21 Chemistry of the Nonmetals

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The electrical charge that creates this bolt of lightning also changes some of the oxygen in the air to ozone.

For what can so fire us,
Enrapture, inspire us,
As Oxygen? What so
delicious to quaff?
It is so stimulating,
And so titillating,
E'en grey-beards turn
freshy, dance, caper,
and laugh.

—JOHN SHIELD
Oxygen Gas

Approximately 18 elements are classified as nonmetals; they lie above and to the right of the "stairway" that runs diagonally across the periodic table (Figure 21.1). As the word "nonmetal" implies, these elements do not show metallic properties; in the solid state they are brittle as opposed to ductile, insulators rather than conductors. Most of the nonmetals, particularly those in Groups 15 to 17 of the periodic table, are molecular in nature (e.g., N_2, O_2, F_2). The noble gases (Group 18) consist of individual atoms attracted to each other by weak dispersion forces. Carbon in Group 14 has a network covalent structure.

As indicated in Figure 21.1, this chapter concentrates on the more common and/or more reactive nonmetals, namely,

- nitrogen and phosphorus in Group 15.
- oxygen and sulfur in Group 16.
- the halogens (F, Cl, Br, I) in Group 17.

We will consider

- the properties of these elements and methods of preparing them (Section 21-1).
- their hydrogen compounds (Section 21-2).
- their oxides (Section 21-3).
- their oxoacids and oxoanions (Section 21-4).

Chapter Outline

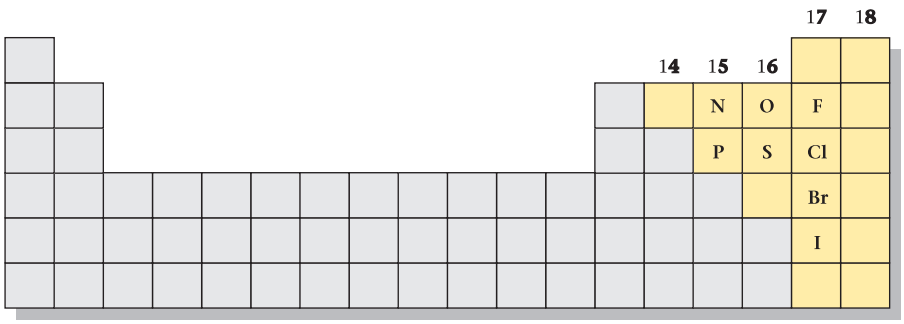


Figure 21.1 Nonmetals and the periodic table. The location of all nonmetals in the periodic table is shown in yellow. Symbols are given for the nonmetallic elements discussed in this chapter.

21-1 The Elements and Their Preparation

Table 21.1 lists some of the properties of the eight nonmetals considered in this chapter. Notice that all of these elements are molecular; those of low molar mass (N_2, O_2, F_2, Cl_2) are gases at room temperature and atmospheric pressure (Figure 21.2). Stronger dispersion forces cause the nonmetals of higher molar mass to be either liquids (Br_2) or solids (I_2, P_4, S_8).

Chemical Reactivity

Of the eight nonmetals listed in Table 21.1, *nitrogen* is by far the least reactive. Its inertness is due to the strength of the triple bond holding the N_2 molecule together (bond enthalpy (B.E.) for $N{\equiv}N$ = 941 kJ/mol). This same factor explains why virtually all chemical explosives are compounds of nitrogen (e.g., nitroglycerin, trinitrotoluene, ammonium nitrate, lead azide). These compounds detonate exothermically to form molecular nitrogen. The reactions with ammonium nitrate and lead azide are

$$2NH_4NO_3(s) \longrightarrow 4H_2O(l) + O_2(g) + 2N_2(g) \qquad \Delta H^\circ = -412 \text{ kJ}$$

$$Pb(N_3)_2(s) \longrightarrow Pb(s) + 3N_2(g) \qquad \Delta H^\circ = -476 \text{ kJ}$$

Fluorine is the most reactive of all elements, in part because of the weakness of the F—F bond (B.E. F—F = 153 kJ/mol), but mostly because it is such a

Table 21.1 Properties of Nonmetallic Elements

	Nitrogen	Phosphorus	Oxygen	Sulfur	Fluorine	Chlorine	Bromine	Iodine
Outer electron configuration	$2s^22p^3$	$3s^23p^3$	$2s^22p^4$	$3s^23p^4$	$2s^22p^5$	$3s^23p^5$	$4s^24p^5$	$5s^25p^5$
Molecular formula	N_2	P_4	O_2	S_8	F_2	Cl_2	Br_2	I_2
Molar mass (g/mol)	28	124	32	257	38	71	160	254
State (25°C, 1 atm)	gas	solid	gas	solid	gas	gas	liquid	solid
Melting point (°C)	−210	44	−218	119	−220	−101	−7	114
Boiling point (°C)	−196	280	−183	444	−188	−34	59	184
Bond enthalpy* (kJ/mol)	941	200	498	226	153	243	193	151
E°_{red}	—	—	—	—	+2.889 V	+1.360 V	+1.077 V	+0.534 V

*In the element (triple bond in N_2, double bond in O_2).

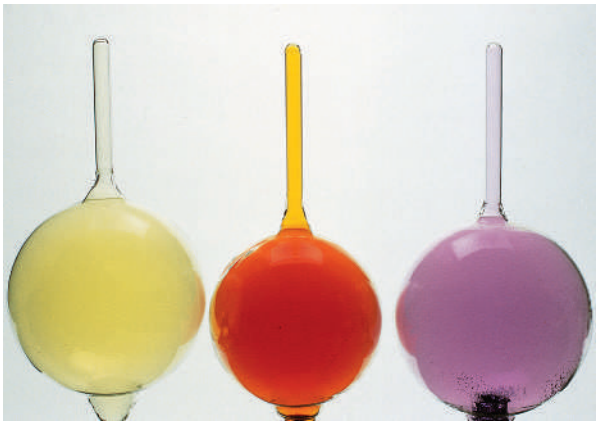


Figure 21.2 Chlorine (Cl_2), bromine (Br_2), and iodine (I_2). The bulbs contain *(left to right)* gaseous chlorine and the vapors in equilibrium with liquid bromine and solid iodine.

powerful oxidizing agent ($E^\circ_{red} = +2.889$ V). Fluorine combines with every element in the periodic table except He and Ne. With a few metals, it forms a surface film of metal fluoride, which adheres tightly enough to prevent further reaction. This is the case with nickel, where the product is NiF_2. Fluorine gas is ordinarily stored in containers made of a nickel alloy, such as stainless steel (Fe, Cr, Ni) or Monel (Ni, Cu). Fluorine also reacts with many compounds including water, which is oxidized to a mixture of O_2, O_3, H_2O_2, and OF_2.

Fluorine is the most electronegative element.

Chlorine is somewhat less reactive than fluorine. Although it reacts with nearly all metals (Figure 21.3), heating is often required. This reflects the relatively strong bond in the Cl_2 molecule (B.E. Cl—Cl = 243 kJ/mol). Chlorine disproportionates in water, forming Cl^- ions (O.N. Cl = −1) and HClO molecules (O.N. Cl = +1).

A species disproportionates when it is oxidized and reduced at the same time.

$$Cl_2(g) + H_2O \rightleftharpoons Cl^-(aq) + H^+(aq) + HClO(aq)$$

The hypochlorous acid, HClO, formed by this reaction is a powerful oxidizing agent ($E^\circ_{red} = +1.630$ V); it kills bacteria, apparently by destroying certain enzymes essential to their metabolism (Figure 21.4). The taste and odor that we

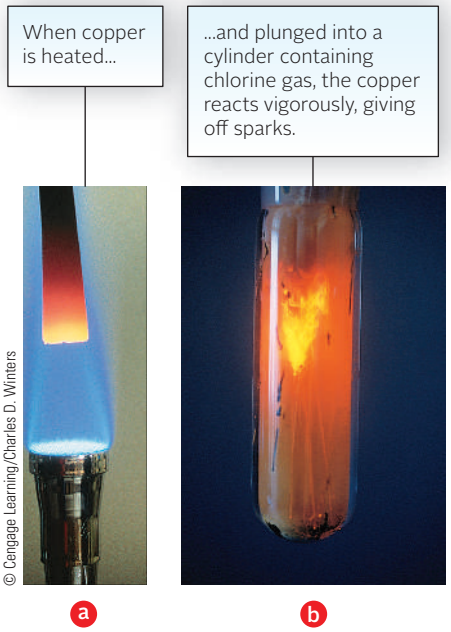


Figure 21.3 Reaction of chlorine with copper. The equation for the reaction is

$$Cu(s) + Cl_2(g) \longrightarrow CuCl_2(s)$$

Figure 21.4 Chlorinated water. The oxidizing power of chlorine-containing chemicals keeps swimming pool water free of disease-causing microorganisms.

associate with "chlorinated water" are actually due to compounds such as CH_3NHCl, produced by the action of hypochlorous acid on bacteria.

EXAMPLE 21.1

Consider the reaction between chlorine gas and water.

$$Cl_2(g) + H_2O \rightleftharpoons Cl^-(aq) + H^+(aq) + HClO(aq)$$

a Write the expression for the equilibrium constant K.

STRATEGY

Recall that in the K expression

- gases enter as partial pressures in atmospheres.
- aqueous species enter as concentrations in molarity.
- water is not included.
- products are written in the numerator raised to their coefficient in the balanced equation.
- reactants are written in the denominator raised to their coefficient in the balanced equation.

SOLUTION

K expression	$K = \dfrac{[HClO][Cl^-][H^+]}{P_{Cl_2}}$

b At the temperature of the reaction, $K = 2.7 \times 10^{-5}$. What is the concentration of HClO in equilibrium with chlorine gas at 1.0 atm?

ANALYSIS

Information given:	$P_{Cl_2}(1.0\ atm)$, $K(2.7 \times 10^{-5})$
Information implied:	from (a) K expression
Asked for:	[HClO]

STRATEGY

Substitute into the K expression obtained in (a).

Let x = [HClO]

Note that the stoichiometric ratios of HClO, H^+, and Cl^- are 1:1:1, thus $[HClO] = [H^+] = [Cl^-] = x$

SOLUTION

[HClO]	$2.7 \times 10^{-5} = \dfrac{(x)(x)(x)}{1.0} \longrightarrow x^3 = 2.7 \times 10^{-5} \longrightarrow x = 0.030\ M$

The oxidizing power of the halogens makes them hazardous to work with. Fluorine is the most dangerous, but it is very unlikely that you will ever come across it in a teaching laboratory. You are most likely to encounter chlorine as its saturated water solution, called "chlorine water." Remember that the pressure of chlorine gas over this solution (if it is freshly prepared) is 1 atm and that chlorine was used as a poison gas in World War I. Use small quantities of chlorine water and don't breathe the vapors. Bromine, although not as strong an oxidizing agent as chlorine, can cause severe burns if it comes in contact with your skin, particularly if it gets under your fingernails.

Of the four halogens, iodine is the weakest oxidizing agent. "Tincture of iodine," a 10% solution of I_2 in alcohol, is sometimes used as an antiseptic. Hospitals most often use a product called "povidone-iodine," a quite powerful

iodine-containing antiseptic and disinfectant, which can be diluted with water to the desired strength. These applications of molecular iodine should not delude you into thinking that the solid is harmless. On the contrary, if $I_2(s)$ is allowed to remain in contact with your skin, it can cause painful burns that are slow to heal.

Occurrence and Preparation

Of the eight nonmetals considered here, three (nitrogen, oxygen, and sulfur) occur in nature in elemental form. *Nitrogen* and *oxygen* are obtained from air, where their mole fractions are 0.7808 and 0.2095, respectively. When liquid air at −200°C (73 K) is allowed to warm, the first substance that boils off is nitrogen (bp N_2 = 77 K). After most of the nitrogen has been removed, further warming gives oxygen (bp O_2 = 90 K). About 2×10^{10} kg of O_2 and lesser amounts of N_2 are produced annually in the United States from liquid air.

At the close of the Civil War in 1865, oil prospectors in Louisiana discovered (to their disgust) elemental *sulfur* in the caprock of vast salt domes up to 20 km^2 in area. The sulfur lies 60 to 600 m below the surface of the earth. The process used to mine sulfur is named after its inventor, Herman Frasch (1851–1914), an American chemical engineer (born in Germany). A diagram of the **Frasch process** is shown in Figure 21.5. The sulfur is heated to its melting point (119°C) by pumping superheated water at 165°C down one of three concentric pipes. Compressed air is used to bring the sulfur to the surface. The air and sulfur form a frothy mixture that rises through the middle pipe. On cooling, the sulfur solidifies, filling huge vats that may be 0.5 km long. The sulfur obtained in this way has a purity approaching 99.9%.

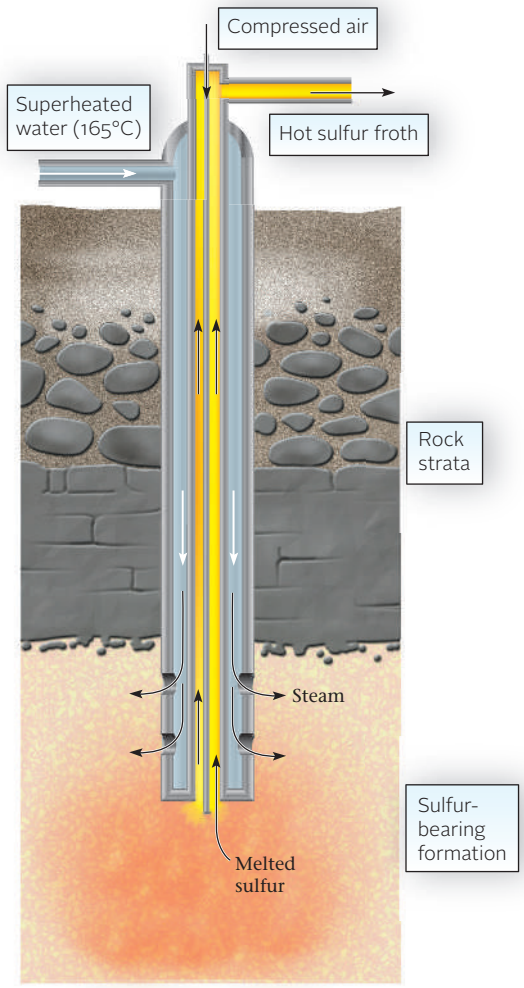


Figure 21.5 Frasch process for mining sulfur. Superheated water at 165°C is sent down through the outer pipe to form a pool of molten sulfur (mp = 119°C) at the base. Compressed air, pumped down the inner pipe, brings the sulfur to the surface. Sulfur deposits are often 100 m or more beneath the earth's surface, covered with quicksand and rock.

Br_2 and I_2 can be obtained from seawater.

The *halogens* are far too reactive to occur in nature as the free elements. Instead, they are found as halide anions:

- F^- in the mineral calcium fluoride, CaF_2 (fluorite).
- Cl^- in huge underground deposits of sodium chloride, NaCl (rock salt), underlying parts of Oklahoma, Texas, and Kansas.
- $Br^-(aq)$ and $I^-(aq)$ in brine wells in Arkansas (conc. $Br^- = 0.05\ M$) and Michigan (conc. $I^- = 0.001\ M$), respectively.

The fluoride and chloride ions are very difficult to oxidize ($E^\circ_{ox}\ F^- = -2.889$ V; $E^\circ_{ox}\ Cl^- = -1.360$ V). Hence the elements fluorine and chlorine are ordinarily prepared by electrolytic oxidation, using a high voltage. As pointed out in Chapter 17, chlorine is prepared by the electrolysis of aqueous sodium chloride:

$$2Cl^-(aq) + 2H_2O \longrightarrow Cl_2(g) + H_2(g) + 2OH^-(aq)$$

The process used to prepare fluorine was developed by Henri Moissan (1852–1907) in Paris in 1886. It won him one of the early (1906) Nobel Prizes in chemistry. The electrolyte is a mixture of HF and KF in a 2:1 mole ratio. At 100°C, fluorine is generated by the decomposition of hydrogen fluoride:

$$2HF(l) \longrightarrow H_2(g) + F_2(g)$$

Potassium fluoride furnishes the ions required to carry the electric current.

Bromide and iodide ions are easier to oxidize ($E^\circ_{ox}\ Br^- = -1.077$ V; $E^\circ_{ox}\ I^- = -0.534$ V), so bromine and iodine can be prepared by chemical oxidation. Commonly, the oxidizing agent is chlorine gas ($E^\circ_{red} = +1.360$ V):

$$Cl_2(g) + 2Br^-(aq) \longrightarrow 2Cl^-(aq) + Br_2(l)$$
$$Cl_2(g) + 2I^-(aq) \longrightarrow 2Cl^-(aq) + I_2(s)$$

21-2 Hydrogen Compounds of Nonmetals

Table 21.2 lists some of the more important hydrogen compounds of the nonmetals. (Those of carbon are discussed in Chapter 22.) The physical states listed are those observed at 25°C and 1 atm. The remainder of this section discusses the chemical properties of the compounds shown in boldface in the table.

Ammonia, NH_3

Ammonia has a sharp, irritating odor and is toxic at high concentrations.

Ammonia is one of the most important industrial chemicals; more than ten million tons of NH_3 are produced annually in the United States. You will recall (Chapter 12) that it is made by the Haber process

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad 450°C,\ 200–600\ atm,\ solid\ catalyst$$

Table 21.2 Hydrogen Compounds of the Nonmetals

Group 15	Group 16	Group 17
Ammonia, $NH_3(g)$	Water, $H_2O(l)$	**Hydrogen fluoride, $HF(g)$**
Hydrazine, $N_2H_4(l)$	**Hydrogen peroxide, $H_2O_2(l)$**	
Hydrazoic acid, $HN_3(l)$		
Phosphine, $PH_3(g)$	**Hydrogen sulfide, $H_2S(g)$**	**Hydrogen chloride, $HCl(g)$**
Diphosphine, $P_2H_4(l)$		
		Hydrogen bromide, $HBr(g)$
		Hydrogen iodide, $HI(g)$

Ammonia is used to make fertilizers and a host of different nitrogen compounds, notably nitric acid, HNO_3.

The NH_3 molecule acts as a *Brønsted-Lowry base* in water, accepting a proton from a water molecule:

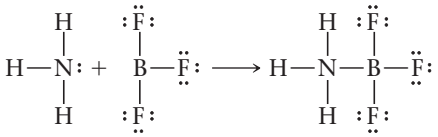
$$NH_3(aq) + H_2O \rightleftharpoons NH_4^+(aq) + OH^-(aq) \qquad K_b = 1.8 \times 10^{-5}$$

Ammonia can also act as a *Lewis base* when it reacts with a metal cation to form a complex ion

$$2NH_3(aq) + Ag^+(aq) \longrightarrow Ag(NH_3)_2^+(aq)$$

The NH_3 molecule donates an electron pair to Ag^+.

or with an electron-deficient compound such as boron trifluoride:



Lewis base Lewis acid

Ammonia is often used to precipitate insoluble metal hydroxides such as $Al(OH)_3$. The OH^- ions formed when ammonia reacts with water precipitate the cation from solution as the hydroxide. The overall equation for the reaction is

$$Al^{3+}(aq) + 3NH_3(aq) + 3H_2O \longrightarrow Al(OH)_3(s) + 3NH_4^+(aq)$$

Nitrogen cannot have an oxidation number lower than −3, which means that when NH_3 takes part in a redox reaction, it always acts as a *reducing agent*. Ammonia may be oxidized to elementary nitrogen or to a compound of nitrogen. An important redox reaction of ammonia is that with hypochlorite ion:

$$2NH_3(aq) + ClO^-(aq) \longrightarrow N_2H_4(aq) + Cl^-(aq) + H_2O$$

Hydrazine, N_2H_4, is made commercially by this process. Certain byproducts of this reaction, notably NH_2Cl and $NHCl_2$, are both toxic and explosive, so solutions of household bleach and ammonia should never be mixed with one another.

Hydrogen Sulfide, H_2S

In water solution, hydrogen sulfide acts as a *Brønsted-Lowry acid;* it can donate a proton to a water molecule:

$$H_2S(aq) + H_2O \rightleftharpoons HS^-(aq) + H_3O^+(aq) \qquad K_a = 1.0 \times 10^{-7}$$

Like ammonia, hydrogen sulfide can act as a precipitating agent toward metal cations. The reaction with Cd^{2+} is typical:

$$Cd^{2+}(aq) + H_2S(aq) \longrightarrow CdS(s) + 2H^+(aq)$$

Like ammonia, hydrogen sulfide (O.N. S = −2) can act only as a reducing agent when it takes part in redox reactions. Most often the H_2S is oxidized to elementary sulfur, as in the reaction

$$2H_2S(aq) + O_2(g) \longrightarrow 2S(s) + 2H_2O$$

The sulfur formed is often very finely dispersed, which explains why aqueous solutions of hydrogen sulfide in contact with air have a milky appearance.

If you've worked with H_2S in the laboratory, you won't soon forget its rotten-egg odor. In a sense, it's fortunate that hydrogen sulfide has such a distinctive odor. This gas is highly toxic, as poisonous as HCN. At a concentration of 10 parts per million, H_2S can cause headaches and nausea; at 100 ppm it can be fatal.

EXAMPLE 21.2

When a solution containing Cu^{2+} is treated with hydrogen sulfide, a black precipitate forms. When another portion of the solution is treated with ammonia, a blue precipitate forms. This precipitate dissolves in excess ammonia to form a deep blue solution containing the $Cu(NH_3)_4^{2+}$ ion. Write balanced net ionic equations to explain these observations.

STRATEGY AND SOLUTION

1. The black precipitate is CuS.

$$Cu^{2+}(aq) + H_2S(aq) \longrightarrow CuS(s) + 2H^+(aq)$$

2. An aqueous solution of ammonia consists of NH_3 and H_2O. Since the blue precipitate must be $Cu(OH)_2$, water has to be a reactant.

$$Cu^{2+}(aq) + 2NH_3(aq) + 2H_2O \longrightarrow Cu(OH)_2(s) + 2NH_4^+(aq)$$

3. The precipitate, $Cu(OH)_2$, reacts with excess ammonia to form $Cu(NH_3)_4^{2+}$.

$$Cu(OH)_2(s) + 4NH_3(aq) \longrightarrow Cu(NH_3)_4^{2+}(aq) + 2OH^-(aq)$$

Figure 21.6 Disproportionation of H_2O_2, catalyzed by MnO_2.

Hydrogen Peroxide

In hydrogen peroxide, oxygen has an oxidation number of −1, intermediate between the extremes for the element, 0 and −2. This means that H_2O_2 can act as either an oxidizing agent, in which case it is reduced to H_2O, or as a reducing agent, when it is oxidized to O_2. In practice, hydrogen peroxide is an extremely strong oxidizing agent:

$$H_2O_2(aq) + 2H^+(aq) + 2e^- \longrightarrow 2H_2O \qquad E^\circ_{red} = +1.763\ V$$

but a very weak reducing agent:

$$H_2O_2(aq) \longrightarrow O_2(g) + 2H^+(aq) + 2e^- \qquad E^\circ_{ox} = -0.695\ V$$

Hydrogen peroxide tends to decompose in water, which explains why its solutions soon lose their oxidizing power. The reaction involved is *disproportionation*, combining the two half-reactions referred to above:

$$\begin{aligned} H_2O_2(aq) + 2H^+(aq) + 2e^- &\longrightarrow 2H_2O & E^\circ_{red} &= +1.763\ V \\ H_2O_2(aq) &\longrightarrow O_2(g) + 2H^+(aq) + 2e^- & E^\circ_{ox} &= -0.695\ V \\ \hline 2H_2O_2(aq) &\longrightarrow O_2(g) + 2H_2O & E^\circ &= +1.068\ V \end{aligned}$$

Half of the H_2O_2 molecules are reduced to H_2O; half are oxidized to O_2.

This reaction (Figure 21.6) is catalyzed by a wide variety of materials, including I^- ions, MnO_2, metal surfaces (Pt, Ag), and even by traces of OH^- ions dissolved from glass.

You are most likely to come across hydrogen peroxide as its water solution. Solutions available in a drugstore for medicinal use contain 3% to 6% by mass of H_2O_2. Industrially, concentrations as high as 86% H_2O_2 are available. All water solutions of hydrogen peroxide contain stabilizers to prevent disproportionation from taking place during storage.

EXAMPLE 21.3

Using Table 17.1, decide whether hydrogen peroxide will react with (oxidize or reduce) the following ions in acid solution at standard concentrations:

I^-, Sn^{2+}, and Co^{2+}

STRATEGY

1. Since H_2O_2 disproportionates, it can either be reduced (and oxidize the ions) or be oxidized (and reduce the ions).
2. For a redox reaction to occur where H_2O_2 is reduced,

E°_{red} H_2O_2(1.763 V) + E°_{ox} ion > 0

continued

3. For a redox reaction to occur where H_2O_2 is oxidized,

$E°_{ox}$ $H_2O_2(-0.695\ V)$ + $E°_{red}$ ion > 0

SOLUTION

I^-	
oxidation	$(E°_{ox}\ I^- = -0.534\ V) + (E°_{red}\ H_2O_2 = 1.763\ V) > 0$ H_2O_2 can oxidize I^- to I_2.
reduction	Table 17.1 shows no reduction potential for I^-.
Sn^{2+}	
oxidation	$(E°_{ox}\ Sn^{2+} = -0.154\ V) + (E°_{red}\ H_2O_2 = 1.763\ V) > 0$ H_2O_2 can oxidize Sn^{2+} to Sn^{4+}.
reduction	$(E°_{red}\ Sn^{2+} = -0.141\ V) + (E°_{ox}\ H_2O_2 = -0.695\ V) < 0$ H_2O_2 cannot reduce Sn^{2+} to Sn.
Co^{2+}	
oxidation	$(E°_{ox}\ Co^{2+} = -1.953\ V) + (E°_{red}\ H_2O_2 = 1.763\ V) < 0$ H_2O_2 cannot oxidize Co^{2+} to Co^{3+}.
reduction	$(E°_{red}\ Co^{2+} = -0.282\ V) + (E°_{ox}\ H_2O_2 = -0.695\ V) < 0$ H_2O_2 cannot reduce Co^{2+} to Co.

Hydrogen Fluoride and Hydrogen Chloride

The most common hydrogen halides are HF (U.S. production = 3×10^8 kg/yr) and HCl (3×10^9 kg/yr). They are most familiar as water solutions, referred to as hydrofluoric acid and hydrochloric acid, respectively. Recall (Chapter 13) that hydrofluoric acid is weak, incompletely dissociated in water, whereas HCl is a strong acid.

$$HF(aq) \rightleftharpoons H^+(aq) + F^-(aq) \qquad K_a = 6.9 \times 10^{-4}$$
$$HCl(aq) \longrightarrow H^+(aq) + Cl^-(aq) \qquad K_a \longrightarrow \infty$$

The difference in K_a values is due largely to the difference in bond strength. The H—F bond (bond enthalpy = 565 kJ/mol) is much stronger than the H—Cl bond (bond enthalpy = 431 kJ/mol).

Hydrofluoric and hydrochloric acids undergo very similar reactions with bases such as OH^- or CO_3^{2-} ions. The equations for these reactions look somewhat different because of the difference in acid strength. Thus for the reaction of hydrochloric acid with a solution of sodium hydroxide, the equation is simply

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O$$

With hydrofluoric acid, the equation is

$$HF(aq) + OH^-(aq) \longrightarrow H_2O + F^-(aq)$$

Hydrochloric acid contains H^+ and Cl^- ions; hydrofluoric acid contains mostly HF molecules.

HF appears in this equation because aqueous hydrofluoric acid is weak, containing many more HF molecules than H^+ ions. Similarly, for the reaction of these two acids with a solution of sodium carbonate:

hydrochloric acid: $2H^+(aq) + CO_3^{2-}(aq) \longrightarrow CO_2(g) + H_2O$

hydrofluoric acid: $2HF(aq) + CO_3^{2-}(aq) \longrightarrow CO_2(g) + H_2O + 2F^-(aq)$

Concentrated hydrofluoric acid reacts with glass, which can be considered to be a mixture of SiO_2 and ionic silicates such as calcium silicate, $CaSiO_3$:

$$SiO_2(s) + 4HF(aq) \longrightarrow SiF_4(g) + 2H_2O$$
$$CaSiO_3(s) + 6HF(aq) \longrightarrow SiF_4(g) + CaF_2(s) + 3H_2O$$

As you might guess, HF solutions are never stored in glass bottles; plastic is used instead. Hydrofluoric acid is sometimes used to etch glass. The glass object is

How do you suppose HF(*aq*) was stored B.P. (before plastics)?

Figure 21.7 A test for limestone. Geologists use a few drops of hydrochloric acid to identify limestone, which is calcium carbonate.

first covered with a thin protective coating of wax or plastic. Then the coating is removed from the area to be etched and the glass is exposed to the HF solution. Thermometer stems and burets can be etched or light bulbs frosted in this way.

Hydrogen fluoride is a very unpleasant chemical to work with. If spilled on the skin, it removes Ca^{2+} ions from the tissues, forming insoluble CaF_2. A white patch forms that is agonizingly painful to the touch. To make matters worse, HF is a local anesthetic, so a person may be unaware of what is happening until it is too late.

Rest assured that you will never have occasion to use hydrofluoric acid in the general chemistry laboratory. Neither are you likely to come in contact with HBr or HI, both of which are relatively expensive. Hydrochloric acid, on the other hand, is a workhorse chemical of the teaching laboratory. It is commonly available as "dilute HCl" (6 *M*) or "concentrated HCl" (12 *M*). You will use it as a source of H^+ ions for such purposes as

- dissolving insoluble carbonates, like limestone (Figure 21.7), or hydroxides.

$$Ag_2CO_3(s) + 2H^+(aq) \longrightarrow 2Ag^+(aq) + CO_2(g) + H_2O$$
$$Zn(OH)_2(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + 2H_2O$$

- converting a weak base such as NH_3 to its conjugate acid.

$$NH_3(aq) + H^+(aq) \longrightarrow NH_4^+(aq)$$

- generating $H_2(g)$ by reaction with a metal.

$$Zn(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$$

EXAMPLE 21.4

Write balanced net ionic equations to explain why

(a) aluminum hydroxide dissolves in hydrochloric acid.

(b) carbon dioxide gas is evolved when calcium carbonate is treated with hydrochloric acid.

(c) carbon dioxide gas is evolved when calcium carbonate is treated with hydrofluoric acid.

STRATEGY AND SOLUTION

(a) When a precipitate is said to dissolve, it means that the solid is broken up into its component ions.

$$Al(OH)_3(s) \longrightarrow Al^{3+}(aq) + 3OH^-(aq)$$

The OH^- ion then reacts with the appropriate ion contributed by HCl, in this case H^+

$$OH^-(aq) + H^+(aq) \longrightarrow H_2O$$

The reaction is

$$Al(OH)_3(s) + 3H^+(aq) \longrightarrow Al^{3+}(aq) + 3H_2O$$

(b) Recall that a carbonate (CO_3^{2-}) reacts with an acid by releasing CO_2 and water. In this case, the reacting species is H^+ because HCl is a strong acid (Chapter 4).

$$CaCO_3(s) + 2H^+(aq) \longrightarrow Ca^{2+}(aq) + CO_2(g) + H_2O$$

(c) As in (b), CO_2 is evolved, but the reacting species is HF because it is a weak acid.

$$CaCO_3(s) + 2HF(aq) \longrightarrow Ca^{2+}(aq) + CO_2(g) + 2F^-(aq) + H_2O$$

21-3 Oxygen Compounds of Nonmetals

Table 21.3 lists some of the more familiar nonmetal oxides. Curiously enough, only 5 of the 21 compounds shown are thermodynamically stable at 25°C and 1 atm (P_4O_{10}, P_4O_6, SO_3, SO_2, I_2O_5). The others, including all of the oxides of nitrogen and chlorine, have positive free energies of formation at 25°C and 1 atm. For example, ΔG_f° $NO_2(g)$ = +51.3 kJ; ΔG_f° $ClO_2(g)$ = +120.6 kJ. Kinetically, these compounds stay around long enough to have an extensive chemistry.

Table 21.3 Nonmetal Oxides*

Group 15	Group 16	Group 17
$N_2O_5(s)$, $N_2O_4(g)$, $NO_2(g)$		$OF_2(g)$, $O_2F_2(g)$
$N_2O_3(d)$, $NO(g)$, $N_2O(g)$		
$P_4O_{10}(s)$, $P_4O_6(s)$	**$SO_3(l)$, $SO_2(g)$**	$Cl_2O_7(l)$, $Cl_2O_6(l)$
		$ClO_2(g)$, $Cl_2O(g)$
		$BrO_2(d)$, $Br_2O(d)$
		$I_2O_5(s)$, $I_4O_9(s)$, $I_2O_4(s)$

*The states listed are those observed at 25°C and 1 atm. Compounds that decompose below 25°C are listed as (*d*). Oxides shown in boldface are discussed in the text.

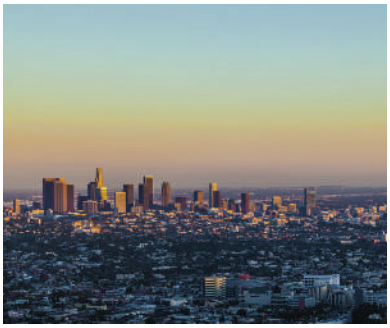
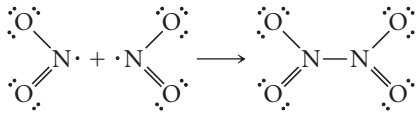


Figure 21.8 Smog over Los Angeles. From a distance, you can clearly see the layer of smog containing reddish-brown nitrogen dioxide.

Nitrogen dioxide, a reddish-brown gas, is a major factor in the formation of photochemical smog (Figure 21.8). Chlorine dioxide, a yellow gas, is widely used as an industrial bleach and water purifier, even though it tends to explode at partial pressures higher than 50 mm Hg.

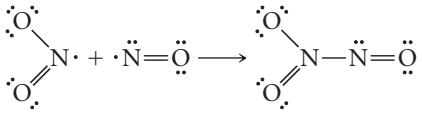
Molecular Structures of Nonmetal Oxides

The Lewis structures of the oxides of nitrogen are shown in Figure 21.9. Two of these species, NO and NO_2, are paramagnetic, with one unpaired electron. When nitrogen dioxide is cooled, it dimerizes; the unpaired electrons combine to form a single bond between the two nitrogen atoms:



$$2NO_2(g) \rightleftharpoons N_2O_4(g)$$

A similar reaction occurs when an equimolar mixture of NO and NO_2 is cooled. Two odd electrons, one from each molecule, pair off to form an N—N bond:



$$NO_2(g) + NO(g) \rightleftharpoons N_2O_3(g)$$

At −20°C, dinitrogen trioxide separates from the mixture as a blue liquid.

Dimerization occurs when two identical molecules combine.

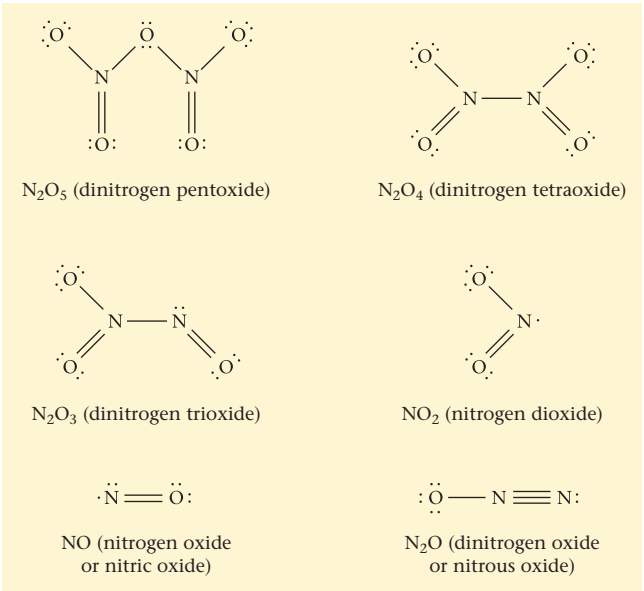


Figure 21.9 Lewis structures of the oxides of nitrogen. Many other resonance forms are possible.

Nitric oxide (NO) is a minor but villainous component of the atmosphere. It is involved in the formation of both smog (Chapter 11) and acid rain (Chapter 14). You may be surprised to learn that small amounts of NO are also produced in the human body, where it has a generally beneficial effect. In particular, it has the ability to dilate blood vessels, lowering blood pressure and reducing the likelihood of strokes or heart attacks. Beyond that, NO is effective in treating what television commercials refer to as "erectile dysfunction"; it increases blood flow to the penis.

Perhaps the best known oxide of nitrogen is N_2O, commonly called nitrous oxide or "laughing gas." Nitrous oxide is frequently used as an anesthetic, particularly in dentistry. It is also the propellant gas used in whipped cream containers; N_2O is nontoxic, virtually tasteless, and quite soluble in vegetable oils. The N_2O molecule, like all those in Figure 21.9, can be represented as a resonance hybrid.

EXAMPLE 21.5

Consider the N_2O molecule shown in Figure 21.9. Draw another resonance form of N_2O and determine its bond angle and polarity.

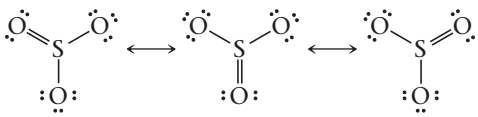
STRATEGY

Recall the discussion in Chapter 7 (Sections 7-1, 7-2, and 7-3) where the principles of resonance, molecular geometry, and polarity are considered.

SOLUTION

resonance forms	:Ö=N=N̈: or :O≡N—N̈:
bond angle	The molecule is linear. Its bond angle is 180°.
polarity	The molecule has two different atoms bonded to the central atom N. The molecule is polar.

The structures of SO_2 and SO_3 were referred to in Chapter 7. These molecules are often cited as examples of resonance; sulfur trioxide, for example, has three equivalent resonance structures:



As you might expect, the SO_3 molecule is nonpolar, with 120° bond angles.

Of the two oxides of phosphorus, P_4O_6 and P_4O_{10}, the latter is the more stable; it is formed when white phosphorus burns in air:

In a limited supply of air, some P_4O_6 is formed.

$$P_4(s) + 5O_2(g) \longrightarrow P_4O_{10}(s)$$

Note from Figure 21.10 that in both oxides, as in P_4 itself, the four phosphorus atoms are at the corners of a tetrahedron. The P_4O_6 molecule can be visualized as derived from P_4 by inserting an oxygen atom between each pair of phosphorus atoms. In P_4O_{10}, an extra oxygen atom is bonded to each phosphorus.

Reactions of Nonmetal Oxides with Water

Many nonmetal oxides are acidic in the sense that they react with water to form acids. Looking at the reaction

$$SO_3(g) + H_2O(l) \longrightarrow H_2SO_4(l)$$

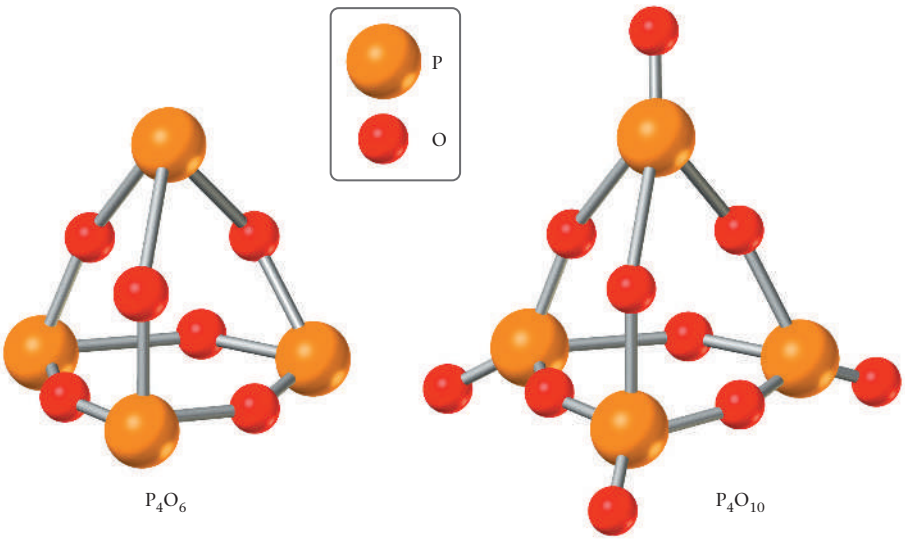


Figure 21.10 Ball-and-stick models of the oxides of phosphorus.

you can see that sulfur trioxide is an *acidic oxide*. Notice that in this reaction, the nonmetal does not change oxidation number; sulfur is in the +6 state in both SO_3 and H_2SO_4. Other acidic oxides include N_2O_5 and N_2O_3:

$$\text{+5 nitrogen:} \quad N_2O_5(s) + H_2O(l) \longrightarrow 2HNO_3(l)$$
$$\text{+3 nitrogen:} \quad N_2O_3(g) + H_2O(l) \longrightarrow 2HNO_2(aq)$$

The products are nitric acid, HNO_3, and an aqueous solution of nitrous acid, HNO_2.

One of the most important reactions of this type involves the +5 oxide of phosphorus, P_4O_{10}. Here the product is phosphoric acid, H_3PO_4:

$$P_4O_{10}(s) + 6H_2O(l) \longrightarrow 4H_3PO_4(s)$$

This reaction is used to prepare high-purity phosphoric acid and salts of that acid for use in food products (Figure 21.11). Phosphoric acid, H_3PO_4, is added in small amounts to soft drinks to give them a tart taste. It is present to the extent of about 0.05 mass percent in colas, 0.01 mass percent in root beers.

Figure 21.11 Household products containing phosphoric acid or its salts.

EXAMPLE 21.6

Give the formula of the oxide that reacts with water to form H_3PO_3, HClO, and H_2SO_3.

STRATEGY

Refer to Table 21.3. Find an oxide in which the central atom has the same oxidation number as the acid.

SOLUTION

H_3PO_3	oxidation number: +3; oxide with oxidation number +3: P_4O_6
HClO	oxidation number: +1; oxide with oxidation number +1: Cl_2O
H_2SO_3	oxidation number: +4; oxide with oxidation number +4: SO_2

21-4 Oxoacids and Oxoanions

Table 21.4 lists some of the more important oxoacids of the nonmetals. In all these compounds, the ionizable hydrogen atoms are bonded to oxygen, not to the central nonmetal atom. Dissociation of one or more protons from the oxoacid gives the corresponding oxoanion (Figure 21.12).

Table 21.4 Oxoacids of the Nonmetals

Group 15	Group 16	Group 17
HNO_3, HNO_2*		
H_3PO_4, H_3PO_3	H_2SO_4, H_2SO_3*	$HClO_4$, $HClO_3$*, $HClO_2$*, HClO*
		$HBrO_4$*, $HBrO_3$*, HBrO*
		HIO_4, H_5IO_6, HIO_3, HIO*

*These compounds cannot be isolated from water solution.

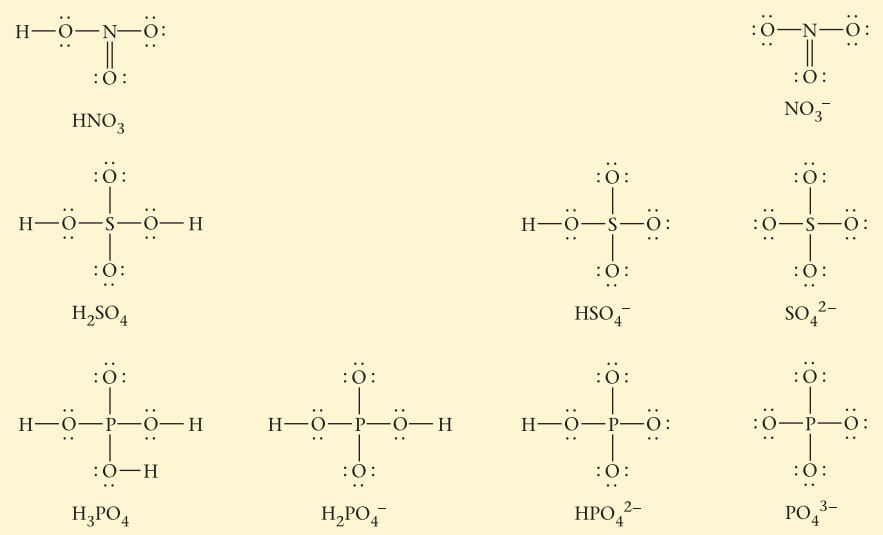


Figure 21.12 **Lewis structures of the oxoacids HNO_3, H_2SO_4, H_3PO_4, and the oxoanions derived from them.**

In this section we discuss the principles that allow you to predict the relative acid strengths of oxoacids such as those listed in Table 21.4. Then we consider their strengths as oxidizing and/or reducing agents. Finally, we take a closer look at the chemistry of three important oxoacids: HNO_3, H_2SO_4, and H_3PO_4.

Acid Strength

The acid equilibrium constants of the oxoacids of the halogens are listed in Table 21.5. Notice that the value of K_a increases with

- ***increasing oxidation number of the central atom*** ($HClO < HClO_2 < HClO_3 < HClO_4$)
- ***increasing electronegativity of the central atom*** ($HIO < HBrO < HClO$)

Table 21.5 Equilibrium Constants of Oxoacids of the Halogens

Oxid. State		K_a		K_a		K_a
+7	$HClO_4$	$\sim 10^7$	$HBrO_4$	$\sim 10^6$	HIO_4*	1.4×10^1
+5	$HClO_3$	$\sim 10^3$	$HBrO_3$	3.0	HIO_3	1.6×10^{-1}
+3	$HClO_2$	1.0×10^{-2}	—	—	—	—
+1	HClO	2.8×10^{-8}	HBrO	2.6×10^{-9}	HIO	2.4×10^{-11}

*Estimated; in water solution the stable species is H_5IO_6, whose first K_a value is 5×10^{-4}.

These trends are general ones, observed with other oxoacids of the nonmetals. Recall, for example, that nitric acid, HNO_3 (O.N. N = +5), is a strong acid, completely ionized in water. In contrast, nitrous acid, HNO_2 (O.N. N = +3), is a weak acid ($K_a = 6.0 \times 10^{-4}$). The electronegativity effect shows up with the strengths of the oxoacids of sulfur and selenium:

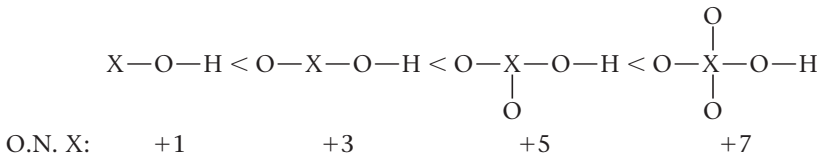
K_{a1} $H_2SO_3 = 1.7 \times 10^{-2}$ K_{a1} $H_2SeO_3 = 2.7 \times 10^{-3}$ (E.N. S = 2.6, Se = 2.5)

Trends in acid strength can be explained in terms of molecular structure. In an oxoacid molecule, the hydrogen atom that dissociates is bonded to oxygen, which in turn is bonded to a nonmetal atom, X. The ionization in water of an oxoacid H—O—X can be represented as

$$H—O—X(aq) \rightleftharpoons H^+(aq) + XO^-(aq)$$

For a proton, with its +1 charge, to separate from the molecule, the electron density around the oxygen should be as low as possible. This will weaken the O—H bond and favor ionization. The electron density around the oxygen atom is decreased when:

- ***X is a highly electronegative atom such as Cl.*** This draws electrons away from the oxygen atom and makes hypochlorous acid stronger than hypoiodous acid.
- ***Additional, strongly electronegative oxygen atoms are bonded to X.*** These tend to draw electrons away from the oxygen atom bonded to H. Thus we would predict that the ease of dissociation of a proton, and hence K_a, should increase in the following order, from left to right:



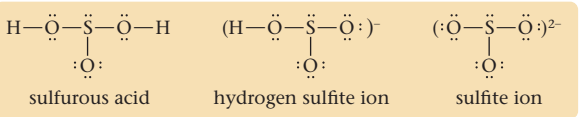
EXAMPLE 21.7

Consider sulfurous acid, H_2SO_3.

a Show its Lewis structure and that of the HSO_3^- and SO_3^{2-} ions.

STRATEGY AND SOLUTION

Reread the discussion on writing Lewis structures in Chapter 7.



b How would its acid strength compare with that of H_2SO_4? H_2TeO_3?

STRATEGY AND SOLUTION

1. Predict acid strength on the basis of electronegativity when the central atoms of the acids being compared are different.

H_2SO_3	vs	H_2TeO_3
S	more electronegative than	Te

H_2SO_3 is a stronger acid than H_2TeO_3.

continued

2. Predict acid strength on the basis of oxidation number when the central atoms of the acids being compared are identical.

H_2SO_3 vs H_2SO_4

oxidation number of S: +4 oxidation number of S: +6

H_2SO_4 is a stronger acid than H_2SO_3.

Oxidizing and Reducing Strength

Many of the reactions of oxoacids and oxoanions involve oxidation and reduction. There are certain general principles that apply, regardless of the particular species involved.

Many oxoanions are very powerful oxidizing agents.

1. ***A species in which a nonmetal is in its highest oxidation state can act only as an oxidizing agent, never as a reducing agent.*** Consider, for example, the ClO_4^- ion, in which chlorine is in its highest oxidation state, +7. In any redox reaction in which this ion takes part, chlorine must be reduced to a lower oxidation state. When that happens, the ClO_4^- ions act as an oxidizing agent, taking electrons away from something else. The same argument applies to

   - the SO_4^{2-} ion (highest O.N. S = +6).
   - the NO_3^- ion (highest O.N. N = +5).

   Note that, in general, *the highest oxidation number of a nonmetal is given by the second digit of its group number* (17 for Cl, 16 for S, 15 for N).
2. ***A species in which a nonmetal is in an intermediate oxidation state can act as either an oxidizing agent or a reducing agent.*** Consider, for example, the ClO_3^- ion (O.N. Cl = +5). It can be oxidized to the perchlorate ion, in which case ClO_3^- acts as a reducing agent:

   $$ClO_3^-(aq) + H_2O \longrightarrow ClO_4^-(aq) + 2H^+(aq) + 2e^- \qquad E^\circ_{ox} = -1.226\ V$$

   Alternatively, the ClO_3^- ion can be reduced, perhaps to a Cl^- ion. When that occurs, ClO_3^- acts as an oxidizing agent:

   $$ClO_3^-(aq) + 6H^+(aq) + 6e^- \longrightarrow Cl^-(aq) + 3H_2O \qquad E^\circ_{red} = +1.442\ V$$

   Notice that the ClO_3^- ion is a much stronger oxidizing agent (E°_{red} = +1.442 V) than reducing agent (E°_{ox} = −1.226 V). This is generally true of oxoanions and oxoacids in an intermediate oxidation state, at least in acidic solution. Compare, for example,

   $HClO$ E°_{red} (to Cl_2) = +1.630 V; E°_{ox} (to $HClO_2$) = −1.157 V
   HNO_2 E°_{red} (to NO) = +1.036 V; E°_{ox} (to NO_2) = −1.056 V
3. ***Sometimes, with a species such as ClO_3^-, oxidation and reduction occur together, resulting in disproportionation:***

   $$4ClO_3^-(aq) \longrightarrow 3ClO_4^-(aq) + Cl^-(aq) \qquad E^\circ = +0.216\ V$$

   In general, a ***species in an intermediate oxidation state is expected to disproportionate if the sum $E^\circ_{ox} + E^\circ_{red}$ is a positive number.***
4. ***The oxidizing strength of an oxoacid or oxoanion is greatest at high [H^+] (low pH). Conversely, its reducing strength is greatest at low [H^+] (high pH).*** This principle has a simple explanation. Looking back at the half-equations

above, you can see that

- when ClO_3^- acts as an oxidizing agent, the H^+ ion is a reactant, so increasing its concentration makes the process more spontaneous.
- when ClO_3^- acts as a reducing agent, the H^+ ion is a product; to make the process more spontaneous, $[H^+]$ should be lowered.

EXAMPLE 21.8

Calculate E_{red} and E_{ox} at 25°C for the ClO_3^- ion in neutral solution, at pH 7.00, assuming all other species are at standard concentration ($E^\circ_{red} = +1.442$ V; $E^\circ_{ox} = -1.226$ V). Will the ClO_3^- ion disproportionate at pH 7.00?

ANALYSIS

Information given:	ClO_3^-: E°_{red} (1.442 V); E°_{ox} (−1.226 V) pH (7.00); T (25°C) All species besides ClO_3^- are at 1.00 M.
Asked for:	Will ClO_3^- disproportionate at the given pH?

STRATEGY

1. Write a half-equation for the reduction of ClO_3^-.
2. Calculate E_{red} by substituting into the Nernst equation for 25°C.

$$E_{red} = E^\circ_{red} - \frac{0.0257}{n} \ln Q$$

3. Write a half-equation for the oxidation of ClO_3^-.
4. Calculate E_{ox} by substituting into the Nernst equation for 25°C.

$$E_{ox} = E^\circ_{ox} - \frac{0.0257}{n} \ln Q$$

5. Find E.

$$E = E_{red} + E_{ox}$$

If $E > 0$, ClO_3^- will disproportionate.

SOLUTION

1. Reduction half-reaction: $ClO_3^-(aq) + 6H^+(aq) + 6e^- \longrightarrow Cl^-(aq) + 3H_2O$

2. E_{red}:

$$E_{red} = 1.442 - \frac{0.0257}{6} \ln \frac{[Cl^-]}{[ClO_3^-][H^+]^6} = 1.442 - \frac{0.0257}{6} \ln \frac{(1)}{(1)(1.00 \times 10^{-7})^6}$$

$$E_{red} = 1.028 \text{ V}$$

3. Oxidation half-reaction: $ClO_3^-(aq) + H_2O \longrightarrow ClO_4^-(aq) + 2H^+(aq) + 2e^-$

4. E_{ox}:

$$E_{ox} = -1.226 - \frac{0.0257}{2} \ln \frac{[ClO_4^-][H^+]^2}{[ClO_3^-]} = -1.226 - \frac{0.0257}{2} \ln \frac{(1)(1 \times 10^{-7})^2}{(1)}$$

$$E_{ox} = -0.812 \text{ V}$$

5. E:

$$E = E_{red} + E_{ox} = 1.028 + (-0.812) = 0.216 \text{ V}$$

Disproportionation should occur.

END POINT

Notice that E is the same as E°, +0.216 V. You could have predicted that (and saved a lot of work!), because the overall equation for the disproportionation

$$4ClO_3^-(aq) \longrightarrow 3ClO_4^-(aq) + Cl^-(aq)$$

does not involve H^+ or OH^- ions.

Nitric Acid, HNO_3

Commercially, nitric acid is made by a three-step process developed by the German physical chemist Wilhelm Ostwald (1853–1932). The starting material is ammonia, which is burned in an excess of air at 900°C, using a platinum-rhodium catalyst:

$$4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g)$$

The gaseous mixture formed is cooled and mixed with more air to convert NO to NO_2:

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$

Finally, nitrogen dioxide is bubbled through water to produce nitric acid:

$$3NO_2(g) + H_2O(l) \longrightarrow NO(g) + 2HNO_3(aq)$$

Nitric acid is a strong acid, completely ionized to H^+ and NO_3^- ions in dilute water solution:

$$HNO_3(aq) \longrightarrow H^+(aq) + NO_3^-(aq)$$

Many of the reactions of nitric acid are those associated with all strong acids. For example, dilute (6 *M*) nitric acid can be used to dissolve aluminum hydroxide:

$$Al(OH)_3(s) + 3H^+(aq) \longrightarrow Al^{3+}(aq) + 3H_2O$$

or to generate carbon dioxide gas from calcium carbonate:

$$CaCO_3(s) + 2H^+(aq) \longrightarrow Ca^{2+}(aq) + CO_2(g) + H_2O$$

Referring back to Example 21.4, you will find that these equations are identical with those written for the reactions of hydrochloric acid with $Al(OH)_3$ and $CaCO_3$. It is the H^+ ion that reacts in either case: Cl^- and NO_3^- ions take no part in the reactions and hence do not appear in the equation.

Concentrated (16 *M*) nitric acid is a strong oxidizing agent; the nitrate ion is reduced to nitrogen dioxide. This happens when 16 *M* HNO_3 reacts with copper metal (Figure 21.13):

$$Cu(s) + 4H^+(aq) + 2NO_3^-(aq) \longrightarrow Cu^{2+}(aq) + 2NO_2(g) + 2H_2O$$

Dilute nitric acid (6 *M*) gives a wide variety of reduction products, depending on the nature of the reducing agent. With inactive metals such as copper ($E^\circ_{ox} = -0.339$ V), the major product is usually NO (O.N. N = +2):

$$3Cu(s) + 2NO_3^-(aq) + 8H^+(aq) \longrightarrow 3Cu^{2+}(aq) + 2NO(g) + 4H_2O$$

With very dilute acid and a strong reducing agent such as zinc ($E^\circ_{ox} = +0.762$ V) reduction may go all the way to the NH_4^+ ion (O.N. N = −3):

$$4Zn(s) + NO_3^-(aq) + 10H^+(aq) \longrightarrow 4Zn^{2+}(aq) + NH_4^+(aq) + 3H_2O$$

As you would expect, the oxidizing strength of the NO_3^- ion drops off sharply as pH increases; the reduction voltage (to NO) is +0.964 V at pH 0, +0.412 V at pH 7, and −0.140 V at pH 14. The nitrate ion is a very weak oxidizing agent in basic solution.

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Figure 21.13 A copper penny dissolving in nitric acid. Copper metal is comparatively inactive, but it reacts with concentrated nitric acid. The brown fumes are $NO_2(g)$, a reduction product of HNO_3. The copper is oxidized to Cu^{2+} ions, which impart their color to the solution. (The penny is an old one made of solid copper. Newer pennies have a coating of copper over a zinc core.)

EXAMPLE 21.9

Write a balanced net ionic equation for the reaction of nitric acid with insoluble copper(II) sulfide; the products include Cu^{2+}, S(*s*), and $NO_2(g)$.

STRATEGY

1. Recall the general procedure for writing and balancing redox equations from Chapter 17.
2. Note that HNO_3 is a strong acid, so it should be represented as H^+ and NO_3^- ions.

continued

SOLUTION	
Skeleton half-equations	oxidation: $CuS(s) \longrightarrow S(s)$ reduction: $NO_3^-(aq) \longrightarrow NO_2(g)$
Balanced half-reactions	oxidation: $CuS(s) \longrightarrow S(s) + Cu^{2+}(aq) + 2e^-$ reduction: $NO_3^-(aq) + 2H^+(aq) + e^-(aq) \longrightarrow NO_2(g) + H_2O$
Overall reaction	$CuS(s) \longrightarrow S(s) + Cu^{2+}(aq) + 2e^-$ $2(NO_3^-(aq) + 2H^+(aq) + e^-(aq) \longrightarrow NO_2(g) + H_2O)$ $CuS(s) + 2NO_3^-(aq) + 4H^+(aq) \longrightarrow Cu^{2+}(aq) + S(s) + 2NO_2(g) + 2H_2O$

Concentrated nitric acid (16 *M*) is colorless when pure. In sunlight, it turns yellow (Figure 21.14) because it decomposes to $NO_2(g)$:

$$4HNO_3(aq) \longrightarrow 4NO_2(g) + 2H_2O + O_2(g)$$

The yellow color that appears on your skin if it comes in contact with nitric acid has quite a different explanation. Nitric acid reacts with proteins to give a yellow material called xanthoprotein.

You can always smell NO_2 over 16 *M* HNO_3.

Sulfuric Acid, H_2SO_4

Sulfuric acid is made commercially by a three-step *contact process*. First, elemental sulfur is burned in air to form sulfur dioxide:

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

The sulfur dioxide is converted to sulfur trioxide by bringing it into contact with oxygen on the surface of a solid catalyst:

$$SO_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow SO_3(g)$$

The catalyst used is vanadium (V) oxide, V_2O_5, at a temperature of 450°C to 600°C. Sulfur trioxide is an acidic oxide that reacts with water to form sulfuric acid.

$$SO_3(g) + H_2O(l) \longrightarrow H_2SO_4(l)$$

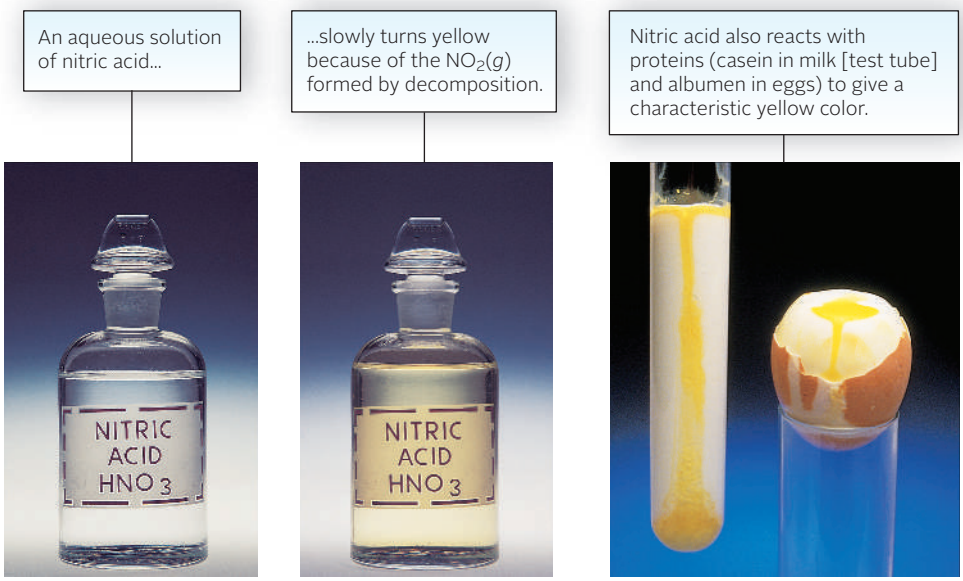

Figure 21.14 Nitric acid. Its decomposition and reaction with proteins.

Sulfuric acid is a strong acid, completely ionized to H^+ and HSO_4^- ions in dilute water solution. The HSO_4^- ion, in contrast, is only partially ionized.

$$H_2SO_4(aq) \longrightarrow H^+(aq) + HSO_4^-(aq) \qquad K_a \longrightarrow \infty$$
$$HSO_4^-(aq) \rightleftharpoons H^+(aq) + SO_4^{2-}(aq) \qquad K_a = 1.0 \times 10^{-2}$$

Most of the H^+ ions come from the first ionization; in 0.10 *M* H_2SO_4, $[H^+] = 0.11$ *M*.

Sulfuric acid is a relatively weak oxidizing agent; most often it is reduced to sulfur dioxide:

$$SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \longrightarrow SO_2(g) + 2H_2O \qquad E^\circ_{red} = +0.155\ V$$

This is the case when copper metal is oxidized by hot concentrated sulfuric acid:

$$Cu(s) + 4H^+(aq) + SO_4^{2-}(aq) \longrightarrow Cu^{2+}(aq) + 2H_2O + SO_2(g)$$

When dilute sulfuric acid (3 *M*) reacts with metals, it is ordinarily the H^+ ion rather than the SO_4^{2-} ion that is reduced. For example, zinc reacts with dilute sulfuric acid to form hydrogen gas:

$$Zn(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$$

Concentrated sulfuric acid, in addition to being an acid and an oxidizing agent, is also a dehydrating agent. Small amounts of water can be removed from organic liquids such as gasoline by extraction with sulfuric acid. Sometimes it is even possible to remove the elements of water from a compound by treating it with 18 *M* H_2SO_4. This happens with table sugar, $C_{12}H_{22}O_{11}$; the product is a black char that is mostly carbon (Figure 21.15).

$$C_{12}H_{22}O_{11}(s) \longrightarrow 12C(s) + 11H_2O$$

When concentrated sulfuric acid dissolves in water, a great deal of heat is given off, nearly 100 kJ per mole of H_2SO_4. Sometimes enough heat is evolved to bring the solution to the boiling point. To prevent this and to avoid splattering, the acid should be added slowly to water, with constant stirring. If it comes in contact with the skin, concentrated sulfuric acid can cause painful chemical burns. Never add water to concentrated H_2SO_4!

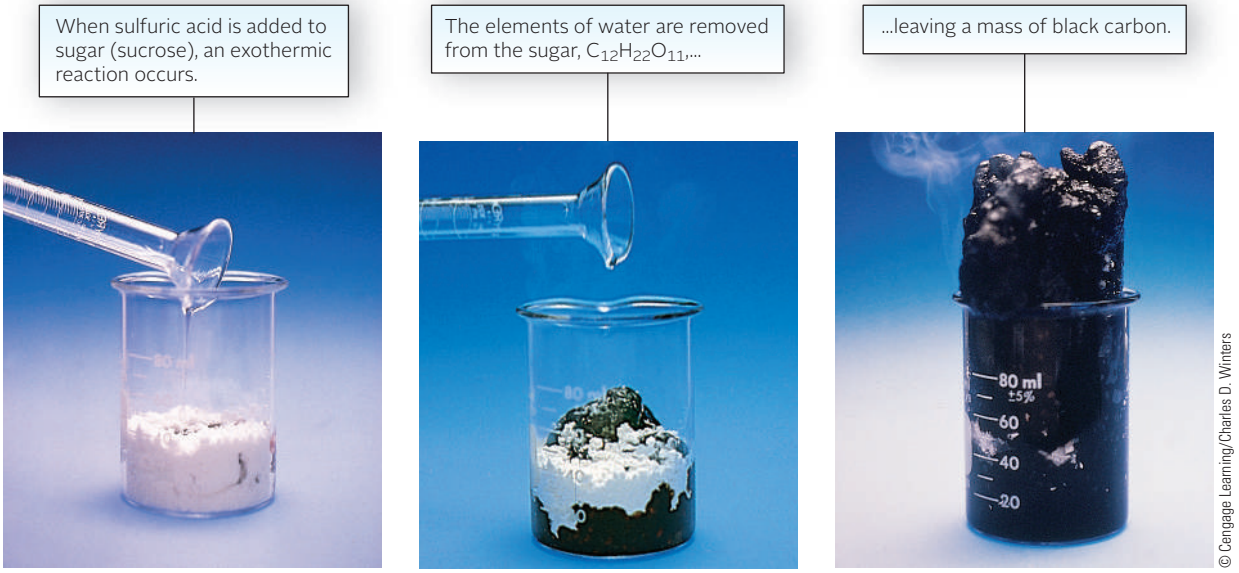

Figure 21.15 Sugar plus sulfuric acid.

Phosphoric Acid, H_3PO_4

In water solution, +5 phosphorus can be present as

- the H_3PO_4 molecule ($K_a = 7.1 \times 10^{-3}$), which is a (relatively strong) weak acid. A 0.10 *M* solution of H_3PO_4 has a pH of 1.6.
- the $H_2PO_4^-$ ion ($K_a = 6.2 \times 10^{-8}$; $K_b = 1.4 \times 10^{-12}$) is a (very) weak acid. A 0.10 *M* solution of NaH_2PO_4 has a pH of 4.
- the HPO_4^{2-} ion ($K_a = 4.5 \times 10^{-13}$; $K_b = 1.6 \times 10^{-7}$) is a (very) weak base. A 0.10 *M* solution of Na_2HPO_4 has a pH of 10.
- the PO_4^{3-} ion ($K_b = 2.2 \times 10^{-2}$) is a (relatively strong) weak base. A 0.10 *M* solution of Na_3PO_4 has a pH of 12.7.

Of the three compounds NaH_2PO_4, Na_2HPO_4, and Na_3PO_4, two are used as cleaning agents: NaH_2PO_4 in acid-type cleaners, Na_3PO_4 in strongly basic cleaners. The principal use of Na_2HPO_4 is in the manufacture of cheese. Around 1915, J. L. Kraft (1874–1953) discovered that this compound is an excellent emulsifying agent. To this day no one quite understands why this happens.

A great many "phosphates" are used in commercial fertilizers. Perhaps the most important of these is calcium dihydrogen phosphate, $Ca(H_2PO_4)_2$. In relatively pure form, this compound is known as "triple superphosphate of lime." A 1:2 mol mixture of $Ca(H_2PO_4)_2$ and gypsum, $CaSO_4 \cdot 2H_2O$, is commonly referred to as "superphosphate of lime."

CHEMISTRY **BEYOND** THE CLASSROOM

Arsenic and Selenium

Arsenic and selenium, which fall directly below phosphorus and sulfur in the periodic table, are of interest for a variety of reasons. Arsenic is a true metalloid. A metallic form, called gray arsenic, has an electrical conductivity approaching that of lead. Another **allotrope**, yellow arsenic, is distinctly nonmetallic; it has the molecular formula As_4, analogous to white phosphorus, P_4. Selenium is properly classified as a nonmetal, although one of its allotropes has a somewhat metallic appearance and is a semiconductor. Another form of selenium has the molecular formula Se_8, analogous to sulfur.

The principal use of elemental arsenic is in its alloys with lead. Lead shot, formed by allowing drops of molten metal to fall through air, contains from 0.5% to 2.0% arsenic. Selenium has long been used as an additive in glassmaking. Particles of colloidally dispersed selenium give the ruby red color seen in traffic lights and stained glass windows (Figure A).

Physiological Properties

The "arsenic poison" referred to in true-crime dramas is actually the oxide of arsenic, As_2O_3, rather than the element itself. Less than 0.1 g of this white, slightly soluble powder can be fatal. The classic symptoms of acute arsenic poisoning involve various unpleasant gastrointestinal disturbances, severe abdominal pain, and burning of the mouth and throat.

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Figure A Stained glass colors. Addition of a selenium compound produces red glass, and an addition of a cobalt compound produces blue glass.

In the modern forensic chemistry laboratory (Figure B) arsenic is detected by analysis of hair samples, where the element tends to concentrate in chronic arsenic poisoning. A single strand of hair is sufficient to establish the presence or absence of the element. The technique most commonly used is neutron activation analysis, described in Chapter 18. If the concentration found is greater than about 0.0003%, poisoning is indicated; normal arsenic levels are much lower than this.

This technique was applied in the early 1960s to a lock of hair taken from Napoleon Bonaparte (1769–1821) on

Photo courtesy of S. Ruven Smith

Figure B A forensic toxicology laboratory. The young woman is working on a research project in the laboratory at Hartford Hospital.

St. Helena. Arsenic levels of up to 50 times normal suggested he may have been a victim of poisoning, perhaps on orders from the French royal family.

Arsenic is a known human carcinogen, found in drinking water in many parts of the world. The World Health Organization (WHO) has set the upper limit for arsenic in drinking water at ten parts per billion (10 ppb). The legal limit in the United States, set by the Environmental Protection Agency (EPA) is 50 ppb.

It has long been known that high concentrations of selenium are toxic. The cattle disease known picturesquely as "blind staggers" arises from grazing on grass growing in soil with a high selenium content. It is now known, however, that selenium is an essential element in human nutrition. A selenium-containing enzyme, glutathione peroxidase, in combination with vitamin E, destroys harmful free radicals in the body.

There is considerable evidence to suggest that selenium compounds are anticarcinogens. For one thing, tests with laboratory animals show that the incidence and size of malignant tumors are reduced when a solution containing Na_2SeO_3 is injected at the part per million level. Beyond that evidence, statistical studies show an inverse correlation between selenium levels in the soil and the incidence of certain types of cancer.

Key Concepts

1. Carry out equilibrium calculations for solution reactions. **(Example 21.1; Problems 43–48)**
2. Apply the Gibbs-Helmholtz equation. **(Example 21.2; Problems 49–54)**
3. Write balanced net ionic equations for solution reactions. **(Examples 21.3, 21.5, and 21.10; Problems 15–26)**
4. Draw Lewis structures for compounds of the nonmetals. **(Examples 21.6 and 21.8; Problems 27–34)**
5. Relate oxoacids to the corresponding oxides and compare their acid strengths. **(Examples 21.7 and 21.8; Problems 7, 8, 63)**
6. Carry out electrochemical calculations involving $E°$, the Nernst equation, and/or electrolysis. **(Examples 21.4 and 21.9; Problems 55–62)**

Summary Problem

Consider bromine, whose chemistry is quite similar to that of chlorine.

(a) Write equations for the reaction of bromine with I^- ions; for the reaction of Br_2 with water (disproportionation).

(b) Write equations for the preparation of bromine by the electrolysis of aqueous NaBr; by the reaction of chlorine with bromide ions in aqueous solution.

(c) Write equations for the reaction of hydrobromic acid with OH^- ions; with CO_3^{2-} ions; with ammonia.

(d) Consider the species Br^-, Br_2, BrO^-, and BrO_4^-. In a redox reaction, which of these species can act only as an oxidizing agent? only as a reducing agent? Which can act as either oxidizing or reducing agents?

(e) When aqueous sodium bromide is heated with a concentrated solution of sulfuric acid, the products include liquid bromine and sulfur dioxide. Write a balanced equation for the redox reaction involved.

(f) Write Lewis structures for the following species: Br^-, BrO^-, BrO_4^-. What is the bond angle in the BrO_4^- ion? For which of these ions is the conjugate acid the weakest?

(g) Give the formula for the acidic oxide of HBrO. Knowing that K_a of HBrO is 2.6×10^{-9}, calculate the ratio [HBrO]/[BrO^-] at pH 10.00.

(h) For the reduction of HBrO to Br^-, what is the change in voltage when the pH increases by one unit?

Answers

(a) $Br_2(l) + 2I^-(aq) \longrightarrow 2Br^-(aq) + I_2(s)$
$Br_2(l) + H_2O \longrightarrow HBrO(aq) + H^+(aq) + Br^-(aq)$

(b) $2Br^-(aq) + 2H_2O \longrightarrow Br_2(l) + H_2(g) + 2OH^-(aq)$
$2Br^-(aq) + Cl_2(aq) \longrightarrow Br_2(l) + 2Cl^-(aq)$

(c) $H^+(aq) + OH^-(aq) \longrightarrow H_2O$
$2H^+(aq) + CO_3^{2-}(aq) \longrightarrow CO_2(g) + H_2O$
$H^+(aq) + NH_3(aq) \longrightarrow NH_4^+(aq)$

(d) BrO_4^-; Br^-; Br_2 or BrO^-

(e) $2Br^-(aq) + SO_4^{2-}(aq) + 4H^+(aq) \longrightarrow Br_2(l) + SO_2(g) + 2H_2O$

(f) $[:\ddot{\underset{\cdot\cdot}{Br}}:]^-$ $[:\ddot{\underset{\cdot\cdot}{Br}}—\ddot{\underset{\cdot\cdot}{O}}:]^-$ $[:\ddot{\underset{\cdot\cdot}{O}}—\underset{\underset{:\ddot{\underset{\cdot\cdot}{O}}:}{|}}{\overset{\overset{:\ddot{\underset{\cdot\cdot}{O}}:}{|}}{Br}}—\ddot{\underset{\cdot\cdot}{O}}:]^-$ 109.5°; BrO^-

(g) Br_2O; 0.038

(h) −0.0296 V

Questions and Problems

Even-numbered questions and Challenge Problems have answers in Appendix 5 and fully worked solutions in the *Student Solutions Manual*.

21-1 The Elements and Their Preparation

21-2 Hydrogen Compounds of Nonmetals

21-3 Oxygen Compounds of Nonmetals

21-4 Oxoacids and Oxoanions

Formulas, Equations, and Reactions

1. Name the following species.
(a) HIO_4 (b) BrO_2^- (c) HIO (d) $NaClO_3$

2. Name the following compounds.
(a) $HBrO_3$ (b) KIO
(c) $NaClO_2$ (d) $NaBrO_4$

3. Write the formula for each of the following compounds.
(a) chloric acid (b) periodic acid
(c) hypobromous acid (d) hydriodic acid

4. Write the formula for each of the following compounds.
(a) potassium bromite (b) calcium bromide
(c) sodium periodate (d) magnesium hypochlorite

5. Write the formula of a compound of each of the following elements that *cannot* act as an oxidizing agent.
(a) N (b) S (c) Cl

6. Write the formula of an oxoanion of each of the following elements that *cannot* act as a reducing agent.
(a) N (b) S (c) Cl

7. Give the formula for the acidic oxide of
(a) HNO_3 (b) HNO_2 (c) H_2SO_4

8. Write the formula of the acid formed when each of these acidic oxides reacts with water.
(a) SO_2 (b) Cl_2O (c) P_4O_6

9. Write the formulas of the following compounds.
(a) ammonia (b) laughing gas
(c) hydrogen peroxide (d) sulfur trioxide

10. Write the formulas for the following compounds.
(a) sodium azide (b) sulfurous acid
(c) hydrazine (d) sodium dihydrogen phosphate

11. Write the formula of a compound of hydrogen with
(a) nitrogen, which is a gas at 25°C and 1 atm.
(b) phosphorus, which is a liquid at 25°C and 1 atm.
(c) oxygen, which contains an O—O bond.

12. Write the formula of a compound of hydrogen with
(a) sulfur.
(b) nitrogen, which is a liquid at 25°C and 1 atm.
(c) phosphorus, which is a poisonous gas at 25°C and 1 atm.

13. Give the formula of
(a) an anion in which S has an oxidation number of −2.
(b) two anions in which S has an oxidation number of +4.
(c) two different acids of sulfur.

14. Give the formula of a compound of nitrogen that is
(a) a weak base. (b) a strong acid.
(c) a weak acid. (d) capable of oxidizing copper.

15. Write a balanced net ionic equation for
(a) the electrolytic decomposition of hydrogen fluoride.
(b) the oxidation of iodide ion to iodine by hydrogen peroxide in acidic solution. Hydrogen peroxide is reduced to water.

16. Write a balanced net ionic equation for
(a) the oxidation of iodide to iodine by sulfate ion in acidic solution. Sulfur dioxide gas is also produced.
(b) The preparation of iodine from an iodide salt and chlorine gas.

17. Write a balanced net ionic equation for the disproportionation reaction
(a) of iodine to give iodate and iodide ions in basic solution.
(b) of chlorine gas to chloride and perchlorate ions in basic solution.

18. Write a balanced net ionic equation for the disproportionation reaction of
(a) hypochlorous acid to chlorine gas and chlorous acid in acidic solution.
(b) chlorate ion to perchlorate and chlorite ions.

19. Complete and balance the following equations. If no reaction occurs, write NR.
(a) $Cl_2(g) + I^-(aq) \longrightarrow$ (b) $F_2(g) + Br^-(aq) \longrightarrow$
(c) $I_2(s) + Cl^-(aq) \longrightarrow$ (d) $Br_2(l) + I^-(aq) \longrightarrow$

20. Complete and balance the following equations. If no reaction occurs, write NR.
(a) $Cl_2(g) + Br^-(aq) \longrightarrow$ (b) $I_2(s) + Cl^-(aq) \longrightarrow$
(c) $I_2(s) + Br^-(aq) \longrightarrow$ (d) $Br_2(l) + Cl^-(aq) \longrightarrow$

21. Write a balanced equation for the preparation of
(a) F_2 from HF. (b) Br_2 from NaBr.
(c) NH_4^+ from NH_3.

22. Write a balanced equation for the preparation of
(a) N_2 from $Pb(N_3)_2$. (b) O_2 from O_3.
(c) S from H_2S.

23. Write a balanced equation for the reaction of ammonia with
(a) Cu^{2+} (b) H^+ (c) Al^{3+}

24. Write a balanced equation for the reaction of hydrogen sulfide with
(a) Cd^{2+} (b) OH^- (c) $O_2(g)$

25. Write a balanced net ionic equation for the reaction of nitric acid with
(a) a solution of $Ca(OH)_2$.
(b) Ag(*s*); assume the nitrate ion is reduced to $NO_2(g)$.
(c) Cd(*s*); assume the nitrate ion is reduced to $N_2(g)$.

26. Write a balanced net ionic equation for the reaction of sulfuric acid with
(a) $CaCO_3(s)$.
(b) a solution of NaOH.
(c) Cu; assume the SO_4^{2-} ion is reduced to SO_2.

Molecular Structure

27. Give the Lewis structure of
(a) NO_2 (b) NO (c) SO_2 (d) SO_3

28. Give the Lewis structure of
(a) Cl_2O (b) N_2O (c) P_4 (d) N_2

29. Which of the molecules in Question 27 are polar?
30. Which of the molecules in Question 28 are polar?
31. Give the Lewis structure of
(**a**) HNO_3 (**b**) H_2SO_4 (**c**) H_3PO_4
32. Give the Lewis structures of the conjugate bases of the species in Question 31.
33. Give the Lewis structure of
(**a**) the strongest oxoacid of bromine.
(**b**) a hydrogen compound of nitrogen in which there is an —N—N— bond.
(**c**) an acid added to cola drinks.
34. Give the Lewis structure of
(**a**) an oxide of nitrogen in the +5 state.
(**b**) the strongest oxoacid of nitrogen.
(**c**) a tetrahedral oxoanion of sulfur.

Stoichiometry

35. The average concentration of bromine (as bromide) in seawater is 65 ppm. Calculate
(**a**) the volume of seawater (d = 64.0 lb/ft^3) in cubic feet required to produce one kilogram of liquid bromine.
(**b**) the volume of chlorine gas in liters, measured at 20°C and 762 mm Hg, required to react with this volume of seawater.
36. A 425-gal tank is filled with water containing 175 g of sodium iodide. How many liters of chlorine gas at 758 mm Hg and 25°C will be required to oxidize all the iodide to iodine?
37. Iodine can be prepared by allowing an aqueous solution of hydrogen iodide to react with manganese dioxide, MnO_2. The reaction is

$$2I^-(aq) + 4H^+(aq) + MnO_2(s) \longrightarrow Mn^{2+}(aq) + 2H_2O + I_2(s)$$

If an excess of hydrogen iodide is added to 0.200 g of MnO_2, how many grams of iodine are obtained, assuming 100% yield?
38. When a solution of hydrogen bromide is prepared, 1.283 L of HBr gas at 25°C and 0.974 atm is bubbled into 250.0 mL of water. Assuming all the HBr dissolves with no volume change, what is the molarity of the hydrobromic acid solution produced?
39. When ammonium nitrate explodes, nitrogen, steam, and oxygen gas are produced. If the explosion is carried out by heating one kilogram of ammonium nitrate sealed in a rigid bomb with a volume of one liter, what is the total pressure produced by the gases before the bomb ruptures? Assume that the reaction goes to completion and that the final temperature is 500°C (3 significant figures).
40. Sulfur dioxide can be removed from the smokestack emissions of power plants by reacting it with hydrogen sulfide, producing sulfur and water. What volume of hydrogen sulfide at 27°C and 755 mm Hg is required to remove the sulfur dioxide produced by a power plant that burns one metric ton of coal containing 5.0% sulfur by mass? How many grams of sulfur are produced by the reaction of H_2S with SO_2?
41. A 1.500-g sample containing sodium nitrate was heated to form $NaNO_2$ and O_2. The oxygen evolved was collected over water at 23°C and 752 mm Hg; its volume was 125.0 mL. Calculate the percentage of $NaNO_3$ in the sample. The vapor pressure of water at 23°C is 21.07 mm Hg.
42. Chlorine can remove the foul smell of H_2S in water. The reaction is

$$H_2S(aq) + Cl_2(aq) \longrightarrow 2H^+(aq) + 2Cl^-(aq) + S(s)$$

If the contaminated water has 5.0 ppm hydrogen sulfide by mass, what volume of chlorine gas at STP is required to remove all the H_2S from 1.00×10^3 gallons of water (d = 1.00 g/mL)? What is the pH of the solution after treatment with chlorine?

Equilibria

43. The equilibrium constant at 25°C for the reaction

$$Br_2(l) + H_2O \rightleftharpoons H^+(aq) + Br^-(aq) + HBrO(aq)$$

is 1.2×10^{-9}. This is the system present in a bottle of "bromine water." Assuming that HBrO does not ionize appreciably, what is the pH of the bromine water?
44. Calculate the pH and the equilibrium concentration of HClO in a 0.10 M solution of hypochlorous acid. K_a HClO = 2.8×10^{-8}.
45. At equilibrium, a gas mixture has a partial pressure of 0.7324 atm for HBr and 2.80×10^{-3} atm for both hydrogen and bromine gases. What is K for the formation of two moles of HBr from H_2 and Br_2?
46. Given

$$HF(aq) \rightleftharpoons H^+(aq) + F^-(aq) \quad K_a = 6.9 \times 10^{-4}$$
$$HF(aq) + F^-(aq) \rightleftharpoons HF_2^-(aq) \quad K = 2.7$$

calculate K for the reaction

$$2HF(aq) \rightleftharpoons H^+(aq) + HF_2^-(aq)$$

47. What is the concentration of fluoride ion in a water solution saturated with BaF_2, $K_{sp} = 1.8 \times 10^{-7}$?
48. Calculate the solubility in grams per 100 mL of BaF_2 in a 0.10 M $BaCl_2$ solution.

Thermodynamics

49. Determine whether the following redox reaction is spontaneous at 25°C and 1 atm:

$$2KIO_3(s) + Cl_2(g) \longrightarrow 2KClO_3(s) + I_2(s)$$

Use data in Appendix 1 and the following information: ΔH_f° $KIO_3(s)$ = −501.4 kJ/mol, S° $KIO_3(s)$ = 151.5 J/mol·K. What is the lowest temperature at which the reaction is spontaneous?
50. Follow the directions for Problem 49 for the reaction

$$2KBrO_3(s) + Cl_2(g) \longrightarrow 2KClO_3(s) + Br_2(l)$$

The following thermodynamic data may be useful:

ΔH_f° $KBrO_3$ = −360.2 kJ/mol; S° $KBrO_3$ = 149.2 J/mol·K
51. Consider the equilibrium system

$$HF(aq) \rightleftharpoons H^+(aq) + F^-(aq)$$

Given ΔH_f° $HF(aq)$ = −320.1 kJ/mol,
ΔH_f° $F^-(aq)$ = −332.6 kJ/mol; S° $F^-(aq)$ = −13.8 J/mol·K;
K_a HF = 6.9×10^{-4} at 25°C
calculate S° for $HF(aq)$.
52. Applying the tables in Appendix 1 to

$$4HCl(g) + O_2(g) \longrightarrow 2Cl_2(g) + 2H_2O(l)$$

determine

(a) whether the reaction is spontaneous at 25°C and 1 atm.
(b) K for the reaction at 25°C.

53. Consider the reaction

$$4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g)$$

(a) Calculate $\Delta H°$ for this reaction. Is it exothermic or endothermic?
(b) Would you expect $\Delta S°$ to be positive or negative? Calculate $\Delta S°$.
(c) Is the reaction spontaneous at 25°C and 1 atm?
(d) At what temperature, if any, is the reaction at equilibrium at 1 atm pressure?

54. Data are given in Appendix 1 for white phosphorus, $P_4(s)$. $P_4(g)$ has the following thermodynamic values: $\Delta H_f° = 58.9$ kJ/mol, $S° = 280.0$ J/K·mol. What is the temperature at which white phosphorus sublimes at 1 atm pressure?

Electrochemistry

55. In the electrolysis of a KI solution, using 5.00 V, how much electrical energy in kilojoules is consumed when one mole of I_2 is formed?

56. If an electrolytic cell producing fluorine uses a current of 7.00×10^3 A (at 10.0 V), how many grams of fluorine gas can be produced in two days (assuming that the cell operates continuously at 95% efficiency)?

57. Sodium hypochlorite is produced by the electrolysis of cold sodium chloride solution. How long must a cell operate to produce 1.500×10^3 L of 5.00% NaClO by mass if the cell current is 2.00×10^3 A? Assume that the density of the solution is 1.00 g/cm^3.

58. Sodium perchlorate is produced by the electrolysis of sodium chlorate. If a current of 1.50×10^3 A passes through an electrolytic cell, how many kilograms of sodium perchlorate are produced in an eight-hour run?

59. Taking $E°_{ox}$ $H_2O_2 = -0.695$ V, determine which of the following species will be reduced by hydrogen peroxide (use Table 17.1 to find $E°_{red}$ values).
(a) $Cr_2O_7^{2-}$ (b) Fe^{2+} (c) I_2 (d) Br_2

60. Taking $E°_{red}$ $H_2O_2 = +1.763$ V, determine which of the following species will be oxidized by hydrogen peroxide (use Table 17.1 to find $E°_{ox}$ values).
(a) Co^{2+} (b) Cl^- (c) Fe^{2+} (d) Sn^{2+}

61. Consider the reduction of nitrate ion in acidic solution to nitrogen oxide ($E°_{red} = 0.964$ V) by sulfur dioxide that is oxidized to sulfate ion ($E°_{red} = 0.155$ V). Calculate the voltage of a cell involving this reaction in which all the gases have pressures of 1.00 atm, all the ionic species (except H^+) are at 0.100 M, and the pH is 4.30.

62. For the reaction in Problem 61 if gas pressures are at 1.00 atm and ionic species are at 0.100 M (except H^+), at what pH will the voltage be 1.000 V?

Unclassified

63. Choose the strongest acid from each group.
(a) HClO, HBrO, HIO (b) HIO, HIO_3, HIO_4
(c) HIO, $HBrO_2$, $HBrO_4$

64. What intermolecular forces are present in the following?
(a) Cl_2 (b) HBr (c) HF
(d) $HClO_4$ (e) MgI_2

65. Write a balanced equation for the reaction of hydrofluoric acid with SiO_2. What volume of 2.0 M HF is required to react with one gram of silicon dioxide?

66. State the oxidation number of N in
(a) NO_2^- (b) NO_2 (c) HNO_3 (d) NH_4^+

67. The density of sulfur vapor at one atmosphere pressure and 973 K is 0.8012 g/L. What is the molecular formula of the vapor?

68. Give the formula of a substance discussed in this chapter that is used
(a) to disinfect water. (b) in safety matches.
(c) to prepare hydrazine. (d) to etch glass.

69. Why does concentrated nitric acid often have a yellow color even though pure HNO_3 is colorless?

70. Explain why
(a) acid strength increases as the oxidation number of the central nonmetal atom increases.
(b) nitrogen dioxide is paramagnetic.
(c) the oxidizing strength of an oxoanion is inversely related to pH.
(d) sugar turns black when treated with concentrated sulfuric acid.

Challenge Problems

71. Suppose you wish to calculate the mass of sulfuric acid that can be obtained from an underground deposit of sulfur 1.00 km^2 in area. What additional information do you need to make this calculation?

72. The reaction

$$4HF(aq) + SiO_2(aq) \longrightarrow SiF_4(aq) + 2H_2O$$

can be used to release gold that is distributed in certain quartz (SiO_2) veins of hydrothermal origin. If the quartz contains 1.0×10^{-3}% Au by weight and the gold has a market value of $425 per troy ounce, would the process be economically feasible if commercial HF (50% by weight, $d = 1.17$ g/cm^3) costs 75¢ a liter? (1 troy ounce = 31.1 g.)

73. The amount of sodium hypochlorite in a bleach solution can be determined by using a given volume of bleach to oxidize excess iodide ion to iodine; ClO^- is reduced to Cl^-. The amount of iodine produced by the redox reaction is determined by titration with sodium thiosulfate, $Na_2S_2O_3$; I_2 is reduced to I^-. The sodium thiosulfate is oxidized to sodium tetrathionate, $Na_2S_4O_6$. In this analysis, potassium iodide was added in excess to 5.00 mL of bleach ($d = 1.00$ g/cm^3). If 25.00 mL of 0.0700 M $Na_2S_2O_3$ was required to reduce all the iodine produced by the bleach back to iodide, what is the mass percent of NaClO in the bleach?

74. What is the minimum amount of sodium azide, NaN_3, that can be added to an automobile airbag to give a volume of 20.0 L of $N_2(g)$ on inflation? Make any reasonable assumptions required to obtain an answer, but state what these assumptions are.