbonic acid solutions. Partial neutralization produces HCO<sub>3</sub><sup>-</sup>, and complete neutralization gives CO<sub>3</sub><sup>2-</sup>. The HCO<sub>3</sub><sup>-</sup> ion is a stronger base than acid ( $K_b = 2.3 \times 10^{-8}$ ;  $K_a = 5.6 \times 10^{-11}$ ). The carbonate ion is much more strongly basic ( $K_b = 1.8 \times 10^{-4}$ ).

The principal carbonate minerals are calcite (CaCO<sub>3</sub>), magnesite (MgCO<sub>3</sub>), dolomite [MgCa(CO<sub>3</sub>)<sub>2</sub>], and siderite (FeCO<sub>3</sub>). Calcite is the principal mineral in limestone and the main constituent of marble, chalk, pearls, coral reefs, and the shells of marine animals such as clams and oysters. Although CaCO<sub>3</sub> has low solubility in pure water, it dissolves readily in acidic solutions with evolution of CO<sub>2</sub>:

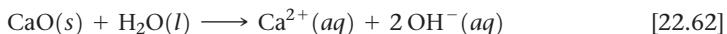


Because water containing CO<sub>2</sub> is slightly acidic (Equation 22.59), CaCO<sub>3</sub> dissolves slowly in this medium:



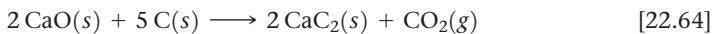
This reaction occurs when surface waters move underground through limestone deposits. It is the principal way Ca<sup>2+</sup> enters groundwater, producing *hard water*, (water with a high mineral content, containing especially Ca<sup>2+</sup> and Mg<sup>2+</sup> ions). If the limestone deposit is deep enough underground, dissolution of the limestone produces a cave.

One of the most important reactions of CaCO<sub>3</sub> is its decomposition into CaO and CO<sub>2</sub> at elevated temperatures (Equation 22.56). Because calcium oxide, known as lime or quicklime, reacts with water to form Ca(OH)<sub>2</sub>, it is an important commercial base. It is also important in making mortar, the mixture of sand, water, and CaO used to bind bricks, blocks, or rocks together. Calcium oxide reacts with water and CO<sub>2</sub> to form CaCO<sub>3</sub>, which binds the sand in the mortar:

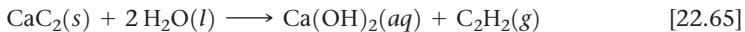


## Carbides

The binary compounds of carbon with metals, metalloids, and certain nonmetals are called **carbides**. The more active metals form *ionic carbides*, and the most common of these contain the *acetylide* ion (C<sub>2</sub><sup>2-</sup>). This ion is isoelectronic with N<sub>2</sub>, and its Lewis structure, [:C≡C:]<sup>2-</sup>, has a carbon–carbon triple bond. The most important ionic carbide is calcium carbide (CaC<sub>2</sub>), produced by the reduction of CaO with carbon at high temperature:



The carbide ion is a very strong base that reacts with water to form acetylene (H—C≡C—H):



Calcium carbide is therefore a convenient solid source of acetylene, which is used in welding (Figure 22.11).

*Interstitial carbides* are formed by many transition metals. The carbon atoms occupy open spaces (interstices) between the metal atoms in a manner analogous to the interstitial hydrides. This process generally makes the metal harder. Tungsten carbide (WC), for example, is very hard and very heat-resistant and, thus, used to make cutting tools.

*Covalent carbides* are formed by boron and silicon. Silicon carbide (SiC), known as Carborundum®, is used as an abrasive and in cutting tools. Almost as hard as diamond, SiC has a diamond-like structure with alternating Si and C atoms.

## Self-Assessment Exercise

**22.35** The hydrogen carbonate ion is amphiprotic. Will the pH of a solution of  $\text{NaHCO}_3$  be acidic, neutral, or basic?

- (a) Acidic
- (b) Neutral
- (c) Basic

## Exercises

**22.36** Give the chemical formula for (a) fullerene, (b) potassium cyanide, (c) zinc carbide, (d) zinc acetylide, (e) carbon disulfide.

**22.37** Complete and balance the following equations:

- (a)  $\text{CO}_2(g) + \text{OH}^-(aq) \longrightarrow$
- (b)  $\text{NaHCO}_3(s) + \text{H}^+(aq) \longrightarrow$
- (c)  $\text{CaO}(s) + \text{C}(s) \xrightarrow{\Delta} \text{CaC}(s)$
- (d)  $\text{C}(s) + \text{H}_2\text{O}(g) \xrightarrow{\Delta} \text{CO}(g) + \text{H}_2(g)$
- (e)  $\text{CuO}(s) + \text{CO}(g) \longrightarrow$

**22.38** Write a balanced equation for each of the following reactions: (a) Burning magnesium metal in a carbon dioxide atmosphere reduces the  $\text{CO}_2$  to carbon. (b) In photosynthesis, solar energy is used to produce glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) and  $\text{O}_2$  from carbon dioxide and water. (c) When carbonate salts dissolve in water, they produce basic solutions.

22.35 (c)

Answers to Self-Assessment Exercise



## 22.10 | The Other Group 14 Elements: Si, Ge, Sn, and Pb

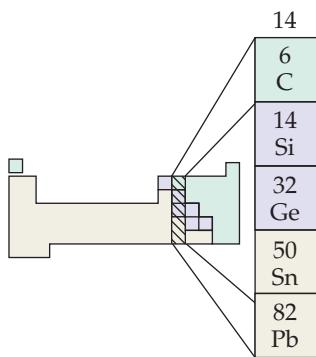


*Asbestos* is a general term applied to a group of fibrous silicate minerals. The structure of these minerals is either chains of silicate tetrahedra or sheets formed into rolls. The result is that the minerals have a fibrous character. Asbestos minerals were once widely used as thermal insulation, especially in high-temperature applications, because of the great chemical stability of the silicate structure. In addition, the fibers can be woven into asbestos cloth, which was once used for fireproof curtains and other applications.

However, the fibrous structure of asbestos minerals poses a health risk, because the fibers readily penetrate soft tissues, such as the lungs, where they can cause diseases, including cancer. The use of asbestos as a common building material has, therefore, been discontinued.

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

- Understand the occurrence of silicates and some uses of silicon



The trend from nonmetallic to metallic character as we go down a family is strikingly evident in Group 14. Carbon is a nonmetal; silicon and germanium are metalloids; tin and lead are metals. In this section, we consider a few general characteristics of Group 14 and then look more thoroughly at silicon.

### General Characteristics of the Group 14 Elements

The Group 14 elements possess the outer-shell electron configuration  $ns^2np^2$ . The electronegativities of the elements are generally low (Table 22.8); carbides that formally contain  $C^{4-}$  ions are observed only in the case of a few compounds of carbon with very active metals. Tin is unusual as it can form the  $Sn^{4+}$  ion, however the +4 oxidation state is common and is found in the vast majority of the compounds of the Group 14 elements. The +2 oxidation state is also found in the chemistry of germanium, tin, and lead and it is the principal oxidation state for lead. Carbon usually forms a maximum of four bonds. The other members of the family are able to form more than four bonds.

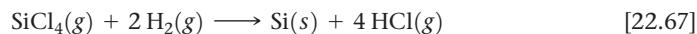
Table 22.8 shows that the strength of a bond between two atoms of a given element decreases as we go down Group 14. Carbon–carbon bonds are quite strong. Carbon, therefore, has a striking ability to form compounds in which carbon atoms are bonded to one another in extended chains and rings, which accounts for the large number of organic compounds that exist. Other elements can form chains and rings, but these bonds are far less important in the chemistries of these other elements. The Si–Si bond strength (226 kJ/mol), for example, is much lower than the Si–O bond strength (386 kJ/mol). As a result, the chemistry of silicon is dominated by the formation of Si–O bonds, and Si–Si bonds play a minor role.

### Occurrence and Preparation of Silicon

Silicon is the second most abundant element, after oxygen, in Earth's crust. It occurs in  $SiO_2$  and in an enormous variety of silicate minerals. The element is obtained by the reduction of molten silicon dioxide with carbon at high temperature:



Elemental silicon has a diamond-like structure. Crystalline silicon is a gray metallic-looking solid that melts at 1410 °C. The element is a semiconductor, as we saw in Chapters 7 and 12, and is used to make solar cells and transistors for computer chips. To be used as a semiconductor, it must be extremely pure, possessing less than  $10^{-7}\%$  (1 ppb) impurities. One method of purification is to treat the element with  $Cl_2$  to form  $SiCl_4$ , a volatile liquid that is purified by fractional distillation and then converted back to elemental silicon by reduction with  $H_2$ :



**TABLE 22.8 Some Properties of the Group 14 Elements**

Property	C	Si	Ge	Sn	Pb
Atomic radius (pm)	76	111	120	139	146
First ionization energy (kJ/mol)	1086	786	762	709	716
Electronegativity	2.5	1.8	1.8	1.8	1.9
X–X single-bond enthalpy (kJ/mol)	348	226	188	151	—

The process known as *zone refining* can further purify the element (Figure 22.30). As a heated coil is passed slowly along a silicon rod, a narrow band of the element is melted. As the molten section is swept slowly along the length of the rod, the impurities concentrate in this section, following it to the end of the rod. The purified top portion of the rod crystallizes as 99.99999999% pure silicon.

## Silicates

Silicon dioxide and other compounds that contain silicon and oxygen make up over 90% of Earth's crust. In **silicates**, a silicon atom is surrounded by four oxygens and silicon is found in its most common oxidation state, +4. The orthosilicate ion,  $\text{SiO}_4^{4-}$ , is found in very few silicate minerals, but we can view it as the “building block” for many mineral structures. As Figure 22.31 shows, adjacent tetrahedra can be linked by a common oxygen atom. Two tetrahedra joined in this way, called the *disilicate* ion, contain two Si atoms and seven O atoms. Silicon and oxygen are in the +4 and -2 oxidation states, respectively, in all silicates, so the overall charge of any silicate ion must be consistent with these oxidation states. For example, the charge on  $\text{Si}_2\text{O}_7$  is  $(2)(+4) + (7)(-2) = -6$ ; it is the  $\text{Si}_2\text{O}_7^{6-}$  ion.

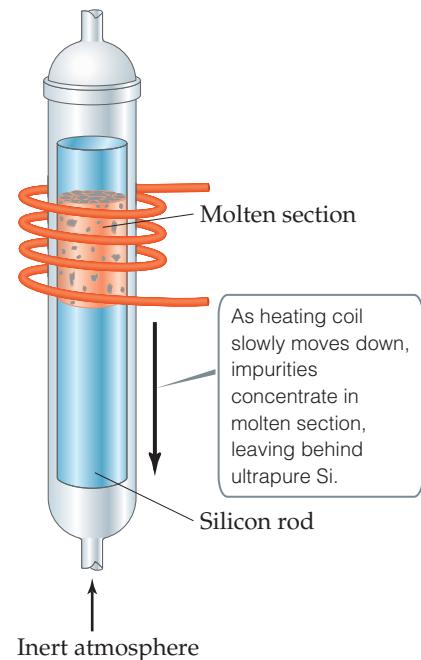
In most silicate minerals, silicate tetrahedra are linked together to form chains, sheets, or three-dimensional structures. We can connect two vertices of each tetrahedron to two other tetrahedra, for example, leading to an infinite chain with an  $\cdots \text{O}—\text{Si}—\text{O}—\text{Si} \cdots$  backbone as shown in Figure 22.31(b). Notice that each silicon in this structure has two unshared (terminal) oxygens and two shared (bridging) oxygens. The stoichiometry is then  $2(1) + 2(1/2) = 3$  oxygens per silicon. Thus, the formula unit for this chain is  $\text{SiO}_3^{2-}$ . The mineral *enstatite* ( $\text{MgSiO}_3$ ) has this kind of structure, consisting of rows of single-strand silicate chains with  $\text{Mg}^{2+}$  ions between the strands to balance charge.

In Figure 22.31(c), each silicate tetrahedron is linked to three others, forming an infinite sheet structure. Each silicon in this structure has one unshared oxygen and three shared oxygens. The stoichiometry is then  $1(1) + 3(1/2) = 2\frac{1}{2}$  oxygens per silicon. The simplest formula of this sheet is  $\text{Si}_2\text{O}_5^{2-}$ . The mineral *talc*, also known as talcum powder, has the formula  $\text{Mg}_3(\text{Si}_2\text{O}_5)_2(\text{OH})_2$  and is based on this sheet structure. The  $\text{Mg}^{2+}$  and  $\text{OH}^-$  ions lie between the silicate sheets. The slippery feel of talcum powder is due to the silicate sheets sliding relative to one another.

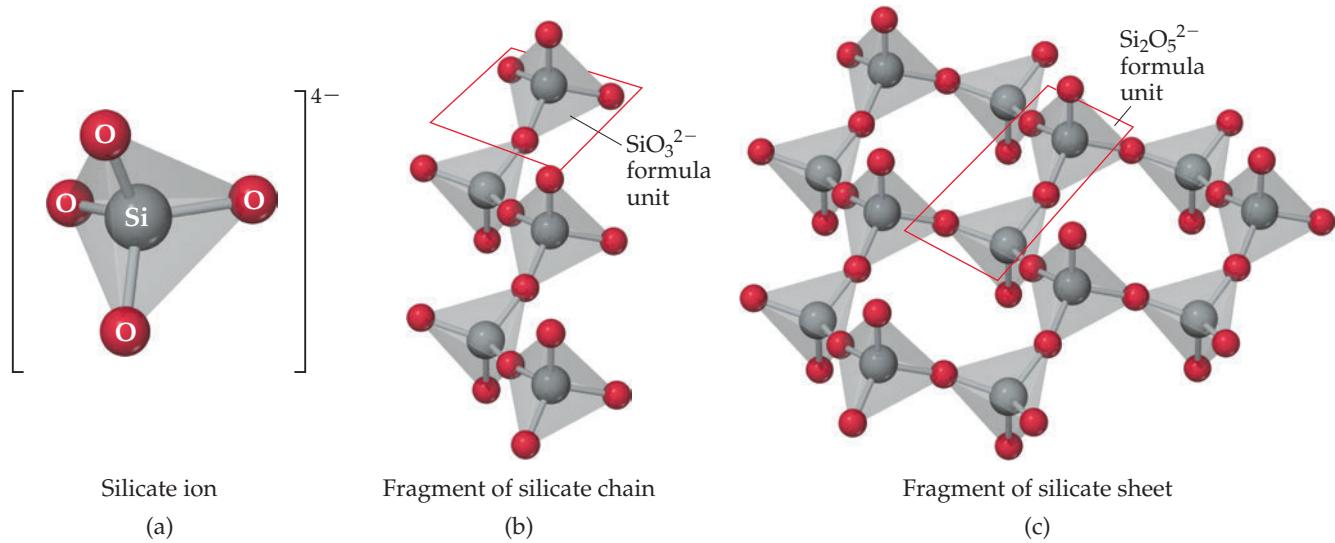
When all four vertices of each  $\text{SiO}_4$  tetrahedron are linked to other tetrahedra, the structure extends in three dimensions. This linking of the tetrahedra forms quartz ( $\text{SiO}_2$ ). Because the structure is locked together in a three-dimensional array much like diamond, quartz is harder than strand- or sheet-type silicates.

## Go Figure

What limits the range of temperatures you can use for zone refining of silicon?



▲ Figure 22.30 Zone-refining apparatus for the production of ultrapure silicon.



▲ Figure 22.31 Silicate chains and sheets.



## Sample Exercise 22.6

### Determining an Empirical Formula

The mineral *chrysotile* is a noncarcinogenic asbestos mineral that is based on the sheet structure shown in Figure 22.31(c). In addition to silicate tetrahedra, the mineral contains  $Mg^{2+}$  and  $OH^-$  ions. Analysis of the mineral shows that there are 1.5 Mg atoms per Si atom. What is the empirical formula for chrysotile?

### SOLUTION

**Analyze** A mineral is described that has a sheet silicate structure with  $Mg^{2+}$  and  $OH^-$  ions to balance charge and 1.5 Mg for each 1 Si. We are asked to write the empirical formula for the mineral.

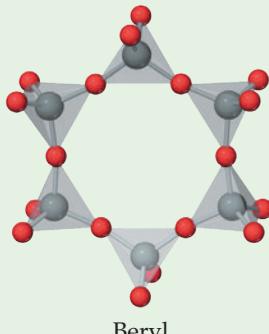
**Plan** As shown in Figure 22.31(c), the silicate sheet structure has the simplest formula  $Si_2O_5^{2-}$ . We first add  $Mg^{2+}$  to give the proper Mg:Si ratio. We then add  $OH^-$  ions to obtain a neutral compound.

### Solve

The observation that the Mg:Si ratio equals 1.5 is consistent with three  $Mg^{2+}$  ions per  $Si_2O_5^{2-}$  unit. The addition of three  $Mg^{2+}$  ions would make  $Mg_3(Si_2O_5)^{4-}$ . In order to achieve charge balance in the mineral, there must be four  $OH^-$  per  $Si_2O_5^{2-}$ . Thus, the formula of chrysotile is  $Mg_3(Si_2O_5)(OH)_4$ . Since this is not reducible to a simpler formula, this is the empirical formula.

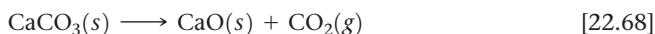
### ► Practice Exercise

In the mineral beryl, six silicate tetrahedra are connected to form a ring as shown here. The negative charge of this polyanion is balanced by  $Be^{2+}$  and  $Al^{3+}$  cations. If elemental analysis gives a Be:Si ratio of 1:2 and an Al:Si ratio of 1:3 what is the empirical formula of beryl: (a)  $Be_2Al_3Si_6O_{19}$ , (b)  $Be_3Al_2(SiO_4)_6$ , (c)  $Be_3Al_2Si_6O_{18}$ , (d)  $BeAl_2Si_6O_{15}$ ?



## Glass

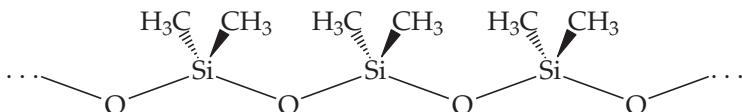
Quartz melts at approximately  $1600^\circ C$ , forming a tacky liquid. In the course of melting, many silicon–oxygen bonds are broken. When the liquid cools rapidly, silicon–oxygen bonds are re-formed before the atoms are able to arrange themselves in a regular fashion. An amorphous solid, known as quartz glass or silica glass, results. Many substances can be added to  $SiO_2$  to cause it to melt at a lower temperature. The common **glass** used in windows and bottles, known as soda-lime glass, contains  $CaO$  and  $Na_2O$  in addition to  $SiO_2$  from sand. The  $CaO$  and  $Na_2O$  are produced by heating two inexpensive chemicals, limestone ( $CaCO_3$ ) and soda ash ( $Na_2CO_3$ ), which decompose at high temperatures:



Other substances can be added to soda-lime glass to produce color or to change the properties of the glass in various ways. The addition of  $CoO$ , for example, produces the deep blue color of “cobalt glass.” Replacing  $Na_2O$  with  $K_2O$  results in a harder glass that has a higher melting point. Replacing  $CaO$  with  $PbO$  results in a denser “lead crystal” glass with a higher refractive index. Lead crystal is used for decorative glassware; the higher refractive index gives this glass a particularly sparkling appearance. Addition of non-metal oxides, such as  $B_2O_3$  and  $P_4O_{10}$ , which form network structures related to the silicates, also changes the properties of the glass. Adding  $B_2O_3$  creates a “borosilicate” glass with a higher melting point and a greater ability to withstand temperature changes. Such glasses, sold commercially under trade names such as Pyrex® and Kimax®, are used where resistance to thermal shock is important, such as in laboratory glassware or coffeemakers.

## Silicones

Silicones consist of O—Si—O chains in which the two remaining bonding positions on each silicon are occupied by organic groups such as  $CH_3$ :



Depending on chain length and degree of cross-linking, silicones can be either oils or rubber-like materials. Silicones are nontoxic and have good stability toward heat, light, oxygen, and water. They are used commercially in a wide variety of products, including lubricants, car polishes, sealants, and gaskets. They are also used for waterproofing fabrics. When applied to a fabric, the oxygen atoms form hydrogen bonds with the molecules on the surface of the fabric. The hydrophobic (water-repelling) organic groups of the silicone are then left pointing away from the surface as a barrier.

## Self-Assessment Exercise

- 22.39** Sodium metasilicate has the formula Na<sub>2</sub>SiO<sub>3</sub>. What structure do you expect for the silicate ions?  
**(a)** Individual units  
**(b)** Chains      **(c)** Sheets  
**(d)** 3-D network

## Exercises

- 22.40** Select the member of Group 14 that best fits each description: **(a)** has the greatest tendency to form multiple bonds with itself, **(b)** forms polymeric structures with oxygen, **(c)** is a metal with +2 and +4 oxidation states.  
**22.41** Speculate as to why carbon forms carbonate rather than silicate analogs.

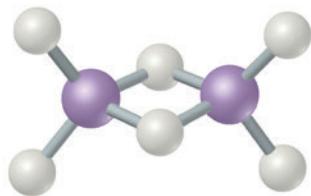
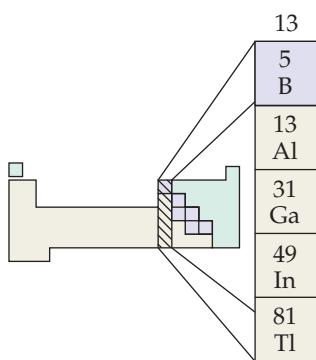
- 22.42** **(a)** Determine the number of sodium ions in the chemical formula of albite, Na<sub>x</sub>AlSi<sub>3</sub>O<sub>8</sub>. **(b)** Determine the number of hydroxide ions in the chemical formula of tremolite, Ca<sub>2</sub>Mg<sub>5</sub>(Si<sub>4</sub>O<sub>11</sub>)<sub>2</sub>(OH)<sub>x</sub>.

22.39 (b)

Answers to Self-Assessment Exercise

## 22.11 | Boron



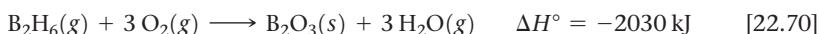


▲ Figure 22.32 The structure of diborane ( $\text{B}_2\text{H}_6$ ).

Boron is the only Group 13 element that can be considered nonmetallic and thus is our final element in this chapter. The element has an extended network structure with a melting point ( $2300^\circ\text{C}$ ) that is intermediate between the melting points of carbon ( $3550^\circ\text{C}$ ) and silicon ( $1410^\circ\text{C}$ ). The electron configuration of boron is  $[\text{He}]2s^22p^1$ .

In the family of compounds called **boranes**, the molecules contain only boron and hydrogen. Because B is less electronegative than H, the B—H bond in these compounds is polarized, with H having the higher electron density. The simplest borane is  $\text{BH}_3$ . This molecule contains only six valence electrons and is therefore an exception to the octet rule. As a result,  $\text{BH}_3$  reacts with itself to form *diborane* ( $\text{B}_2\text{H}_6$ ). This reaction can be viewed as a Lewis acid–base reaction in which one B—H bonding pair of electrons in each  $\text{BH}_3$  molecule is donated to the other. As a result, diborane is an unusual molecule in which hydrogen atoms form a bridge between two B atoms (Figure 22.32). Such hydrogens are called *bridging hydrogens*.

Sharing hydrogen atoms between the two boron atoms compensates somewhat for the deficiency in valence electrons around each boron. Nevertheless, diborane is an extremely reactive molecule, spontaneously flammable in air in a highly exothermic reaction:



Boron and hydrogen form a series of anions called *borane anions*. Salts of the borohydride ion ( $\text{BH}_4^-$ ) are widely used as reducing agents. For example, sodium borohydride ( $\text{NaBH}_4$ ) is a commonly used reducing agent for certain organic compounds.

The only important oxide of boron is boric oxide ( $\text{B}_2\text{O}_3$ ). This substance is the anhydride of boric acid, which we may write as  $\text{H}_3\text{BO}_3$  or  $\text{B}(\text{OH})_3$ . Boric acid is so weak an acid ( $K_a = 5.8 \times 10^{-10}$ ) that solutions of  $\text{H}_3\text{BO}_3$  are used as an eyewash. Upon heating, boric acid loses water by a condensation reaction similar to that described for phosphorus in Section 22.8:

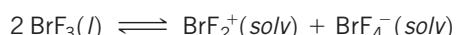


The diprotic acid  $\text{H}_2\text{B}_4\text{O}_7$  is tetraboric acid. The hydrated sodium salt  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$ , called borax, is used in various laundry and cleaning products.

## Sample Integrative Exercise

### Putting Concepts Together

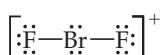
The interhalogen compound  $\text{BrF}_3$  is a volatile, straw-colored liquid. The compound exhibits appreciable electrical conductivity because of autoionization (“solv” refers to  $\text{BrF}_3$  as the solvent):



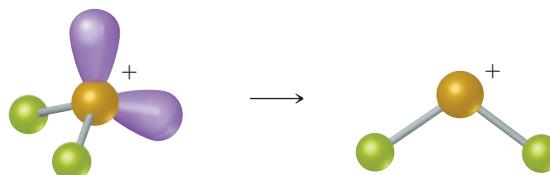
- (a) What are the molecular structures of the  $\text{BrF}_2^+$  and  $\text{BrF}_4^-$  ions?
- (b) The electrical conductivity of  $\text{BrF}_3$  decreases with increasing temperature. Is the autoionization process exothermic or endothermic?
- (c) One chemical characteristic of  $\text{BrF}_3$  is that it acts as a Lewis acid toward fluoride ions. What do we expect will happen when KF is dissolved in  $\text{BrF}_3$ ?

### SOLUTION

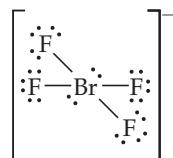
- (a) The  $\text{BrF}_2^+$  ion has  $7 + 2(7) - 1 = 20$  valence-shell electrons. The Lewis structure for the ion is



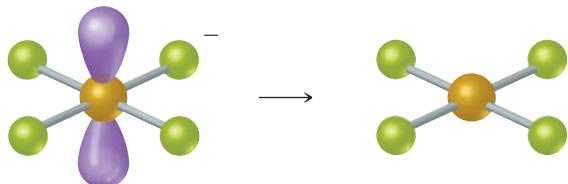
Because there are four electron domains around the central Br atom, the resulting electron domain geometry is tetrahedral. Because bonding pairs of electrons occupy two of these domains, the molecular geometry is bent:



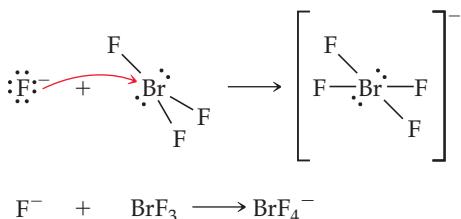
The  $\text{BrF}_4^-$  ion has  $7 + 4(7) + 1 = 36$  electrons, leading to the Lewis structure:



Because there are six electron domains around the central Br atom in this ion, the electron-domain geometry is octahedral. The two nonbonding pairs of electrons are located opposite each other on the octahedron, leading to a square-planar molecular geometry:



- (b) The observation that conductivity decreases as temperature increases indicates that there are fewer ions present in the solution at the higher temperature. Thus, increasing the temperature causes the equilibrium to shift to the left. According to Le Châtelier's principle, this shift indicates that the reaction is exothermic as it proceeds from left to right.
- (c) A Lewis acid is an electron-pair acceptor. The fluoride ion has four valence-shell electron pairs and can act as a Lewis base (an electron-pair donor). Thus, we can envision the following reaction occurring:



## Self-Assessment Exercise

- 22.43** Recall that the hydride ion is  $\text{H}^-$ . What is the oxidation state of boron in sodium borohydride?

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

## Exercises

- 22.44** Write the formulas for the following compounds, and indicate the oxidation state of the Group 14 element or of boron in each: (a) stannous fluoride, (b) germane, (c) diborane, (d) tin(II) sulfate, (e) tin selenide, (f) zinc carbonate.

- 22.45** Write a balanced equation for each of the following reactions: (a) Diborane reacts with water to form boric acid and molecular hydrogen. (b) Upon heating, boric acid undergoes a condensation reaction to form tetraboric acid. (c) Boron oxide dissolves in water to give a solution of boric acid.

22.43 (c)

Answers to Self-Assessment Exercise



## Chapter Summary and Key Terms

### THE PERIODIC TABLE AND CHEMICAL REACTIONS (SECTION 22.1)

The periodic table is useful for organizing and remembering the descriptive chemistry of the elements. Among elements of a given group, size increases with increasing atomic number, and electronegativity and ionization energy decrease. The most nonmetallic elements are found in the upper right portion of the periodic table.

Among the nonmetallic elements, the first member of each group differs dramatically from the other members; it forms a maximum of four bonds to other atoms and exhibits a much greater tendency to form  $\pi$  bonds than the heavier elements in its group.

Because  $O_2$  and  $H_2O$  are abundant in our world, we focus on two important and general reaction types as we discuss the nonmetals: oxidation by  $O_2$  and proton-transfer reactions involving  $H_2O$  or aqueous solutions.

**HYDROGEN (SECTION 22.2)** Hydrogen has three isotopes: **protium** ( $^1H$ ), **deuterium** ( $^2H$ ), and **tritium** ( $^3H$ ). Hydrogen is not a member of any particular periodic group, although it is usually placed above lithium. The hydrogen atom can either lose an electron, forming  $H^+$ , or gain one, forming  $H^-$  (the hydride ion). Because the H—H bond is relatively strong,  $H_2$  is fairly unreactive unless activated by heat or a catalyst. Hydrogen forms a very strong bond to oxygen, so the reactions of  $H_2$  with oxygen-containing compounds usually lead to the formation of  $H_2O$ . The  $H^+(aq)$  ion is able to oxidize many metals, forming  $H_2(g)$ . The electrolysis of water also forms  $H_2(g)$ .

The binary compounds of hydrogen are of three general types: **ionic hydrides** (formed by active metals), **metallic hydrides** (formed by transition metals), and **molecular hydrides** (formed by nonmetals). The ionic hydrides contain the  $H^-$  ion; because this ion is extremely basic, ionic hydrides react with  $H_2O$  to form  $H_2$  and  $OH^-$ .

**GROUP 18: THE NOBLE GASES AND GROUP 17: HALOGENS (SECTIONS 22.3 AND 22.4)** The noble gases (Group 18) exhibit a very limited chemical reactivity because of the exceptional stability of their electron configurations. The xenon fluorides and oxides and  $KrF_2$  are the best-established compounds of the noble gases.

The halogens (Group 17) occur as diatomic molecules. All except fluorine exhibit oxidation states varying from  $-1$  to  $+7$ . Fluorine is the most electronegative element, so it is restricted to the oxidation states  $0$  and  $-1$ . The oxidizing power of the element (the tendency to form the  $-1$  oxidation state) decreases as we proceed down the group.

The hydrogen halides are among the most useful compounds of these elements; these gases dissolve in water to form the hydrohalic acids, such as  $HCl(aq)$ . Hydrofluoric acid reacts with **silica**. The **interhalogens** are compounds formed between two different halogen elements. Chlorine, bromine, and iodine form a series of oxyacids, in which the halogen atom is in a positive oxidation state. These compounds and their associated oxyanions are strong oxidizing agents.

### OXYGEN AND THE OTHER GROUP 16 ELEMENTS (SECTIONS 22.5 AND 22.6)

Oxygen has two allotropes,  $O_2$  and  $O_3$  (ozone). Ozone is unstable compared to  $O_2$ , and it is a stronger oxidizing agent than  $O_2$ . Most reactions of  $O_2$  lead to oxides, compounds in which oxygen is in the  $-2$  oxidation state. The soluble oxides of nonmetals generally produce acidic aqueous solutions; they are called **acidic anhydrides** or **acidic oxides**. In contrast, soluble metal oxides produce basic solutions and are called **basic anhydrides** or **basic oxides**. Many metal oxides that are insoluble in water dissolve in acid, accompanied by the formation of  $H_2O$ .

Peroxides contain O—O bonds and oxygen in the  $-1$  oxidation state. Peroxides are unstable, decomposing to  $O_2$  and oxides. In

such reactions peroxides are simultaneously oxidized and reduced, a process called **disproportionation**. Superoxides contain the  $O_2^-$  ion in which oxygen is in the  $-\frac{1}{2}$  oxidation state.

Sulfur is the most important of the other Group 16 elements. It has several allotropic forms; the most stable one at room temperature consists of  $S_8$  rings. Sulfur forms two oxides,  $SO_2$  and  $SO_3$ , and both are important atmospheric pollutants. Sulfur trioxide is the anhydride of sulfuric acid, the most important sulfur compound and the most-produced industrial chemical. Sulfuric acid is a strong acid and a good dehydrating agent. Sulfur forms several oxyanions as well, including the  $SO_3^{2-}$  (sulfite),  $SO_4^{2-}$  (sulfate), and  $S_2O_3^{2-}$  (thiosulfate) ions. Sulfur is found combined with many metals as a sulfide, in which sulfur is in the  $-2$  oxidation state. These compounds often react with acids to form hydrogen sulfide ( $H_2S$ ), which smells like rotten eggs.

### NITROGEN AND THE OTHER GROUP 15 ELEMENTS (SECTIONS 22.7 AND 22.8)

Nitrogen is found in the atmosphere as  $N_2$  molecules. Molecular nitrogen is chemically very stable because of the strong  $N\equiv N$  bond. Molecular nitrogen can be converted into ammonia via the Haber process. Once the ammonia is made, it can be converted into a variety of different compounds that exhibit nitrogen oxidation states ranging from  $-3$  to  $+5$ . The most important industrial conversion of ammonia is the **Ostwald process**, in which ammonia is oxidized to nitric acid ( $HNO_3$ ).

Nitrogen has three important oxides: nitrous oxide ( $N_2O$ ), nitric oxide ( $NO$ ), and nitrogen dioxide ( $NO_2$ ). Nitrous acid ( $HNO_2$ ) is a weak acid; its conjugate base is the nitrite ion ( $NO_2^-$ ). Another important nitrogen compound is hydrazine ( $N_2H_4$ ).

Phosphorus is the most important of the remaining Group 15 elements. It occurs in nature as phosphate minerals. Phosphorus has several allotropes, including white phosphorus, which consists of  $P_4$  tetrahedra. In reaction with the halogens, phosphorus forms trihalides  $PX_3$  and pentahalides  $PX_5$ . These compounds undergo hydrolysis to produce an oxyacid of phosphorus and  $HX$ .

Phosphorus forms two oxides,  $P_4O_6$  and  $P_4O_{10}$ . Their corresponding acids, phosphorous acid and phosphoric acid, undergo condensation reactions when heated. Phosphorus compounds are important in biochemistry and as fertilizers.

### CARBON AND THE OTHER GROUP 14 ELEMENTS (SECTIONS 22.9 AND 22.10)

The allotropes of carbon include diamond, graphite, fullerenes, carbon nanotubes, and graphene. Amorphous forms of graphite include **charcoal** and **carbon black**. Carbon forms two common oxides,  $CO$  and  $CO_2$ . Aqueous solutions of  $CO_2$  produce the weak diprotic acid carbonic acid ( $H_2CO_3$ ), which is the parent acid of hydrogen carbonate and carbonate salts. Binary compounds of carbon are called **carbides**. Carbides may be ionic, interstitial, or covalent. Calcium carbide ( $CaC_2$ ) contains the strongly basic acetylidyne ion ( $C_2^{2-}$ ), which reacts with water to form acetylene.

The other Group 14 elements show great diversity in physical and chemical properties. Silicon, the second most abundant element, is a semiconductor. It reacts with  $Cl_2$  to form  $SiCl_4$ , a liquid at room temperature, a reaction that is used to help purify silicon from its native minerals. Silicon forms strong Si—O bonds and therefore occurs in a variety of silicate minerals. Silica is  $SiO_2$ ; **silicates** consist of  $SiO_4$  tetrahedra, linked together at their vertices to form chains, sheets, or three-dimensional structures. The most common three-dimensional silicate is quartz ( $SiO_2$ ). **Glass** is an amorphous (non-crystalline) form of  $SiO_2$ . Silicones contain O—Si—O chains with organic groups bonded to the Si atoms. Like silicon, germanium is a metalloid; tin and lead are metallic.

**BORON (SECTION 22.11)** Boron is the only Group 13 element that is a nonmetal. It forms a variety of compounds with hydrogen called boron hydrides, or **boranes**. Diborane ( $\text{B}_2\text{H}_6$ ) has an unusual structure with two hydrogen atoms that bridge between the two

boron atoms. Boranes react with oxygen to form boric oxide ( $\text{B}_2\text{O}_3$ ), in which boron is in the +3 oxidation state. Boric oxide is the anhydride of boric acid ( $\text{H}_3\text{BO}_3$ ). Boric acid readily undergoes condensation reactions.

## Learning Outcomes After studying this chapter, you should be able to:

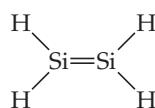
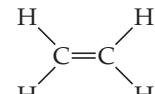
- Use periodic trends to explain the basic differences between the elements of a group or period. (Section 22.1)  
*Related Exercises: 22.57, 22.58, 22.59*
- Explain two ways in which the first element in a group differs from subsequent elements in the group. (Section 22.1)  
*Related Exercises: 22.46, 22.58*
- Be able to determine electron configurations, oxidation numbers, and molecular shapes of elements and compounds. (Sections 22.2–22.11) *Related Exercises: 22.48, 22.67, 22.77*

- Complete and balance chemical equations for common reactions of the nonmetals. (Sections 22.1–22.11)  
*Related Exercises: 22.20, 22.63, 22.84*
- Understand how phosphoric and phosphorous acids undergo condensation reactions. (Section 22.8) *Related Exercise: 22.98*
- Explain how the bonding and structures of silicates relate to their chemical formulas and properties. (Section 22.10)  
*Related Exercises: 22.87, 22.89, 22.102*

## Exercises

### Visualizing Concepts

- 22.46** Which statement identifies which of these two compounds is more stable and explains why? [Section 22.1]

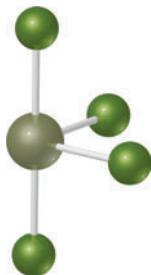


- (a) The carbon compound because C is less electronegative than Si  
 (b) The silicon compound because Si forms stronger sigma bonds than C  
 (c) The carbon compound because C forms stronger multiple bonds than Si  
 (d) The silicon compound because Si forms stronger pi bonds than C

- 22.47** (a) Identify the *type* of chemical reaction represented by the following diagram. (b) Place appropriate charges on the species on both sides of the equation. (c) Write the chemical equation for the reaction. [Section 22.1]

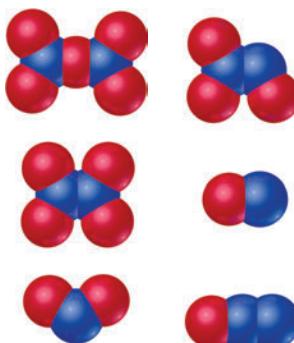


- 22.48** Which of the following species (there may be more than one) is/are likely to have the structure shown here: (a)  $\text{XeF}_4$ , (b)  $\text{BrF}_4^+$ , (c)  $\text{SiF}_4$ , (d)  $\text{TeCl}_4$ , (e)  $\text{HClO}_4$ ? (The colors do not reflect atom identities.) [Sections 22.3, 22.4, 22.6, and 22.10]

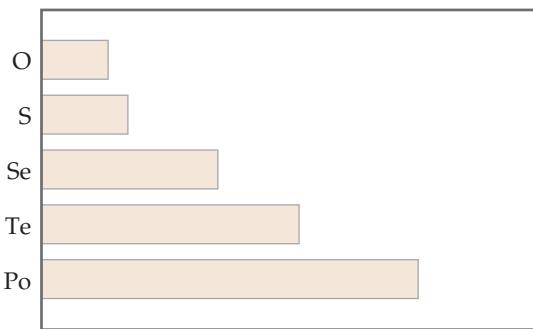


- 22.49** You have two glass bottles, one containing oxygen and one filled with nitrogen. How could you determine which one is which? [Sections 22.5 and 22.7]

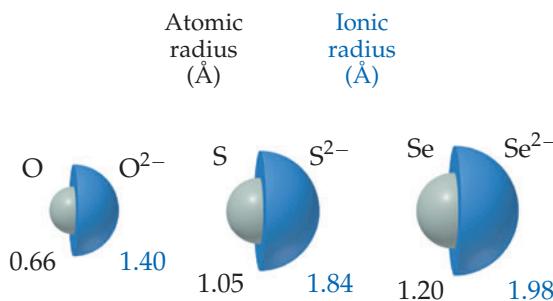
- 22.50** Write the molecular formula and Lewis structure for each of the following oxides of nitrogen: [Section 22.7]



- 22.51** Which property of the Group 16 elements might be the one depicted in the graph shown here: (a) electronegativity, (b) first ionization energy, (c) density, (d) X—X single-bond enthalpy, (e) electron affinity? [Sections 22.5 and 22.6]

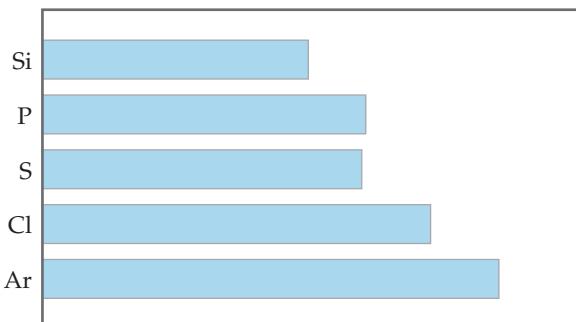


- 22.52** Identify the true statements concerning the atoms and ions of the Group 16 elements. [Sections 22.5 and 22.6]

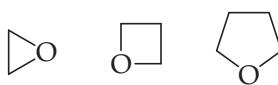


- (a) The ionic radii are larger than the atomic radii because the ions have more electrons than their corresponding atoms.
- (b) Atomic radii increase going down the group because of increasing nuclear charge.
- (c) The ionic radii increase going down the group because of the increase in the principal quantum number of outermost electrons.
- (d) Of these ions,  $\text{Se}^{2-}$  is the strongest base in water because it is largest.

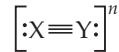
- 22.53** Which property of the third-row nonmetallic elements might be the one depicted here: (a) first ionization energy, (b) atomic radius, (c) electronegativity, (d) melting point, (e) X—X single-bond enthalpy? [Sections 22.3, 22.4, 22.6, 22.8, and 22.10]



- 22.54** Which of the following compounds would you expect to be the most generally reactive, and why? (Each corner in these structures represents a  $\text{CH}_2$  group.) [Section 22.8]



- 22.55** (a) Draw the Lewis structures for at least four species that have the general formula



where X and Y may be the same or different, and n may have a value from +1 to -2. (b) Which of the compounds is likely to be the strongest Brønsted base? Explain. [Sections 22.1, 22.7, and 22.9]

### Periodic Trends and Chemical Reactions (Section 22.1)

- 22.56** Identify each of the following elements as a metal, nonmetal, or metalloid: (a) boron, (b) barium, (c) argon, (d) caesium, (e) yttrium, (f) astatine.

- 22.57** Consider the elements N, F, Si, Rb, Te, and Ir. From this list, select the element that (a) is most electronegative, (b) exhibits a maximum oxidation state of +6, (c) loses an electron most readily, (d) forms  $\pi$  bonds most readily, (e) is a transition metal, (f) forms four covalent bonds to achieve octet.

- 22.58** Which of the following statements are true?

- (a) Both nitrogen and phosphorus can form a pentafluoride compound.
- (b) Although CO is a well-known compound, SiO does not exist under ordinary conditions.
- (c)  $\text{Cl}_2$  is easier to oxidize than  $\text{I}_2$ .
- (d) At room temperature, the stable form of oxygen is  $\text{O}_2$ , whereas that of sulfur is  $\text{S}_8$ .

- 22.59** Complete and balance the following equations:

- (a)  $\text{NaOCH}_3(s) + \text{H}_2\text{O}(l) \longrightarrow$
- (b)  $\text{CuO}(s) + \text{HNO}_3(aq) \longrightarrow$
- (c)  $\text{WO}_3(s) + \text{H}_2(g) \xrightarrow{\Delta} \longrightarrow$
- (d)  $\text{NH}_2\text{OH}(l) + \text{O}_2(g) \longrightarrow$
- (e)  $\text{Al}_4\text{C}_3(s) + \text{H}_2\text{O}(l) \longrightarrow$

### Hydrogen, the Noble Gases, and the Halogens (Sections 22.2, 22.3, and 22.4)

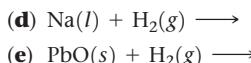
- 22.60** The physical properties of  $\text{D}_2\text{O}$  differ from those of  $\text{H}_2\text{O}$  because

- (a) D has a different electron configuration than O.
- (b) D is radioactive.
- (c) D forms stronger bonds with O than H does.
- (d) D is much more massive than H.

- 22.61** Give a reason why hydrogen might be placed along with the Group 1 elements of the periodic table.

- 22.62** Complete and balance the following equations:

- (a)  $\text{NaH}(s) + \text{H}_2\text{O}(l) \longrightarrow$
- (b)  $\text{Fe}(s) + \text{H}_2\text{SO}_4(aq) \longrightarrow$
- (c)  $\text{H}_2(g) + \text{Br}_2(g) \longrightarrow$



- 22.63** Identify the following hydrides as ionic, metallic, or molecular: (a)  $\text{H}_2\text{S}$ , (b)  $\text{LiH}$ , (c)  $\text{VH}_{0.56}$ .
- 22.64** Describe two characteristics of hydrogen that are favorable for its use as a general energy source in vehicles.
- 22.65** Why does xenon form stable compounds with fluorine, whereas argon does not?
- 22.66** Write the chemical formula for each of the following, and indicate the oxidation state of the halogen or noble-gas atom in each: (a) xenon trioxide difluoride, (b) chlorine dioxide, (c) molybdenum hexafluoride, (d) iodic acid, (e) sodium hypobromite, (f) magnesium iodite.
- 22.67** Name the following compounds and assign oxidation states to the halogens in them: (a)  $\text{Co}(\text{IO}_3)_3$ , (b)  $\text{Ca}(\text{IO}_4)_2$ , (c)  $\text{PF}_6^-$ , (d)  $\text{ICl}_4^-$ , (e)  $\text{HBrO}$ , (f)  $\text{AtH}$ .
- 22.68** Explain each of the following observations: (a) At room temperature  $\text{I}_2$  is a solid,  $\text{Br}_2$  is a liquid, and  $\text{Cl}_2$  and  $\text{F}_2$  are both gases. (b)  $\text{F}_2$  cannot be prepared by electrolytic oxidation of aqueous  $\text{F}^-$  solutions. (c) The boiling point of HF is much higher than those of the other hydrogen halides. (d) The halogens decrease in oxidizing power in the order  $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$ .

## Oxygen and the Other Group 16 Elements (Sections 22.5 and 22.6)

- 22.69** Write balanced equations for each of the following reactions. (a) When mercury(II) oxide is heated, it decomposes to form  $\text{O}_2$  and mercury metal. (b) When copper(II) nitrate is heated strongly, it decomposes to form copper(II) oxide, nitrogen dioxide, and oxygen. (c) Lead(II) sulfide,  $\text{PbS}(s)$ , reacts with ozone to form  $\text{PbSO}_4(s)$  and  $\text{O}_2(g)$ . (d) When heated in air,  $\text{ZnS}(s)$  is converted to  $\text{ZnO}$ . (e) Potassium peroxide reacts with  $\text{CO}_2(g)$  to give potassium carbonate and  $\text{O}_2$ . (f) Oxygen is converted to ozone in the upper atmosphere.
- 22.70** Predict whether each of the following oxides is acidic, basic, amphoteric, or neutral: (a)  $\text{SO}_3$ , (b)  $\text{Li}_2\text{O}$ , (c)  $\text{SnO}$ , (d)  $\text{ZnO}$ .
- 22.71** Write the chemical formula for each of the following compounds, and indicate the oxidation state of the Group 16 elements in each: (a) potassium peroxide, (b) potassium thiosulfate, (c) selenium oxychloride, (d) sodium telluride, (e) magnesium sulfite, (f) selenium hexafluoride.
- 22.72** In aqueous solution, hydrogen sulfide reduces (a)  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$ , (b)  $\text{Br}_2$  to  $\text{Br}^-$ , (c)  $\text{MnO}_4^-$  to  $\text{Mn}^{2+}$ , (d)  $\text{HNO}_3$  to  $\text{NO}_2$ . In all cases, under appropriate conditions, the product is elemental sulfur. Write a balanced net ionic equation for each reaction.
- 22.73** Write the Lewis structure for each of the following species, and indicate the structure of each: (a)  $\text{SeOCl}_2$ ; (b)  $\text{CS}_2$ ; (c) Telluric acid,  $\text{H}_2\text{TeO}_4$  (hydrogen is bonded to oxygen).
- 22.74** Write a balanced equation for each of the following reactions: (a) Sulfur dioxide reacts with water. (b) Solid zinc sulfide reacts with hydrochloric acid. (c) Elemental sulfur reacts with sulfite ion to form thiosulfate. (d) Sulfur trioxide is dissolved in sulfuric acid.

## Nitrogen and the Other Group 15 Elements (Sections 22.7 and 22.8)

- 22.75** Write the chemical formula for each of the following compounds, and indicate the oxidation state of nitrogen in each: (a) sodium azide, (b) ammonium ion, (c) nitrous

acid, (d) magnesium nitride, (e) diazene, (f) sodium nitrate, (g) nitrogen trifluoride, (h) nitric acid.

- 22.76** Write the Lewis structure for each of the following species, describe its geometry, and indicate the oxidation state of the nitrogen: (a)  $\text{HNO}_2$ , (b)  $\text{N}_3^-$ , (c)  $\text{N}_2\text{H}_5^+$ , (d)  $\text{NO}_3^-$ .
- 22.77** Complete and balance the following equations:
- (a)  $\text{Mg}_3\text{N}_2(s) + \text{H}_2\text{O}(l) \longrightarrow$   
 (b)  $\text{NO}(g) + \text{O}_2(g) \longrightarrow$   
 (c)  $\text{N}_2\text{O}_5(g) + \text{H}_2\text{O}(l) \longrightarrow$   
 (d)  $\text{NH}_3(aq) + \text{H}^+(aq) \longrightarrow$   
 (e)  $\text{N}_2\text{H}_4(l) + \text{O}_2(g) \longrightarrow$
- Which ones of these are redox reactions?
- 22.78** Write complete balanced half-reactions for (a) oxidation of nitrous acid to nitrate ion in acidic solution, (b) oxidation of  $\text{N}_2$  to  $\text{N}_2\text{O}$  in acidic solution.
- 22.79** Write a molecular formula for each compound, and indicate the oxidation state of the Group 15 element in each formula: (a) hexafluoroantimonate(V) ion, (b) calcium phosphate, (c) potassium dihydrogen phosphate, (d) arsenic trioxide, (e) tetraphosphorus hexaoxide, (f) arsenic trifluoride.
- 22.80** Account for the following observations: (a) Phosphorus forms a pentachloride, but nitrogen does not. (b)  $\text{H}_3\text{PO}_2$  is a monoprotic acid. (c) Phosphonium salts, such as  $\text{PH}_4\text{Cl}$ , can be formed under anhydrous conditions, but they cannot be made in aqueous solution. (d) White phosphorus is more reactive than red phosphorus.
- 22.81** Write a balanced equation for each of the following reactions: (a) preparation of white phosphorus from calcium phosphate, (b) hydrolysis of  $\text{PBr}_3$ , (c) reduction of  $\text{PBr}_3$  to  $\text{P}_4$  in the gas phase, using  $\text{H}_2$ .
- ## Carbon, the Other Group 14 Elements, and Boron (Sections 22.9, 22.10, and 22.11)
- 22.82** Give the chemical formula for (a) copper(II) carbonate, (b) carbon monoxide, (c) magnesium hydrogen carbonate, (d) lithium acetylide, (e) carbon tetrafluoride.

**22.83** Complete and balance the following equations:

(a)  $\text{ZnCO}_3(s) \xrightarrow{\Delta} \dots$   
 (b)  $\text{BaC}_2(s) + \text{H}_2\text{O}(l) \longrightarrow$   
 (c)  $\text{C}_2\text{H}_2(g) + \text{O}_2(g) \longrightarrow$   
 (d)  $\text{CS}_2(g) + \text{O}_2(g) \longrightarrow$   
 (e)  $\text{Ca}(\text{CN})_2(s) + \text{HBr}(aq) \longrightarrow$

**22.84** Write a balanced equation for each of the following reactions: (a) Hydrogen cyanide is formed commercially by passing a mixture of methane, ammonia, and air over a catalyst at  $800^\circ\text{C}$ . Water is a by-product of the reaction. (b) Baking soda reacts with acids to produce carbon dioxide gas. (c) When barium carbonate reacts in air with sulfur dioxide, barium sulfate and carbon dioxide form.

**22.85** Select the member of Group 14 that best fits each description: (a) has the highest electronegativity, (b) a metalloid which is commonly used in computer chips, (c) is used for shielding for radiation.

**22.86** (a) What is the characteristic geometry about silicon in all silicate minerals? (b) Metasilicic acid has the empirical formula  $\text{H}_2\text{SiO}_3$ . Which of the structures shown in Figure 22.32 would you expect metasilicic acid to have?

**22.87** (a) Determine the number of calcium ions in the chemical formula of the mineral hardystonite,  $\text{Ca}_x\text{Zn}(\text{Si}_2\text{O}_7)$ .

- (b) Determine the number of hydroxide ions in the chemical formula of the mineral pyrophyllite,  $\text{Al}_2(\text{Si}_2\text{O}_5)_2(\text{OH})_x$ .
- 22.88** Write the formulas for the following compounds, and indicate the oxidation state of the Group 14 element or of boron in each: (a) silane, (b) germanium dichloride, (c) tin(II) sulfide, (d) sodium borohydride, (e) lead(IV) nitrate, (f) tin dioxide.

## Additional Exercises

- 22.90** Indicate whether each of the following statements is true or false (a)  $\text{H}_2(g)$  and  $\text{D}_2(g)$  are allotropic forms of hydrogen. (b)  $\text{ClF}_3$  is an interhalogen compound. (c)  $\text{MgO}(s)$  is an acidic anhydride. (d)  $\text{SO}_2(g)$  is an acidic anhydride. (e)  $2\text{H}_3\text{PO}_4(l) \rightarrow \text{H}_4\text{P}_2\text{O}_7(l) + \text{H}_2\text{O}(g)$  is an example of a condensation reaction. (f) Tritium is an isotope of the element hydrogen. (g)  $2\text{SO}_2(g) + \text{O}_2(g) \rightarrow 2\text{SO}_3(g)$  is an example of a disproportionation reaction.
- 22.91** Although the  $\text{ClO}_4^-$  and  $\text{IO}_4^-$  ions have been known for a long time,  $\text{BrO}_4^-$  was not synthesized until 1965. The ion was synthesized by oxidizing the bromate ion with xenon difluoride, producing xenon, hydrofluoric acid, and the perbromate ion. (a) Write the balanced equation for this reaction. (b) What are the oxidation states of Br in the Br-containing species in this reaction?
- 22.92** Write a balanced equation for the reaction of each of the following compounds with water: (a)  $\text{PCl}_5(s)$ , (b)  $\text{CO}_2(g)$ , (c)  $\text{K}_2\text{O}_2(s)$ , (d)  $\text{Mg}_3\text{P}_2(s)$ , (e)  $\text{LiAlH}_4(s)$ , (f)  $\text{Cl}_2\text{O}(g)$ , (g)  $\text{NO}_2(g)$ .
- 22.93** What is the anhydride for each of the following acids: (a)  $\text{H}_2\text{SO}_4$ , (b)  $\text{HClO}_3$ , (c)  $\text{HNO}_2$ , (d)  $\text{H}_2\text{CO}_3$ , (e)  $\text{H}_3\text{PO}_4$ ?
- 22.94** Hydrogen peroxide is capable of oxidizing (a) hydrazine to  $\text{N}_2$  and  $\text{H}_2\text{O}$ , (b)  $\text{SO}_2$  to  $\text{SO}_4^{2-}$ , (c)  $\text{NO}_2^-$  to  $\text{NO}_3^-$ , (d)  $\text{H}_2\text{S}(g)$  to  $\text{S}(s)$ , (e)  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ . Write a balanced net ionic equation for each of these redox reactions.
- 22.95** A sulfuric acid plant produces a considerable amount of heat. This heat is used to generate electricity, which helps reduce operating costs. The synthesis of  $\text{H}_2\text{SO}_4$  consists of three main chemical processes: (a) oxidation of S to  $\text{SO}_2$ , (b) oxidation of  $\text{SO}_2$  to  $\text{SO}_3$ , (c) the dissolving of  $\text{SO}_3$  in  $\text{H}_2\text{SO}_4$  and the subsequent reaction with water to form  $\text{H}_2\text{SO}_4$ . If the third process produces 130 kJ/mol, how much heat is produced in preparing a mole of  $\text{H}_2\text{SO}_4$  from

- 22.89** (a) How does the structure of diborane ( $\text{B}_2\text{H}_6$ ) differ from that of ethane ( $\text{C}_2\text{H}_6$ )? (b) Explain why diborane adopts the geometry that it does. (c) What is the significance of the statement that the hydrogen atoms in diborane are described as “hydridic”?

## Integrative Exercises

- 22.102** (a) How many grams of  $\text{H}_2$  can be stored in 100.0 kg of the alloy  $\text{FeTi}$  if the hydride  $\text{FeTiH}_2$  is formed? (b) What volume does this quantity of  $\text{H}_2$  occupy at STP? (c) If this quantity of hydrogen was combusted in air to produce liquid water, how much energy could be produced?
- 22.103** Using the thermochemical data in Table 22.1 and Appendix C, calculate the average Xe—F bond enthalpies in  $\text{XeF}_2$ ,  $\text{XeF}_4$ , and  $\text{XeF}_6$ , respectively. What is the significance of the trend in these quantities?
- 22.104** Hydrogen gas has a higher fuel value than natural gas on a mass basis but not on a volume basis. Thus, hydrogen is not competitive with natural gas as a fuel transported long distances through pipelines. Calculate the heats of combustion of  $\text{H}_2$  and  $\text{CH}_4$  (the principal component of natural gas) (a) per mole of each, (b) per gram of each, (c) per cubic meter of each at STP. Assume  $\text{H}_2\text{O}(l)$  as a product.

- a mole of S? How much heat is produced in preparing 2000 kg of  $\text{H}_2\text{SO}_4$ ?
- 22.96** (a) What is the oxidation state of P in  $\text{PF}_6^-$  and of N in  $\text{NF}_3$ ? (b) Why doesn't N form  $\text{NF}_6^-$  ion analogous to P?
- 22.97** (a) The  $\text{P}_4$ ,  $\text{P}_4\text{O}_6$  and  $\text{P}_4\text{O}_{10}$  molecules have a common structural feature of four P atoms arranged in a tetrahedron (Figures 22.27 and 22.28). Does this mean that the bonding between the P atoms is the same in all these cases? Explain. (b) Sodium trimetaphosphate ( $\text{Na}_3\text{P}_3\text{O}_9$ ) and sodium tetrametaphosphate ( $\text{Na}_4\text{P}_4\text{O}_{12}$ ) are used as water-softening agents. They contain cyclic  $\text{P}_3\text{O}_9^{3-}$  and  $\text{P}_4\text{O}_{12}^{4-}$  ions, respectively. Propose reasonable structures for these ions.
- 22.98** Write a balanced chemical reaction for the condensation reaction between  $\text{H}_3\text{PO}_4$  molecules to form  $\text{H}_6\text{P}_4\text{O}_{13}$ .
- 22.99** Ultrapure germanium, like silicon, is used in semiconductors. Germanium of “ordinary” purity is prepared by the high-temperature reduction of  $\text{GeO}_2$  with carbon. The Ge is converted to  $\text{GeCl}_4$  by treatment with  $\text{Cl}_2$  and then purified by distillation;  $\text{GeCl}_4$  is then hydrolyzed in water to  $\text{GeO}_2$  and reduced to the elemental form with  $\text{H}_2$ . The element is then zone refined. Write a balanced chemical equation for each of the chemical transformations in the course of forming ultrapure Ge from  $\text{GeO}_2$ .
- 22.100** When aluminum replaces up to half of the silicon atoms in  $\text{SiO}_2$ , a mineral class called feldspars result. The feldspars are the most abundant rock-forming minerals, comprising about 50% of the minerals in Earth's crust. Orthoclase is a feldspar in which Al replaces one-fourth of the Si atoms of  $\text{SiO}_2$ , and charge balance is completed by  $\text{K}^+$  ions. Determine the chemical formula for orthoclase.
- 22.101** (a) Determine the charge of the silicate ion whose composition is  $\text{Si}_4\text{O}_{11}$ . (b) Using Figure 22.32, propose a reasonable description of the structure of this silicate.

- 22.105** Using  $\Delta G_f^\circ$  for NO and  $\text{NO}_2$ , from Appendix C, calculate the equilibrium constant for the oxidation of NO to  $\text{NO}_2$  at 298.0 K as described in equation 22.38.
- 22.106** The solubility of  $\text{Cl}_2$  in 100 g of water at STP is  $310 \text{ cm}^3$ . Assume that this quantity of  $\text{Cl}_2$  is dissolved and equilibrated as follows:
- $$\text{Cl}_2(aq) + \text{H}_2\text{O} \rightleftharpoons \text{Cl}^-(aq) + \text{HClO}(aq) + \text{H}^+(aq)$$
- (a) If the equilibrium constant for this reaction is  $4.7 \times 10^{-4}$ , calculate the equilibrium concentration of  $\text{HClO}$  formed. (b) What is the pH of the final solution?
- 22.107** When ammonium perchlorate decomposes thermally, the products of the reaction are  $\text{N}_2(g)$ ,  $\text{O}_2(g)$ ,  $\text{H}_2\text{O}(g)$ , and  $\text{HCl}(g)$ . (a) Write a balanced equation for the reaction. (Hint: You might find it easier to use fractional coefficients for the products.) (b) Calculate the enthalpy change in the reac-

- tion per mole of  $\text{NH}_4\text{ClO}_4$ . The standard enthalpy of formation of  $\text{NH}_4\text{ClO}_4(s)$  is  $-295.8 \text{ kJ}$ . (c) When  $\text{NH}_4\text{ClO}_4(s)$  is employed in solid-fuel booster rockets, it is packed with powdered aluminum. Given the high temperature needed for  $\text{NH}_4\text{ClO}_4(s)$  decomposition and what the products of the reaction are, what role does the aluminum play? (d) Calculate the volume of all the gases that would be produced at STP, assuming complete reaction of one pound of ammonium perchlorate.
- 22.108** The dissolved oxygen present in any highly pressurized, high-temperature steam boiler can be extremely corrosive to its metal parts. Hydrazine, which is completely miscible with water, can be added to remove oxygen by reacting with it to form nitrogen and water. (a) Write the balanced equation for the reaction between gaseous hydrazine and oxygen. (b) Calculate the enthalpy change accompanying this reaction. (c) Oxygen in air dissolves in water to the extent of 9.1 ppm at  $20^\circ\text{C}$  at sea level. How many grams of hydrazine are required to react with all the oxygen in  $3.0 \times 10^4 \text{ L}$  (the volume of a small swimming pool) under these conditions?
- 22.109** One method proposed for removing  $\text{SO}_2$  from the flue gases of power plants involves scrubbing with an alkali solid such as calcium carbonate to form calcium sulfite and carbon dioxide gas. (a) Write a balanced chemical equation for the reaction. (b) What mass of  $\text{CaCO}_3$  would be required to remove the  $\text{SO}_2$  formed by burning 1000 kg of coal containing 8.0% S by mass? (c) What volume of  $\text{CO}_2$  is formed under standard temperature and pressure? Assume that all reactions are 100% efficient.
- 22.110** The maximum allowable concentration of  $\text{H}_2\text{S}(g)$  in air is 20 mg per kilogram of air (20 ppm by mass). How many grams of  $\text{FeS}$  would be required to react with hydrochloric acid to produce this concentration at 101.3 kPa and  $25^\circ\text{C}$  in an average room measuring  $3.5 \text{ m} \times 6.0 \text{ m} \times 2.5 \text{ m}$ ? (Under these conditions, the average molar mass of air is  $29.0 \text{ g/mol}$ .)
- 22.111** The standard heats of formation of  $\text{H}_2\text{O}(g)$ ,  $\text{H}_2\text{S}(g)$ ,  $\text{H}_2\text{Se}(g)$ , and  $\text{H}_2\text{Te}(g)$  are  $-241.8$ ,  $-20.17$ ,  $+29.7$ , and  $+99.6 \text{ kJ/mol}$ , respectively. The enthalpies necessary to convert the elements in their standard states to one mole of gaseous atoms are 248, 277, 227, and 197 kJ/mol of atoms for O, S, Se, and Te, respectively. The enthalpy for dissociation of  $\text{H}_2$  is 436 kJ/mol. Calculate the average H—O, H—S, H—Se, and H—Te bond enthalpies, and comment on their trend.
- 22.112** Manganese silicide has the empirical formula  $\text{MnSi}$  and melts at  $1280^\circ\text{C}$ . It is insoluble in water but does dissolve in aqueous HF. (a) What type of compound do you expect  $\text{MnSi}$  to be: metallic, molecular, covalent-network, or ionic? (b) Write a likely balanced chemical equation for the reaction of  $\text{MnSi}$  with concentrated aqueous HF.
- 22.113** Nitric acid is a powerful oxidizing agent. Using standard reduction potentials, predict whether the following metals can be oxidized to  $+2$  ions by nitric acid: (a) iron, (b) copper, (c) rhodium, (d) zinc, (e) lead, (f) tin.
- 22.114** Both dimethylhydrazine,  $(\text{CH}_3)_2\text{NNH}_2$ , and methylhydrazine,  $\text{CH}_3\text{NHNH}_2$ , have been used as rocket fuels. When dinitrogen tetroxide ( $\text{N}_2\text{O}_4$ ) is used as the oxidizer, the products are  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ , and  $\text{N}_2$ . If the thrust of the rocket depends on the volume of the products produced, which of the substituted hydrazines produces a greater thrust per gram total mass of oxidizer plus fuel? (Assume that both fuels generate the same temperature and that  $\text{H}_2\text{O}(g)$  is formed.)
- 22.115** Borazine,  $(\text{BH})_3(\text{NH})_3$ , is an analog of  $\text{C}_6\text{H}_6$ , benzene. It can be prepared from the reaction of diborane with ammonia, with hydrogen as another product; or from lithium borohydride and ammonium chloride, with lithium chloride and hydrogen as the other products. (a) Write balanced chemical equations for the production of borazine using both synthetic methods. (b) Draw the Lewis dot structure of borazine. (c) How many grams of borazine can be prepared from 2.00 L of ammonia at STP, assuming diborane is in excess?

## Designing an Experiment

You are given samples of five substances. At room temperature, three are colorless gases, one is a colorless liquid, and one is a white solid. You are told that the substances are  $\text{NF}_3$ ,  $\text{PF}_3$ ,  $\text{PCl}_3$ ,  $\text{PF}_5$ , and  $\text{PCl}_5$ . Let's design experiments to determine which substance is which, using concepts from this and earlier chapters.

(a) Assuming that you don't have access to either the Internet or to a handbook of chemistry (as is the case during your exams!), design

experiments that would allow you to identify the substances. (b) How might you proceed differently if you had access to data from the Internet? (c) Which of the substances could undergo reaction to add more atoms around the central atom? What types of reactions might you choose to test this hypothesis? (d) Based on what you know about intermolecular forces, which of the substances is likely the solid?