

Some Nonmetals and Metalloids

24





Recently mined sulfur awaits shipment.

OUTLINE

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- 24-2 Xenon Compounds

The Halogens (Group VIIA)

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- 24-6 The Hydrogen Halides and Hydrohalic Acids
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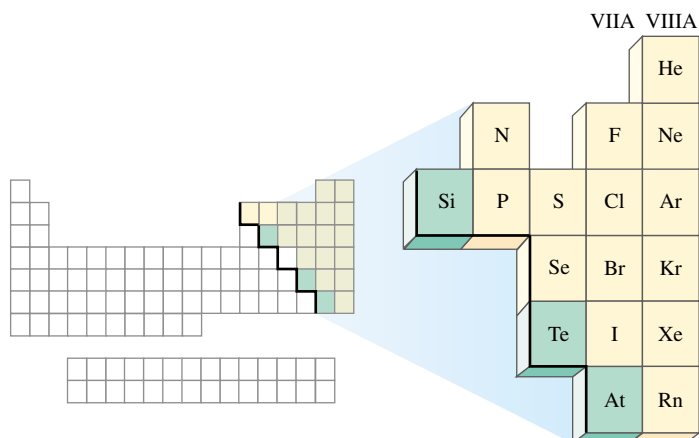
- 24-18 Silicon and the Silicates

OBJECTIVES

After you have studied this chapter, you should be able to

- Describe the occurrence and use of the noble gases
- Describe compounds of the noble gases
- Describe the occurrence and production of the halogens
- Describe some important reactions and compounds of the halogens
- Describe the occurrence and production of sulfur, selenium, and tellurium
- Describe some important reactions and compounds of the heavier Group VIA nonmetals
- Describe the occurrence and production of nitrogen and phosphorus
- Describe some important reactions of nitrogen and phosphorus
- Describe the occurrence and importance of silicon
- Describe a few important compounds of silicon

Only about 20% of the elements are classified as nonmetals. With the exception of H, they are in the upper right-hand corner of the periodic table. In this chapter we shall consider the chemistry and properties of nonmetals and metalloids that illustrate group trends and individuality of elements within groups of nonmetals.



THE NOBLE GASES (GROUP VIII A)

24-1 OCCURRENCE, USES, AND PROPERTIES

The noble gases are very low-boiling gases. Except for radon, they can be isolated by fractional distillation of liquefied air. Radon is collected from the radioactive disintegration of radium salts. Table 24-1 gives the percentage of each noble gas in the atmosphere.

Helium is produced in the United States from some natural gas fields. This source was discovered in 1905 by H. P. Cady and D. F. McFarland at the University of Kansas, when they were asked to analyze a nonflammable component of natural gas from a Kansas gas well. Uses of the noble gases are summarized in Table 24-2.

The noble gases are colorless, tasteless, and odorless. In the liquid and solid states the only forces of attraction among the atoms are very weak dispersion forces. Polarizability and interatomic interactions increase with increasing atomic size, and so melting and boiling points increase with increasing atomic number. The attractive forces among He atoms are so small that He remains liquid at 1 atmosphere pressure even at a temperature of 0.001 K.

Radon is continually produced in small amounts in the uranium radioactive decay sequence (Section 26-11). Radon gas is so unreactive that it eventually escapes from the soil. Measurable concentrations of radon, a radioactive gas, have been observed in basements of many dwellings.

A pressure of about 26 atmospheres is required to solidify He at 0.001 K.

24-2 XENON COMPOUNDS

Until the early 1960s, chemists believed that the Group VIII A elements would not combine chemically with any elements. In 1962, Neil Bartlett (1932–) and his research group at the University of British Columbia were studying the powerful oxidizing agent PtF_6 . They

The noble gases are often called the rare gases. They were formerly called the “inert gases” because it was incorrectly thought that they could not enter into chemical combination.

TABLE 24-1 Percentages (by volume) of Noble Gases in the Atmosphere

He	Ne	Ar	Kr	Xe	Rn
0.0005%	0.015%	0.94%	0.00011%	0.000009%	≈0%

TABLE 24-2 *Uses of the Noble Gases*

Noble Gas	Use	Useful Properties or Reasons
helium	<ol style="list-style-type: none"> 1. Filling of observation balloons and other lighter-than-air craft 2. He/O₂ mixtures, rather than N₂/O₂, for deep-sea breathing 3. Diluent for gaseous anesthetics 4. He/O₂ mixtures for respiratory patients 5. Heat transfer medium for nuclear reactors 6. Industrial applications, such as inert atmosphere for welding easily oxidized metals 7. Liquid He used to maintain very low temperatures in research (cryogenics) 	<p>Nonflammable; 93% of lifting power of flammable hydrogen</p> <p>Low solubility in blood; prevents nitrogen narcosis and “bends”</p> <p>Nonflammable, nonreactive</p> <p>Low density, flows easily through restricted passages</p> <p>Transfers heat readily; does not become radioactive; chemically inert</p> <p>Chemically inert</p> <p>Extremely low boiling point</p>
neon	Neon signs	Even at low Ne pressure, moderate electric current causes bright orange-red glow; can be modified by colored glass or mixing with Ar or Hg vapor
argon	<ol style="list-style-type: none"> 1. Inert atmosphere for welding 2. Filling incandescent light bulbs 	<p>Chemically inert</p> <p>Inert; inhibits vaporization of tungsten filament and blackening of bulbs</p>
krypton	Airport runway and approach lights	Gives longer life to incandescent lights than Ar, but more expensive
xenon	Xe and Kr mixture in high-intensity, short-exposure photographic flash tubes	Both have fast response to electric current
radon	Radiotherapy of cancerous tissues	Radioactive

accidentally prepared and identified O₂⁺PtF₆⁻ by reaction of oxygen with PtF₆. Bartlett reasoned that xenon also should be oxidized by PtF₆ because the first ionization energy of O₂ (1.31 × 10³ kJ/mol) is slightly larger than that of xenon (1.17 × 10³ kJ/mol). He obtained a red crystalline solid initially believed to be Xe⁺PtF₆⁻ but now known to be a more complex compound.

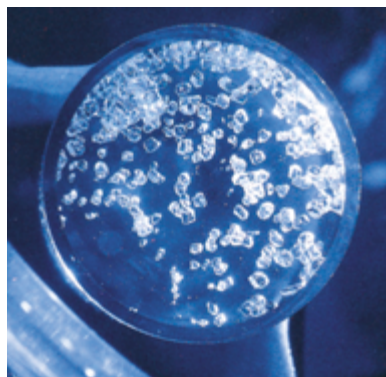
Since Bartlett’s discovery, many other noble gas compounds have been made. All involve very electronegative elements. Most are compounds of Xe, and the best characterized compounds are xenon fluorides. Oxygen compounds are also well known. Reaction of Xe with F₂, an extremely strong oxidizing agent, in different stoichiometric ratios produces xenon difluoride, XeF₂; xenon tetrafluoride, XeF₄; and xenon hexafluoride, XeF₆, all colorless crystals (Table 24-3).

All the xenon fluorides are formed in exothermic reactions. They are reasonably stable, with Xe—F bond energies of about 125 kJ/mol of bonds. For comparison, strong covalent bond energies range from about 170 to 500 kJ/mol, whereas bond energies of hydrogen bonds are typically less than 40 kJ/mol.

THE HALOGENS (GROUP VIIA)

The elements of Group VIIA are known as **halogens** (Greek, “salt formers”). The term “**halides**” is used to describe their binary compounds. The heaviest halogen, astatine, is an artificially produced element of which only short-lived radioactive isotopes are known.

Oxygen is second only to fluorine in electronegativity.



Crystals of the noble gas compound xenon tetrafluoride, XeF₄.

TABLE 24-3 Xenon Fluorides

Compound	Preparation (Molar ratio Xe:F ₂)	Reaction Conditions	e ⁻ Pairs Around Xe	Xe Hybridization, Molecular Geometry*
XeF ₂	1:1–3	400°C or irradiation or elec. discharge	5	sp ³ d, linear
XeF ₄	1:5	Same as for XeF ₂	6	sp ³ d ² , square planar
XeF ₆	1:20	300°C and 60 atm or elec. discharge	7	sp ³ d ³ (?), exact geometry undetermined

*See Tables 8-3, 8-4.

24-3 PROPERTIES

The elemental halogens exist as diatomic molecules containing single covalent bonds. Properties of the halogens show obvious trends (Table 24-4). Their high electronegativities indicate that they attract electrons strongly. Many binary compounds that contain a metal and a halogen are ionic.

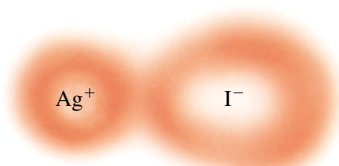
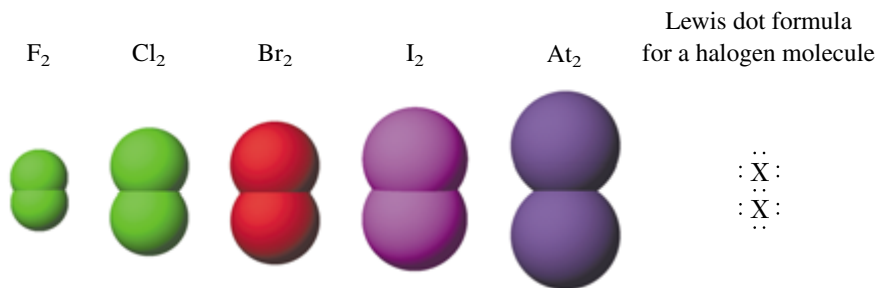
The small fluoride ion (radius = 1.19 Å) is not easily polarized (distorted) by cations, whereas the large iodide ion (radius = 2.06 Å) is. As a result, compounds containing I⁻ ions show greater covalent character than those containing F⁻ ions. The properties of Cl⁻ and Br⁻ ions are intermediate between those of F⁻ and I⁻.

The chemical properties of the halogens resemble one another more closely than do those of elements in any other periodic group, with the exception of the noble gases and possibly the Group IA metals. But their physical properties differ significantly. Melting and boiling points of the halogens increase from F₂ to I₂. This follows their increase in size and increase in ease of polarization of outer-shell electrons by adjacent nuclei, resulting in greater intermolecular attractive (dispersion) forces. All halogens except astatine are decidedly nonmetallic. They show the -1 oxidation number in most of their compounds. Except for fluorine, they also exhibit oxidation numbers of +1, +3, +5, and +7.

TABLE 24-4 Properties of the Halogens

Property	F	Cl	Br	I	At
Physical state (25°C, 1 atm)	gas	gas	liquid	solid	solid
Color	pale yellow	yellow-green	red-brown	violet (g); black (s)	—
Atomic radius (Å)	0.72	1.00	1.14	1.33	1.40
Ionic radius (X ⁻) (Å)	1.19	1.67	1.82	2.06	—
Outer shell e ⁻	2s ² 2p ⁵	3s ² 3p ⁵	4s ² 4p ⁵	5s ² 5p ⁵	6s ² 6p ⁵
First ionization energy (kJ/mol)	1681	1251	1140	1008	890
Electronegativity	4.0	3.0	2.8	2.5	2.1
Melting point (°C, 1 atm)	-220	-101	-7.1	114	—
Boiling point (°C, 1 atm)	-188	-35	59	184	—
X—X bond energy (kJ/mol)	155	242	193	151	—

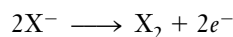
We often represent a halogen atom as X, without specifying a particular halogen.



The diffuse cloud of the I⁻ ion is easily polarized by the small Ag⁺ ion.

24-4 OCCURRENCE, PRODUCTION, AND USES

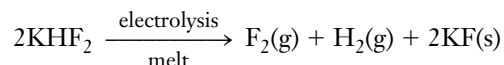
The halogens are so reactive that they do not occur free in nature. The most abundant sources of halogens are halide salts. A primary source of iodine is NaIO₃. The halogens are obtained by oxidation of the halide ions.



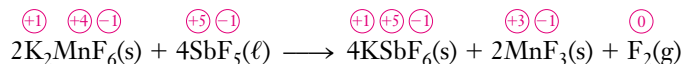
The order of increasing ease of oxidation is F⁻ < Cl⁻ < Br⁻ < I⁻ < At⁻.

Fluorine

Fluorine occurs in large quantities in the minerals *fluorspar* or *fluorite*, CaF₂; *cryolite*, Na₃AlF₆, and *fluorapatite*, Ca₅(PO₄)₃F. It also occurs in small amounts in sea water, teeth, bones, and blood. F₂ is such a strong oxidizing agent that it has not been produced by *direct* chemical oxidation of F⁻ ions. The pale yellow gas is prepared by electrolysis of a molten mixture of KF + HF, or KHF₂, in a Monel metal cell. This must be done under anhydrous conditions because H₂O is more readily oxidized than F⁻.



In 1986, Carl O. Christe discovered that the strong Lewis acid SbF₅ displaces the weaker Lewis acid MnF₄ from the hexafluoromanganate(IV) ion, [MnF₆]²⁻. MnF₄ is thermodynamically unstable, and it decomposes into MnF₃ and F₂. Christe heated a mixture of potassium hexafluoromanganate(IV) and antimony(V) fluoride in a passivated Teflon–stainless steel container at 150°C for 1 hour. He obtained elemental F₂ in better than 40% yield. The overall reaction may be represented as



The reactions of F₂ with other elements are dangerous because of the vigor with which F₂ oxidizes other substances. They must be carried out with *extreme caution!*

Fluorine is used as a fluorinating agent. Many fluorinated organic compounds are stable and nonflammable. They are used as refrigerants, lubricants, plastics (such as Teflon), insecticides, and, until recently, aerosol propellants. Stannous fluoride, SnF₂, is used in toothpaste.

Chlorine

Chlorine (Greek *chloros*, “green”) occurs in abundance in NaCl, KCl, MgCl₂, and CaCl₂ in salt water and in salt beds. It is also present as HCl in gastric juices. The toxic, yellowish green gas is prepared commercially by electrolysis of concentrated aqueous NaCl, in which



Chlorides occur in salt beds.

industrially important H_2 and caustic soda ($NaOH$) are also produced (Section 21-4). More than 26 billion pounds of chlorine was produced in the United States in 1997.

Chlorine is used to produce many commercially important products. Tremendous amounts of it are used in extractive metallurgy and in chlorinating hydrocarbons to produce a variety of compounds (such as polyvinyl chloride, a plastic). Chlorine is present as Cl_2 , $NaClO$, $Ca(ClO)_2$, or $Ca(ClO)Cl$ in household bleaches as well as in bleaches for wood pulp and textiles. Under carefully controlled conditions, Cl_2 is used to kill bacteria in public water supplies.

Bromine

Bromine (Greek *bromos*, “stench”) is less abundant than fluorine and chlorine. In the elemental form it is a dense, freely flowing, corrosive, dark-red liquid with a brownish red vapor at $25^\circ C$. It occurs mainly in $NaBr$, KBr , $MgBr_2$, and $CaBr_2$ in salt water, underground salt brines, and salt beds. The major commercial source for bromine is deep brine wells in Arkansas that contain up to 5000 parts per million (0.5%) of bromide.

Bromine is used in the production of silver bromide for light-sensitive eyeglasses and photographic film; in the production of sodium bromide, a mild sedative; and in methyl bromide, CH_3Br , a soil fumigant that contributes to the destruction of the ozone layer.

Iodine

Iodine (Greek *iodos*, “purple”) is a violet-black crystalline solid with a metallic luster. It exists in equilibrium with a violet vapor at $25^\circ C$. The element can be obtained from dried seaweed or shellfish or from $NaIO_3$ impurities in Chilean nitrate ($NaNO_3$) deposits. It is contained in the growth-regulating hormone thyroxine, produced by the thyroid gland. “Iodized” table salt is about 0.02% KI , which helps prevent goiter, a condition in which the thyroid enlarges. Iodine has been used as an antiseptic and germicide in the form of tincture of iodine, a solution in alcohol.

The preparation of iodine involves reduction of iodate ion from $NaIO_3$ with sodium hydrogen sulfite, $NaHSO_3$.



Iodine is then purified by sublimation (Figure 13-16).



Bromine is a dark red, volatile liquid.



Iodine reacts with starch (as in this potato) to form a deep-blue complex substance.

More recently available is an aqueous solution of an iodine complex of polyvinylpyrrolidone, or “povidone.” It does not sting when applied to open wounds.



Bromine reacts with powdered antimony so vigorously that the flask vibrates.

24-5 REACTIONS OF THE FREE HALOGENS

The free halogens react with most other elements and many compounds. For example, all the Group IA metals react with all the halogens to form simple binary ionic compounds (Section 7-2).

General Reaction	Remarks
$nX_2 + 2M \longrightarrow 2MX_n$	All X_2 with most metals (most vigorous reaction with F_2 and Group IA metals)
$X_2 + nX_2 \longrightarrow 2XX'_n$	Formation of interhalogens ($n = 1, 3, 5, \text{ or } 7$); X is larger than X'
$X_2 + H_2 \longrightarrow 2HX$	With all X_2 .
$3X_2 + 2P \longrightarrow 2PX_3$	With all X_2 , and with As, Sb, Bi replacing P
$5X_2 + 2P \longrightarrow 2PX_5$	Not with I_2 ; also $Sb \longrightarrow SbF_5, SbCl_5$; $As \longrightarrow AsF_5; Bi \longrightarrow BiF_5$
$X_2 + H_2S \longrightarrow S + 2HX$	With all X_2
$X_2 + 2X^- \longrightarrow 2X'^- + X_2$	$F_2 \longrightarrow Cl_2, Br_2, I_2$ $Cl_2 \longrightarrow Br_2, I_2$ $Br_2 \longrightarrow I_2$

The most vigorous reactions are those of F_2 , which usually oxidizes other species to their highest possible oxidation states. Iodine is only a mild oxidizing agent (I^- is a mild reducing agent) and usually does not oxidize substances to high oxidation states. Consider the following reactions of halogens with two metals that exhibit variable oxidation numbers.



Iron and chlorine react to form iron(III) chloride, $FeCl_3$.

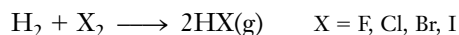
With Fe		With Cu	
$2Fe + 3F_2 \longrightarrow 2FeF_3$ (only)	$\overset{+3}{\text{Fe}}$	$Cu + X_2 \longrightarrow CuX_2$ ($X = F, Cl, Br$)	$\overset{+2}{\text{Cu}}$
$2Fe + 3Cl_2$ (excess) $\longrightarrow 2FeCl_3$	$\overset{+3}{\text{Fe}}$		
$Fe + Cl_2$ (lim. amt.) $\longrightarrow FeCl_2$	$\overset{+2}{\text{Fe}}$		
$Fe + I_2 \longrightarrow FeI_2$ (only)	$\overset{+2}{\text{Fe}}$	$2Cu + I_2 \longrightarrow 2CuI$ (only)	$\overset{+1}{\text{Cu}}$
$Fe^{3+} + I^- \longrightarrow Fe^{2+} + \frac{1}{2}I_2$		$Cu^{2+} + 2I^- \longrightarrow CuI + \frac{1}{2}I_2$	$\overset{+1}{\text{Cu}}$

24-6 THE HYDROGEN HALIDES AND HYDROHALIC ACIDS

The hydrogen halides are colorless gases that dissolve in water to give acidic solutions called hydrohalic acids. The gases have piercing, irritating odors. The abnormally high melting and boiling points of HF are due to its very strong hydrogen bonding (Figure 13-5).

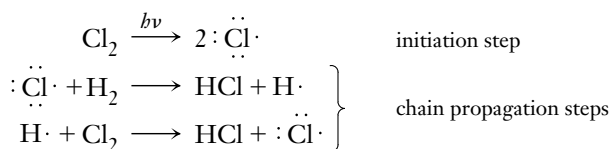
For instance, aqueous solutions of hydrogen fluoride are called hydrofluoric acid.

Hydrogen halides can be prepared by combination of the elements.



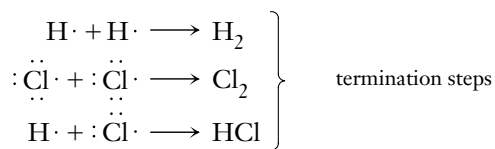
The reaction with F_2 to produce HF is explosive and very dangerous. The reaction producing HCl does not occur significantly in the dark but occurs rapidly by a photochemical **chain reaction** when the mixture is exposed to light. Light energy is absorbed by Cl_2 molecules, which break apart into very reactive chlorine atoms, which have unpaired electrons (**radicals**). These subsequently attack H_2 molecules and produce HCl molecules, leaving hydrogen atoms (also radicals). The hydrogen radicals, in turn, attack Cl_2 molecules to form HCl molecules and chlorine radicals, and the process continues.

A photochemical reaction is one in which a species (usually a molecule) interacts with radiant energy to produce very reactive species. These then undergo further reaction.



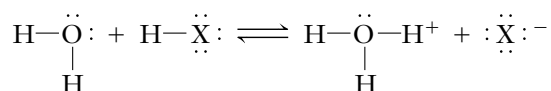
This chain reaction continues as long as there is a significant concentration of radicals.

Termination steps eliminate two radicals and can eventually terminate the reaction.



The reaction of H_2 with Br_2 is also a photochemical reaction. That of H_2 with I_2 is very slow, even at high temperatures and with illumination.

All hydrogen halides react with H_2O to produce *hydrohalic acids* that ionize.



The reaction is essentially complete for dilute aqueous solutions of HCl, HBr, and HI. In dilute aqueous solutions; HF is a weak acid ($K_a = 7.2 \times 10^{-4}$). In concentrated solutions more acidic dimeric $(\text{HF})_2$ units are present (Figure 24-1). They ionize as follows.

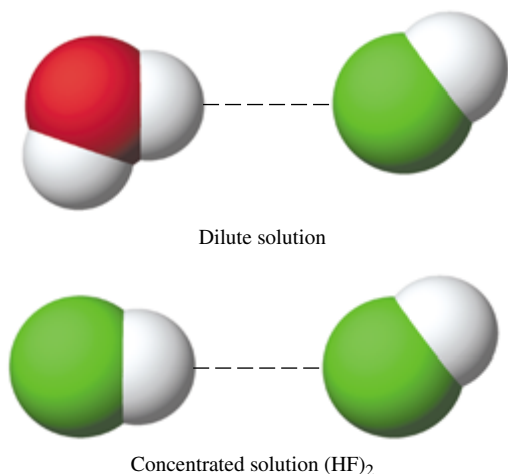
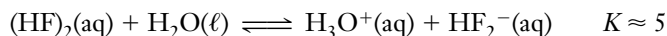
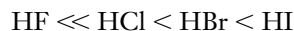


Figure 24-1 Hydrogen bonding (dashed lines) in dilute and concentrated aqueous solutions of hydrofluoric acid, HF.

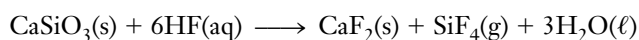


The order of increasing acid strengths of the aqueous hydrohalic acids is:



The only acid used in industry to a greater extent than HCl is H_2SO_4 . Hydrochloric acid is used in the production of metal chlorides, dyes, and many other commercially important products. It is also used on a large scale to dissolve metal oxide coatings from iron and steel prior to galvanizing or enameling.

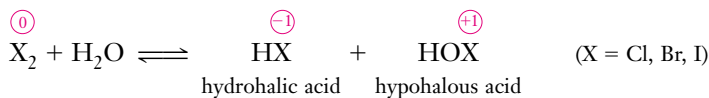
Hydrofluoric acid is used in the production of fluorine-containing compounds and for etching glass. The acid reacts with silicates, such as calcium silicate, CaSiO_3 , in the glass to produce a very volatile and thermodynamically stable compound, silicon tetrafluoride, SiF_4 .



24-7 THE OXOACIDS (TERNARY ACIDS) OF THE HALOGENS

Table 24-5 lists the known oxoacids of the halogens, their sodium salts, and some trends in properties. Only three oxoacids, HClO_4 , HIO_3 , and H_5IO_6 , have been isolated in anhydrous form. The others are known only in aqueous solution. In all these acids the H is bonded through an O.

The only oxoacid of fluorine that has been prepared is unstable hypofluorous acid, HOF. Aqueous *hypohalous acids* (except HOF) can be prepared by reaction of free halogens (Cl_2 , Br_2 , I_2) with cold water. The smaller the halogen, the farther to the right the equilibrium lies.



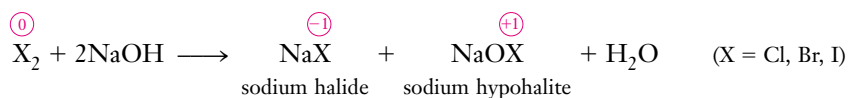
In HOF the oxidation states are $\text{F} = -1$, $\text{H} = +1$, $\text{O} = 0$.

These reactions all involve *disproportionation* of the halogen.

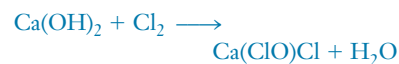
Hypohalite salts can be prepared by reactions of the halogens with *cold* dilute bases.

TABLE 24-5 Oxoacids of the Halogens and Their Salts

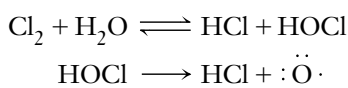
Oxidation State	Acid	Name of Acid	Thermal Stability and Acid Strength	Oxidizing Power of Acid	Sodium Salt	Name of Salt	Thermal Stability	Oxidizing Power and Hydrolysis of Anion	Nature of Halogen
+1	HXO (HOX)	hypohalous acid			NaXO (NaOX)	sodium hypohalite			$\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$
+3	HXO_2	halous acid			NaXO_2	sodium halite			$\text{X} = \text{Cl}, \text{Br} (?)$
+5	HXO_3	halic acid			NaXO_3	sodium halate			$\text{X} = \text{Cl}, \text{Br}, \text{I}$
+7	HXO_4	perhalic acid			NaXO_4	sodium perhalate			$\text{X} = \text{Cl}, \text{Br}, \text{I}$
+7	H_5XO_6	paraperhalic acid			several types	sodium paraperhalates			$\text{X} = \text{I}$ only



Solid household bleaches are usually $\text{Ca}(\text{ClO})\text{Cl}$. This is prepared by reaction of Cl_2 with $\text{Ca}(\text{OH})_2$.



The hypohalites are used as bleaching agents. Sometimes Cl_2 is used as a bleach or as a disinfectant, as in public water supplies. It reacts slowly with H_2O to form HCl and HOCl . The hypochlorous acid then decomposes into HCl and O radicals, which kill bacteria.



These oxygen radicals are very strong oxidizing agents. They are the effective bleaching and disinfecting agent in aqueous solutions of Cl_2 or hypochlorite salts.

Perchloric acid is the strongest of all common acids with respect to ionization. Hot, concentrated perchloric acid is a very strong oxidizing agent that can explode in the presence of reducing agents. Cold, dilute perchloric acid is only a weak oxidizing agent.

SULFUR, SELENIUM, AND TELLURIUM

24-8 OCCURRENCE, PROPERTIES, AND USES

Each Group VIA element is less electronegative than its neighboring halogen. Oxygen and sulfur are clearly nonmetallic, but selenium is less so. Tellurium is usually classified as a metalloid and forms metal-like crystals. Its chemistry is mostly that of a nonmetal. Polonium is a metal. All 29 isotopes of polonium are radioactive.

Irregularities in the properties of elements within a given family increase toward the middle of the periodic table. There are larger differences in the properties of the Group VIA elements than in the properties of the halogens. The properties of elements in the *second period* usually differ significantly from those of other elements in their families, because second-period elements have no low-energy *d* orbitals. So, the properties of oxygen are not very similar to those of the other Group VIA elements (Table 24-6). The maximum number of electrons that O can have in its valence shell is eight. The heavier Group VIA elements—S, Se, Te, and Po—have *d* orbitals in their valence shells; one or

The *d* orbitals do not occur until the third energy level.

TABLE 24-6 Some Properties of Group VIA Elements

Property	O	S	Se	Te	Po
Physical state (1 atm, 25°C)	gas	solid	solid	solid	solid
Color	colorless (very pale blue)	yellow	red-gray to black	brass-colored, metallic luster	—
Outermost electrons	$2s^2 2p^4$	$3s^2 3p^4$	$4s^2 4p^4$	$5s^2 5p^4$	$6s^2 6p^4$
Melting point (1 atm, °C)	-218	112	217	450	254
Boiling point (1 atm, °C)	-183	444	685	990	962
Electronegativity	3.5	2.5	2.4	2.1	1.9
First ionization energy (kJ/mol)	1314	1000	941	869	812
Atomic radius (Å)	0.73	1.03	1.19	1.42	1.68
Ionic (2-) radius (Å)	1.26	1.70	1.84	2.07	—
Common oxidation states	usually -2	-2, +2, +4, +6	-2, +2, +4, +6	-2, +2, +4, +6	-2, +6



◀ Native sulfur. Elemental sulfur is deposited at the edges of some hot springs and geysers. This formation surrounds Emerald Lake in Yosemite National Park.

more of these d orbitals can accommodate additional electrons to form up to six bonds. Thus each of the Group VIA elements except O can bond covalently to as many as six other atoms.

Sulfur

Sulfur makes up about 0.05% of the earth's crust. It was one of the elements known to the ancients. It was used by the Egyptians as a yellow coloring, and it was burned in some religious ceremonies because of the unusual odor it produced; it is the "brimstone" of the Bible. Alchemists tried to incorporate its "yellowness" into other substances to produce gold.

Sulfur occurs as the free element—predominantly S_8 molecules—and in metal sulfides such as galena, PbS ; iron pyrite, FeS_2 ; and cinnabar, HgS . To a lesser extent, it occurs as metal sulfates such as barite, $BaSO_4$, and gypsum, $CaSO_4 \cdot 2H_2O$, and in volcanic gases as H_2S and SO_2 .

Sulfur is found in much naturally occurring organic matter, such as petroleum and coal. Its presence in fossil fuels causes environmental and health problems because many sulfur-containing compounds burn to produce sulfur dioxide, an air pollutant.

Much of the sulfur used in the United States is recovered from sulfur compounds in natural gas and oil. During the oil-refining process, these compounds are reduced to hydrogen sulfide, which is then oxidized to sulfur in the Claus furnace.



Elemental sulfur is mined along the U.S. Gulf Coast by the **Frasch process** (Figure 24-2). Most of it is used in the production of sulfuric acid, H_2SO_4 , the most important of all industrial chemicals. Sulfur is used in the vulcanization of rubber and in the synthesis of many important sulfur-containing organic compounds.

In each of the three physical states, elemental sulfur exists in many forms. The two most stable forms of sulfur, the rhombic (mp $112^\circ C$) and monoclinic (mp $119^\circ C$) crystalline modifications, consist of different arrangements of S_8 molecules. These are puckered rings containing eight sulfur atoms (Figure 2-3) and all S—S single bonds. Above $150^\circ C$, sulfur becomes increasingly viscous and darkens as the S_8 rings break apart into chains that interlock with one another through S—S bonds. The viscosity reaches a maximum at $180^\circ C$, at which point sulfur is dark brown. Above $180^\circ C$, the liquid thins as the chains are broken down into smaller chains. At $444^\circ C$, sulfur boils to give a vapor containing S_8 , S_6 , S_4 , and S_2 molecules.

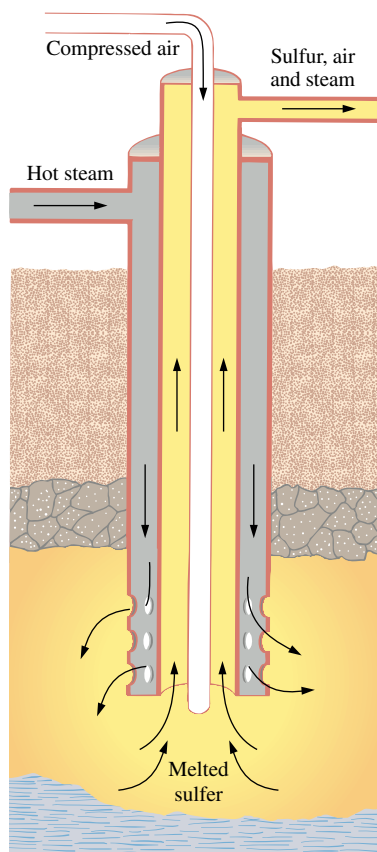
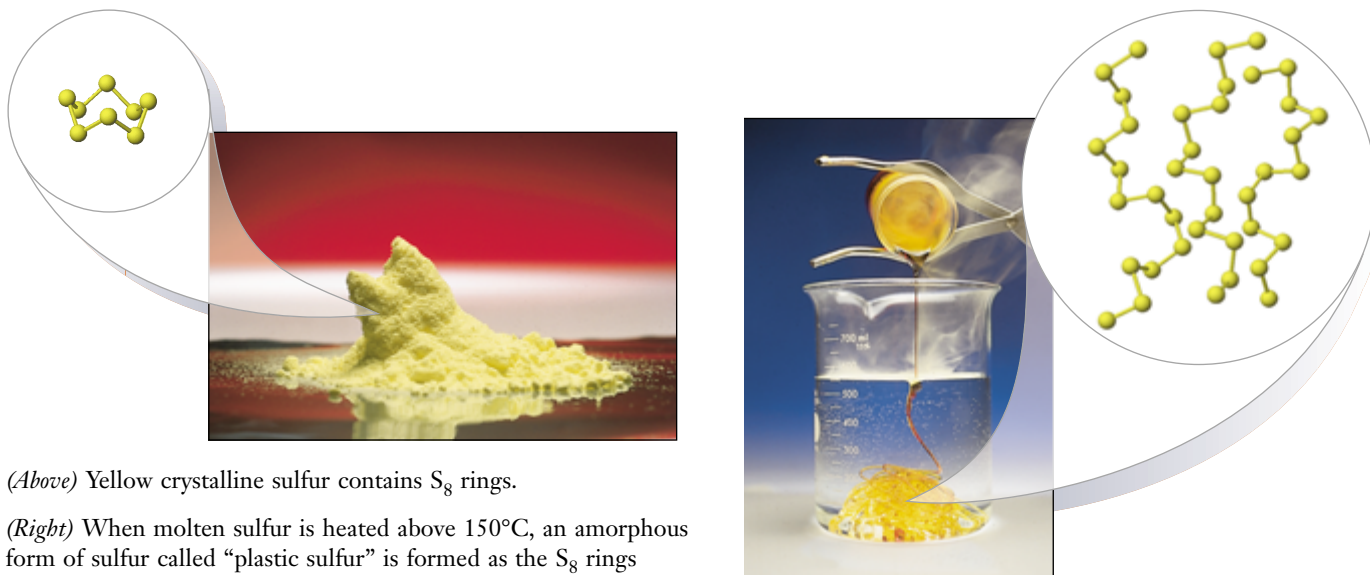


Figure 24-2 The Frasch process for mining sulfur. Three concentric pipes are used. Water at about $170^\circ C$ and a pressure of 100 lb/in^2 (7 kg/cm^2) is forced down the outermost pipe to melt the sulfur. Hot compressed air is pumped down the innermost pipe. It mixes with the molten sulfur to form a froth, which rises through the third pipe.



(Above) Yellow crystalline sulfur contains S_8 rings.

(Right) When molten sulfur is heated above 150°C , an amorphous form of sulfur called “plastic sulfur” is formed as the S_8 rings break and the fragments link to form long chains.

Selenium

Selenium is quite rare ($9 \times 10^{-6}\%$ of the earth’s crust). It occurs mainly as an impurity in sulfur, sulfide, and sulfate deposits. It is obtained from the flue dusts that result from roasting sulfide ores and from the “anode mud” formed in the electrolytic refining of copper. It is used as a red coloring in glass. The gray crystalline allotropic form of selenium has an electrical conductivity that is very light-sensitive, so it is used in photocopy machines and in solar cells.

Tellurium

Tellurium is even less abundant ($2 \times 10^{-7}\%$ of the earth’s crust) than selenium. It occurs mainly in sulfide ores, especially with copper sulfide, and as the tellurides of gold and silver. It, too, is obtained from the “anode mud” from refining of copper. The element forms brass-colored, shiny, hexagonal crystals having low electrical conductivity. It is added to some metals, particularly lead, to increase electrical resistance and improve resistance to heat, corrosion, mechanical shock, and wear.

24-9 REACTIONS OF GROUP VIA ELEMENTS

Some reactions of the Group VIA elements are summarized in the following table.

General Equation	Remarks
$x\text{E} + y\text{M} \longrightarrow \text{M}_y\text{E}_x$	With many metals
$z\text{E} + \text{M}_x\text{E}_y \longrightarrow \text{M}_x\text{E}_{y+z}$	Especially with S, Se
$\text{E} + \text{H}_2 \longrightarrow \text{H}_2\text{E}$	Decreasingly in the series O_2 , S, Se, Te
$\text{E} + 3\text{F}_2 \longrightarrow \text{EF}_6$	With S, Se, Te, and excess F_2
$2\text{E} + \text{Cl}_2 \longrightarrow \text{E}_2\text{Cl}_2$	With S, Se (Te gives TeCl_2); also with Br_2
$\text{E}_2\text{Cl}_2 + \text{Cl}_2 \longrightarrow 2\text{ECl}_2$	With S, Se; also with Br_2
$\text{E} + 2\text{Cl}_2 \longrightarrow \text{ECl}_4$	With S, Se, Te, and excess Cl_2 ; also with Br_2
$\text{E} + \text{O}_2 \longrightarrow \text{EO}_2$	With S (with Se, use $\text{O}_2 + \text{NO}_2$)

E represents a Group VIA element.

24-10 HYDRIDES OF GROUP VIA ELEMENTS

All the Group VIA elements form covalent compounds of the type H_2E ($E = O, S, Se, Te, Po$) in which the Group VIA element is in the -2 oxidation state. H_2O is a liquid that is essential for animal and plant life. H_2S , H_2Se , and H_2Te are colorless, noxious, poisonous gases. They are even more toxic than HCN. Egg protein contains sulfur, and its decomposition forms H_2S , giving off the odor of rotten eggs. H_2Se and H_2Te smell even worse. Their odors are usually ample warning of the presence of these poisonous gases.

Both the melting point and boiling point of water are very much higher than expected by comparison with those of the heavier hydrides (Figure 13-5). This is a consequence of hydrogen bonding in ice and liquid water (Section 13-2) caused by the strongly dipolar nature of water molecules. The electronegativity differences between H and the other VIA elements are much smaller than that between H and O, so no H-bonding occurs in H_2S , H_2Se , or H_2Te .

Aqueous solutions of hydrogen sulfide, selenide, and telluride are acidic; acid strength increases as the group is descended: $H_2S < H_2Se < H_2Te$. The same trend was observed for increasing acidity of the hydrogen halides. The acid ionization constants are

	H_2S	H_2Se	H_2Te
$H_2E \rightleftharpoons H^+ + HE^-$	$K_{a1}: 1.0 \times 10^{-7}$	1.9×10^{-4}	2.3×10^{-3}
$HE^- \rightleftharpoons H^+ + E^{2-}$	$K_{a2}: 1.0 \times 10^{-19}$	$\approx 10^{-11}$	$\approx 1.6 \times 10^{-11}$

H_2S is a stronger acid than H_2O .
The solubility of H_2S in water is
approximately 0.10 mol/L at 25°C.

Here E represents S, Se, or Te.

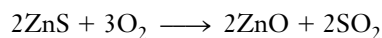
24-11 GROUP VIA OXIDES

Although others exist, the most important VIA oxides are the dioxides, which are acid anhydrides of H_2SO_3 , H_2SeO_3 , and H_2TeO_3 ; and the trioxides, which are anhydrides of H_2SO_4 , H_2SeO_4 , and H_6TeO_6 . Let us consider SO_2 and SO_3 as examples.

Sulfur Dioxide, SO_2

Sulfur dioxide is a colorless, poisonous, corrosive gas with a very irritating odor. Even in small quantities, it causes coughing and nose, throat, and lung irritation. It is an angular molecule with trigonal planar electronic geometry, sp^2 hybridization at the S atom, and resonance stabilization.

Sulfur dioxide is produced in reactions such as the combustion of sulfur-containing fossil fuels and the roasting of sulfide ores.



SO_2 is a waste product of these operations. In the past, it was released into the atmosphere along with some SO_3 produced by its reaction with O_2 . A more environmentally friendly practice now is to trap SO_2 and SO_3 and use them to make H_2SO_4 . Some coal contains up to 5% sulfur, so both SO_2 and SO_3 are present in the flue gases when coal is burned. No way has been found to remove all the SO_2 from flue gases of power plants. One way of removing most of the SO_2 involves the injection of limestone, $CaCO_3$, into the combustion zone of the furnace. Here $CaCO_3$ decomposes to lime, CaO . This then

+4 Oxidation State

Formula	Name
H_2SO_3	sulfurous acid
H_2SeO_3	selenous acid
H_2TeO_3	tellurous acid

+6 Oxidation State

Formula	Name
H_2SO_4	sulfuric acid
H_2SeO_4	selenic acid
H_6TeO_6	telluric acid

If the SO_2 and SO_3 are allowed to
escape into the atmosphere, they cause
highly acidic rain.



Large amounts of SO_2 and H_2S are released during volcanic eruptions.

combines with SO_2 to form calcium sulfite (CaSO_3), an ionic solid, which is collected and disposed of as solid waste



This process is called scrubbing, and a disadvantage of it is the formation of huge quantities of solid waste (CaSO_3 , unreacted CaO , and by-products).

Catalytic oxidation is now used by the smelting industry to convert SO_2 into SO_3 . This is then dissolved in water to make solutions of H_2SO_4 (up to 80% by mass). The gases containing SO_2 are passed through a series of condensers containing catalysts to speed up the reaction. In some cases the impure H_2SO_4 can be used in other operations in the same plant.

Sulfur Trioxide, SO_3

Sulfur trioxide is a liquid that boils at 44.8°C . It is the anhydride of H_2SO_4 . It is formed by the reaction of SO_2 with O_2 . The reaction is very exothermic, but ordinarily very slow. It is catalyzed commercially in the **contact process** by spongy Pt, SiO_2 , or vanadium(V) oxide, V_2O_5 , at high temperatures (400 to 700°C).



The high temperature favors SO_2 and O_2 but allows the reaction to proceed much more rapidly, so it is economically advantageous. The SO_3 is then removed from the gaseous reaction mixture by dissolving it in concentrated H_2SO_4 (95% H_2SO_4 by mass) to produce polysulfuric acids—mainly pyrosulfuric acid, $\text{H}_2\text{S}_2\text{O}_7$. This is called oleum, or fuming sulfuric acid. The addition of fuming sulfuric acid to water produces commercial H_2SO_4 .



In the presence of certain catalysts, sulfur dioxide in polluted air reacts rapidly with O_2 to form SO_3 . Particulate matter, or suspended microparticles, such as NH_4NO_3 and elemental S, act as efficient catalysts.



The rose on the left is in an atmosphere of sulfur dioxide, SO_2 . Gaseous SO_2 and aqueous solutions of HSO_3^- and SO_3^{2-} ions are used as bleaching agents. A similar process is used to bleach wood pulp before it is converted to paper.

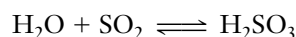
The prefix *pyro* means “heat” or “fire.” Pyrosulfuric acid may also be obtained by heating concentrated sulfuric acid, which results in the elimination of one molecule of water from two molecules of sulfuric acid.



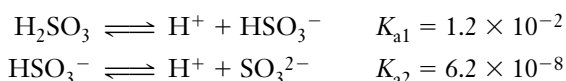
24-12 OXOACIDS OF SULFUR

Sulfurous Acid, H_2SO_3

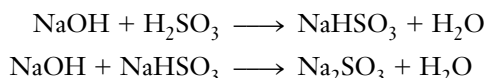
Sulfur dioxide readily dissolves in water to produce solutions of sulfurous acid, H_2SO_3 . The acid has not been isolated in anhydrous form.



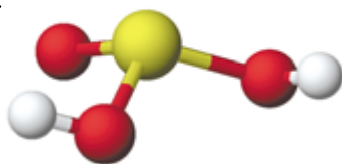
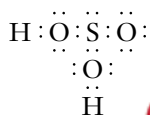
The acid ionizes in two steps in water



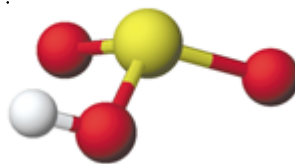
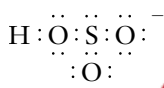
When excess SO_2 is bubbled into aqueous NaOH , sodium hydrogen sulfite, NaHSO_3 is produced. This acid salt can be neutralized with additional NaOH or Na_2CO_3 to produce sodium sulfite.



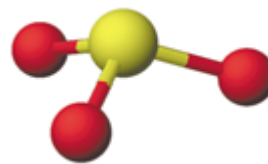
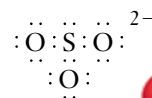
The sulfite ion is pyramidal and has tetrahedral electronic geometry as predicted by the VSEPR theory.



Sulfurous acid, H_2SO_3



Hydrogen sulfite ion, HSO_3^-



Sulfite ion, SO_3^{2-}

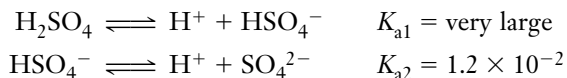
Sulfuric Acid, H_2SO_4

More than 40 million tons of sulfuric acid are produced annually worldwide. The contact process is used for the commercial production of most sulfuric acid. The solution sold commercially as “concentrated sulfuric acid” is 96–98% H_2SO_4 by mass and is about 18 molar H_2SO_4 .

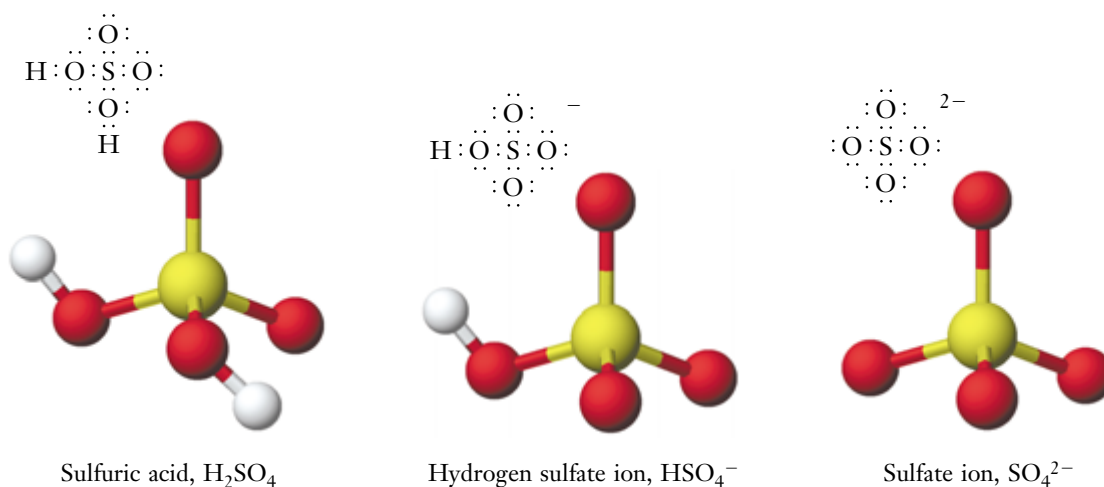
Pure H_2SO_4 is a colorless, oily liquid that freezes at 10.4°C and boils at 290 to 317°C while partially decomposing to SO_3 and water. There is some hydrogen bonding in solid and liquid H_2SO_4 .

Tremendous amounts of heat are evolved when concentrated sulfuric acid is diluted. This illustrates the strong affinity of H_2SO_4 for water. H_2SO_4 is often used as a dehydrating agent. **Dilutions should always be performed by adding the acid to water to avoid spattering the acid.**

Sulfuric acid is a strong acid with respect to the first step of its ionization in water. The second ionization occurs to a lesser extent (Example 18-17).



Pouring concentrated H_2SO_4 into an equal volume of H_2O liberates a lot of heat—enough to raise the temperature of the resulting solution from room temperature to 121°C .



NITROGEN AND PHOSPHORUS

The Group VA elements provide a dramatic illustration of the vertical trends in metallic properties. In this family, nitrogen and phosphorus are nonmetals, arsenic is predominantly nonmetallic, antimony is more metallic, and bismuth is definitely metallic. Properties of the Group VA elements are listed in Table 24-7.

Oxidation states of the VA elements range from -3 to $+5$. Odd-numbered oxidation states are favored. The VA elements form very few monatomic ions. Ions with a charge of $3-$ occur for N and P, as in Mg₃N₂ and Ca₃P₂.

All of the Group VA elements show the -3 oxidation state in covalent compounds such as NH₃ and PH₃. The $+5$ oxidation state is found only in covalent compounds such as phosphorus pentafluoride, PF₅; nitric acid, HNO₃; and phosphoric acid, H₃PO₄; and in polyatomic ions such as NO₃⁻ and PO₄³⁻. Each Group VA element exhibits the $+3$ oxidation state in one of its oxides, for instance, N₂O₃ and P₄O₆. These are acid anhydrides of nitrous acid, HNO₂, and phosphorous acid, H₃PO₃; both are weak acids. No other element exhibits more oxidation states than nitrogen (Table 24-8).

TABLE 24-7 Properties of the Group VA Elements

Property	N	P	As	Sb	Bi
Physical state (1 atm, 25°C)	gas	solid	solid	solid	solid
Color	colorless	red, white, black	yellow, gray	yellow, gray	gray
Outermost electrons	2s ² 2p ³	3s ² 3p ³	4s ² 4p ³	5s ² 5p ³	6s ² 6p ³
Melting point (°C)	-210	44 (white)	813 (gray, 28 atm)*	631 (gray)	271
Boiling point (°C)	-196	280 (white)	sublimes 613	1750	1560
Atomic radius (Å)	0.75	1.10	1.20	1.40	1.50
Electronegativity	3.0	2.1	2.1	1.9	1.8
First ionization energy (kJ/mol)	1402	1012	947	834	703
Oxidation states	-3 to +5	-3 to +5	-3 to +5	-3 to +5	-3 to +5

*Sublimes at lower pressures.

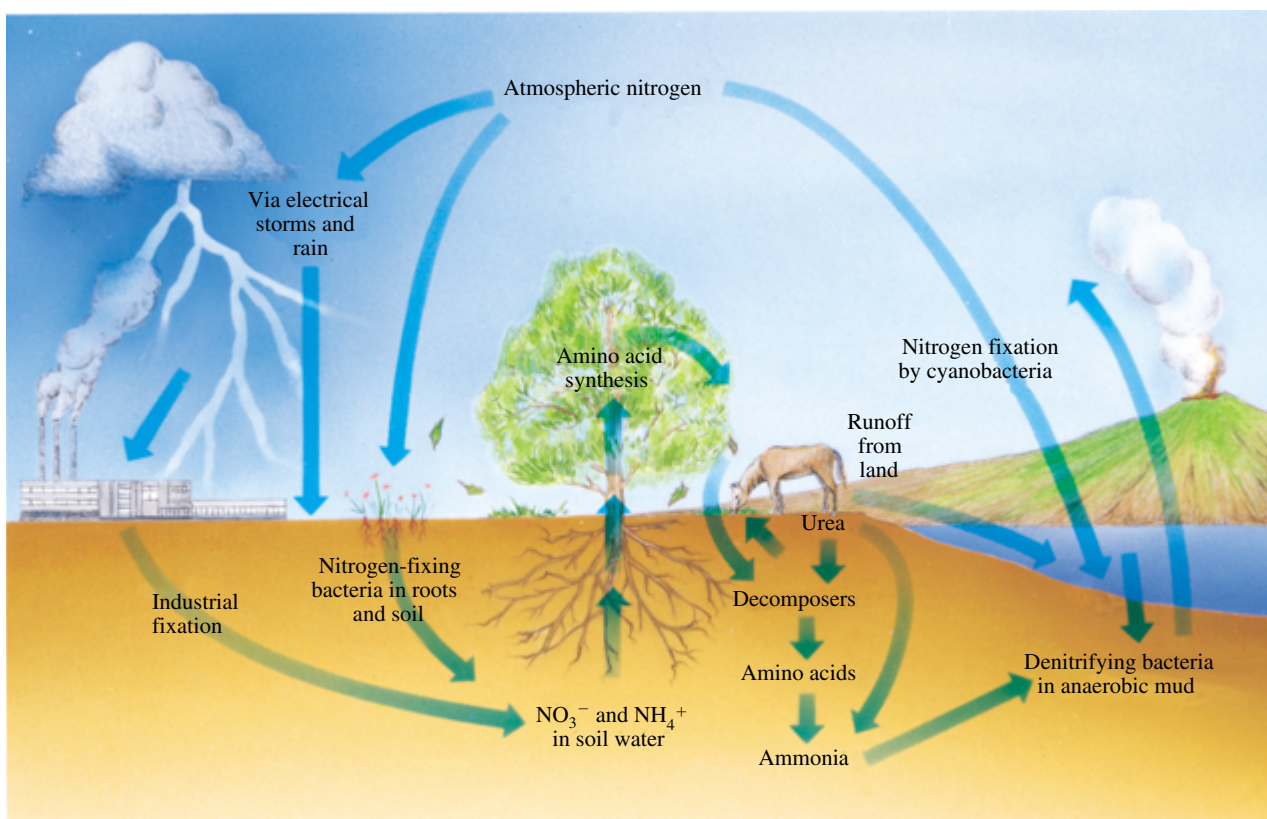
TABLE 24-8 Oxidation States of Nitrogen and Examples

-3	-2	-1	0	+1	+2	+3	+4	+5
NH ₃ ammonia	N ₂ H ₄ hydrazine	NH ₂ OH hydroxylamine	N ₂ nitrogen	N ₂ O dinitrogen oxide	NO nitrogen oxide	N ₂ O ₃ dinitrogen trioxide	NO ₂ nitrogen dioxide	N ₂ O ₅ dinitrogen pentoxide
NH ₄ ⁺ ammonium ion		NH ₂ Cl chloramine		H ₂ N ₂ O ₂ hyponitrous acid		HNO ₂ nitrous acid	N ₂ O ₄ dinitrogen tetroxide	HNO ₃ nitric acid
NH ₂ ⁻ amide ion						NO ₂ ⁻ nitrite ion		NO ₃ ⁻ nitrate ion

24-13 OCCURRENCE OF NITROGEN

Nitrogen, N₂, is a colorless, odorless, tasteless gas that makes up about 75% by mass and 78% by volume of the atmosphere. Nitrogen compounds form only a minor portion of the earth's crust, but all living matter contains nitrogen. The primary natural inorganic deposits of nitrogen are very localized. They consist mostly of KNO₃ and NaNO₃. Most sodium nitrate is mined in Chile.

Every protein contains nitrogen in each of its fundamental amino acid units.



A schematic representation of the nitrogen cycle.

The extreme abundance of N_2 in the atmosphere and the low relative abundance of nitrogen compounds elsewhere are due to the chemical inertness of N_2 molecules. This results from the very high bond energy of the $N\equiv N$ bond (945 kJ/mol).

Although N_2 molecules are relatively unreactive, nature provides mechanisms by which N atoms are incorporated into proteins, nucleic acids, and other nitrogenous compounds. The **nitrogen cycle** is the complex series of reactions by which nitrogen is slowly but continually recycled in the atmosphere (our nitrogen reservoir), lithosphere (earth), and hydrosphere (water).

When N_2 and O_2 molecules collide near a bolt of lightning, they can absorb enough electrical energy to produce molecules of NO. An NO molecule is quite reactive because it contains one unpaired electron. NO reacts readily with O_2 to form nitrogen dioxide, NO_2 . Most NO_2 dissolves in rainwater and falls to the earth's surface. Bacterial enzymes reduce the nitrogen in a series of reactions in which amino acids and proteins are produced. These are then used by plants, eaten by animals, and metabolized. The metabolic products are excreted as nitrogenous compounds such as urea, $(NH_2)_2CO$, and ammonium salts such as $NaNH_4HPO_4$. These can also be enzymatically converted to ammonia, NH_3 , and amino acids.

Nitrogen is converted directly into NH_3 in another way. Members of the class of plants called legumes (including soybeans, alfalfa, and clover) have nodules on their roots. Within the nodules live bacteria that produce an enzyme called nitrogenase. These bacteria extract N_2 directly from air trapped in the soil and convert it into NH_3 . The ability of nitrogenase to catalyze this conversion, called **nitrogen fixation**, at ordinary temperatures and pressures with very high efficiency is a marvel to scientists. They must resort to very extreme and costly conditions to produce NH_3 from nitrogen and hydrogen (the Haber process, Section 17-7).

Ammonia is the source of nitrogen in many fertilizers. Unfortunately, nature does not produce NH_3 and related plant nutrient compounds rapidly enough to provide an adequate food supply for the world's growing population. Commercial synthetic fertilizers have helped to lessen this problem, but at great cost for the energy that is required to produce them.

Nitrogen is sold as compressed gas in cylinders. The boiling point of N_2 is $-195.8^\circ C$ ($-320^\circ F$). N_2 is obtained by fractional distillation of liquid air.



Root nodules on soybeans.



Great advances have been made in cattle breeding in recent decades. Semen from superior bulls can be collected and stored in liquid nitrogen for 30 years or more.

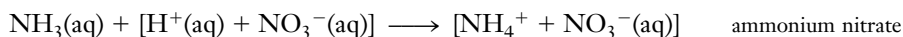
24-14 HYDROGEN COMPOUNDS OF NITROGEN

We have already described ammonia and some of its reactions. Please review Sections 17-7 and 18-4.

Liquid ammonia (bp $-33.4^\circ C$) is used as a solvent for some chemical reactions. It is hydrogen bonded, just as H_2O is, but NH_3 is a much more basic solvent. Its weak *auto-ionization* produces the ammonium ion, NH_4^+ , and the amide ion, NH_2^- . This is similar to H_2O , which ionizes to produce some H_3O^+ and OH^- ions.

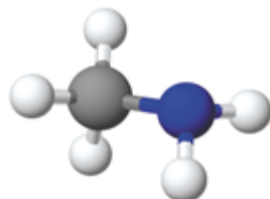
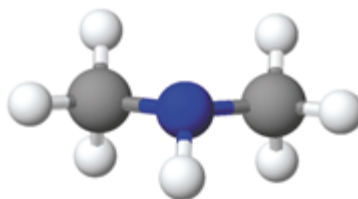
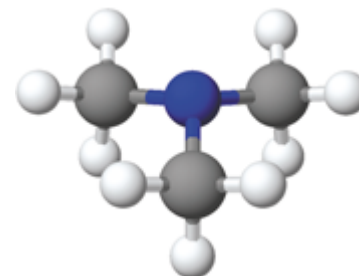


Many ammonium salts are known. Most are very soluble in water. They can be prepared by reactions of ammonia with acids. Reaction with nitric acid gives ammonium nitrate.



Amines are organic compounds that are structurally related to ammonia. We think of them as being derived from NH_3 by the replacement of one or more hydrogens with

organic groups (Sections 18-4 and 27-12). All involve sp^3 -hybridized N. All are weak bases because of the unshared pair of electrons on N.

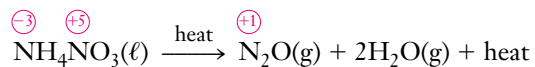
Ammonia, NH_3 Methylamine, CH_3NH_2 Dimethylamine, $(\text{CH}_3)_2\text{NH}$ Trimethylamine, $(\text{CH}_3)_3$

24-15 NITROGEN OXIDES

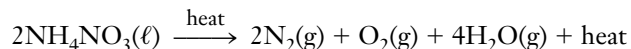
Nitrogen forms several oxides, in which it exhibits positive oxidation states of 1 to 5 (Table 24-8). All have positive free energies of formation, owing to the high dissociation energy of N_2 and O_2 molecules. All are gases except N_2O_5 , a solid that melts at 30.0°C .

Dinitrogen Oxide (+1 Oxidation State)

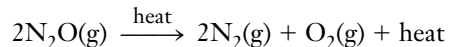
Molten ammonium nitrate undergoes autooxidation–reduction (decomposition) at 170 to 260°C to produce dinitrogen oxide, also called nitrous oxide.



At higher temperatures, explosions occur, producing N_2 , O_2 , and H_2O .



Dinitrogen oxide supports combustion because it produces O_2 when heated.

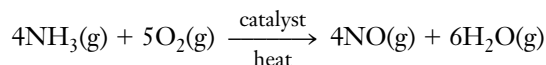


The molecule is linear but unsymmetrical, with a dipole moment of 0.17 D .

Dinitrogen oxide, or nitrous oxide, N_2O , mp -90.8°C , bp -88.8°C .

Nitrogen Oxide (+2 Oxidation State)

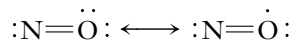
The first step of the Ostwald process (Section 24-16) for producing HNO_3 from NH_3 is used for the commercial preparation of nitrogen oxide, NO .



NO is not produced in large amounts in nature under usual conditions. It is formed by direct reaction of N_2 and O_2 in electrical storms.

Some dentists use N_2O for its mild anesthetic properties. It is also known as laughing gas because of its side effects.

NO is a colorless gas that condenses at -152°C to a blue liquid. Gaseous NO is paramagnetic and contains one unpaired electron per molecule.



Its unpaired electron makes nitric oxide very reactive. Molecules that contain unpaired electrons are called *radicals*. NO reacts with O_2 to form NO_2 , a brown, corrosive gas.



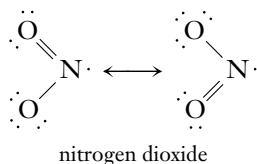
In recent years, researchers have learned that very low concentrations of NO have important roles in a variety of physiological processes, not only in humans, but in such a variety of animals as barnacles, chickens, trout, and fruit flies. It has recently been found to be involved in transmission of signals by nerves, blood clotting, local control of blood flow, the immune system's ability to kill tumor cells and bacteria, and possibly even memory.

Nitrogen Dioxide and Dinitrogen Tetroxide (+4 Oxidation State)

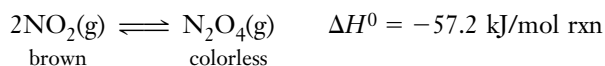
Nitrogen dioxide is formed by reaction of NO with O_2 . It is prepared in the laboratory by heating heavy metal nitrates.



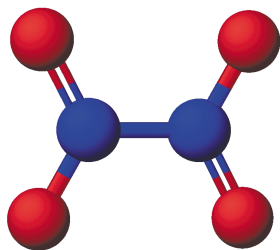
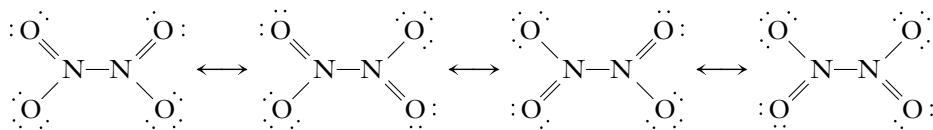
The NO_2 molecule is angular. It is represented by resonance structures.



Because each NO_2 molecule contains one unpaired electron, NO_2 readily dimerizes to form colorless, diamagnetic dinitrogen tetroxide, N_2O_4 , at low temperatures.



The N_2O_4 molecule is also represented by resonance structures.



Dinitrogen tetroxide, N_2O_4 , bp 21.2°C , no unpaired electrons, N—N bond length 1.64 \AA , N—O bond length 1.17 \AA , O—N—O bond angle 126° .



Nitrogen oxide, or nitric oxide, NO, mp -163.6°C , bp -151.8°C , bond distance (1.15 \AA) intermediate between $\text{N}\equiv\text{O}$ (1.06 \AA) and $\text{N}=\text{O}$ (1.20 \AA).



Nitrogen dioxide, NO_2 , mp -11.20°C , one unpaired electron, bond length 1.197 \AA ; brown gas.



CHEMISTRY IN USE

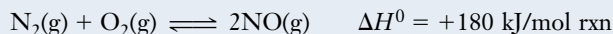


The Environment

Nitrogen Oxides and Photochemical Smog

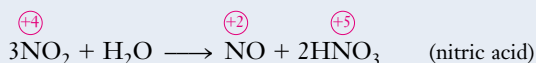
Nitrogen oxides are produced in the atmosphere by natural processes. Human activities contribute only about 10% of all the oxides of nitrogen (collectively referred to as NO_x) in the atmosphere, but the human contribution occurs mostly in urban areas, where the oxides may be present in concentrations a hundred times greater than in rural areas.

Just as NO is produced naturally by the reaction of N_2 and O_2 in electrical storms, it is also produced by the same reaction at the high temperatures of internal combustion engines and furnaces.

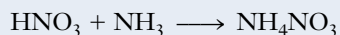


At ordinary temperatures the reaction does not occur to a significant extent. Because it is endothermic, it is favored by high temperatures. Even in internal combustion engines and furnaces, the equilibrium still lies far to the left, so only small amounts of NO are produced and released into the atmosphere. Even very small concentrations of nitrogen oxides cause serious problems, however.

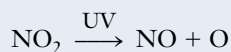
The NO radicals react with O_2 to produce NO_2 radicals. Both NO and NO_2 are quite reactive, and they do considerable damage to plants and animals. NO_2 reacts with H_2O in the air to produce corrosive droplets of HNO_3 and more NO .



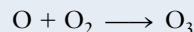
The HNO_3 may be washed out of the air by rainwater (acid rain), or it may react with traces of NH_3 in the air to form solid NH_4NO_3 , a *particulate* pollutant.



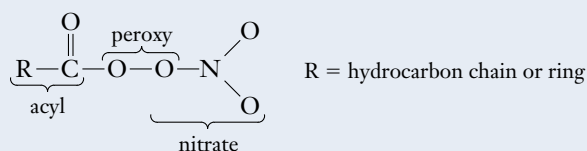
This situation occurs in all urban areas, but the problem is worse in warm, dry climates, which are conducive to light-induced (photochemical) reactions. Here ultraviolet (UV) radiation from the sun produces damaging oxidants. The brownish hazes that often hang over such cities as Los Angeles, Denver, and Mexico City are due to the presence of brown NO_2 . Problems begin in the morning rush hour as NO is exhausted into the air. The NO combines with O_2 to form NO_2 . Then, as the sun rises higher in the sky, NO_2 absorbs UV radiation and breaks down into NO and oxygen radicals.



The extremely reactive O radicals combine with O_2 to produce O_3 (ozone).



Ozone is a powerful oxidizing agent that damages rubber, plastic materials, and all plant and animal life. It also reacts with hydrocarbons from automobile exhaust and evaporated gasoline to form secondary organic pollutants such as aldehydes and ketones (Section 27-11). The **peroxyacyl nitrates (PANs)**, perhaps the worst of the secondary pollutants, are especially damaging photochemical oxidants that are very irritating to the eyes and throat.



Catalytic converters in automobile exhaust systems reduce emissions of oxides of nitrogen.



Photochemical smog casts a haze over urban or industrial areas; its severity depends on the weather.

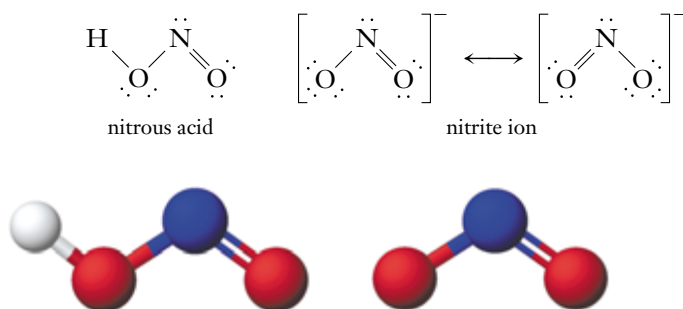
24-16 SOME OXOACIDS OF NITROGEN AND THEIR SALTS

The main oxoacids of nitrogen are nitrous acid, HNO_2 , and nitric acid, HNO_3 .

Nitrous Acid (+3 Oxidation State)

Nitrous acid, HNO_2 , is unstable and cannot be isolated in pure form. It is prepared as a pale blue solution when H_2SO_4 reacts with cold aqueous sodium nitrite. Nitrous acid is a weak acid ($K_a = 4.5 \times 10^{-4}$). It acts as an oxidizing agent toward strong reducing agents and as a reducing agent toward very strong oxidizing agents.

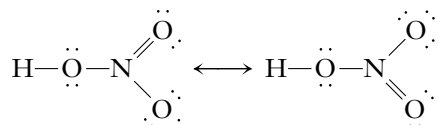
Lewis formulas for nitrous acid and the nitrite ion follow.



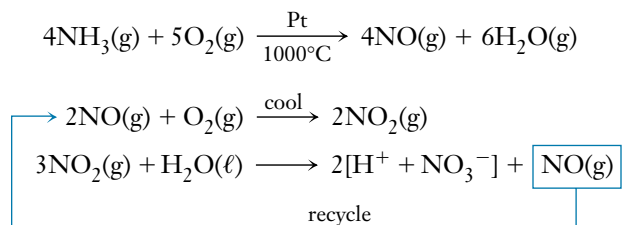
Nitrogen also forms hyponitrous acid, $\text{H}_2\text{N}_2\text{O}_2$, in which N is in the +1 oxidation state, as well as hyponitrite salts such as $\text{Na}_2\text{N}_2\text{O}_2$.

Nitric Acid (+5 Oxidation State)

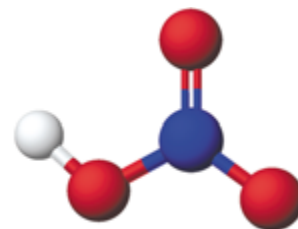
Pure nitric acid, HNO_3 , is a colorless liquid that boils at 83°C . Light or heat causes it to decompose into NO_2 , O_2 , and H_2O . The presence of the NO_2 in partially decomposed aqueous HNO_3 causes its yellow or brown tinge. The Lewis structure of nitric acid is



HNO_3 is commercially prepared by the **Ostwald process**. At high temperatures, NH_3 is catalytically converted to NO , which is cooled and then air-oxidized to NO_2 . Nitrogen dioxide reacts with H_2O to produce HNO_3 and some NO . The NO produced in the third step is then recycled into the second step. More than 18 billion pounds of HNO_3 was produced in the United States in 1997.



Nitric acid is very soluble in water (≈ 16 mol/L). It is a strong acid and a strong oxidizing agent.



Nitric acid, HNO_3 , mp -42°C ; bp 83°C ; bond lengths N—O (terminal) 1.22 Å, N—O (central) 1.41 Å.



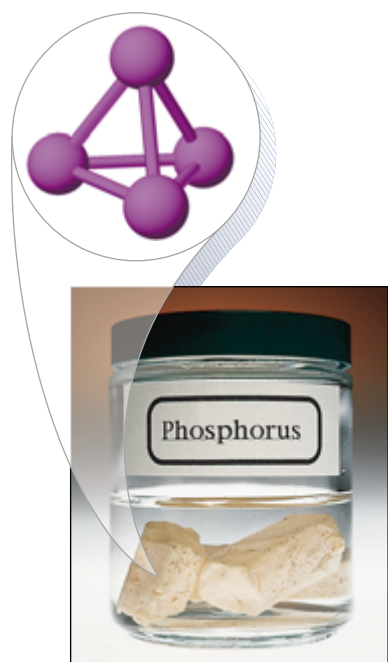
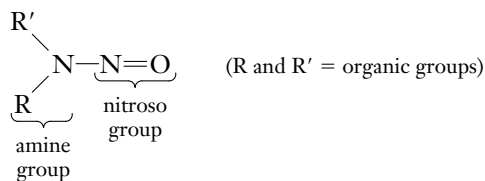
Nitric acid, HNO_3 , reacts with protein-containing materials such as this feather, staining them yellow. Perhaps you have spilled nitric acid on your skin and seen it turn yellow.



Copper (*left beaker*) and zinc (*right beaker*) react with concentrated nitric acid.

NaNO_2 and NaNO_3 as Food Additives

The brown color of “old” meat is the result of oxidation of blood and is objectionable to many consumers. Nitrites and nitrates are added to food to retard this oxidation and also to prevent growth of botulism bacteria. Nitrate ions, NO_3^- , are reduced to NO_2^- ions, which are then converted to NO . This in turn reacts with the brown oxidized form of the heme in blood. This reaction keeps meat red longer. Controversy has arisen, however, concerning the possibility that nitrites combine with amines under the acidic conditions in the stomach to produce carcinogenic *nitrosoamines*.



White phosphorus reacts with air, so it is stored under water. It contains tetrahedral P_4 molecules.

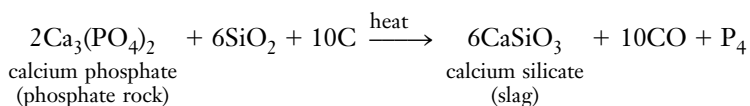
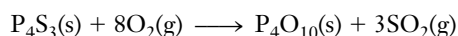
24-17 PHOSPHORUS

Phosphorus is always combined in nature. Phosphorus is present in all living organisms—as organophosphates and in calcium phosphates such as hydroxyapatite, $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$, and fluorapatite, $\text{Ca}_5(\text{PO}_4)_3\text{F}$, in bones and teeth. It also occurs in these and related compounds in phosphate minerals, which are mined mostly in Florida and North Africa.

Industrially, the element is obtained from phosphate minerals by heating them at 1200 to 1500°C in an electric arc furnace with sand (SiO_2) and coke.

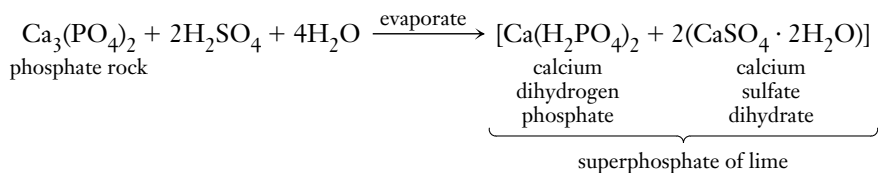


The tips of “strike anywhere” matches contain tetraphosphorus trisulfide and red phosphorus. Friction converts kinetic energy into heat, which initiates a spontaneous reaction.



Vaporized phosphorus is condensed to a white solid (mp = 44.2°C, bp = 280.3°C) under H₂O to prevent oxidation. Even when kept under H₂O, white phosphorus slowly converts to the more stable red phosphorus allotrope (mp = 597°C; sublimes at 431°C). Red phosphorus and tetraphosphorus trisulfide, P₄S₃, are used in matches. They do not burn spontaneously, yet they ignite easily when heated by friction. Both white and red phosphorus are insoluble in water.

The largest use of phosphorus is in fertilizers. Phosphorus is an essential nutrient, and nature’s phosphorus cycle is very slow owing to the low solubility of most natural phosphates. Phosphate fertilizers are therefore essential. To increase the solubility of the natural phosphates, they are treated with H₂SO₄ to produce “superphosphate of lime,” a mixture of two salts. This solid is pulverized and applied as a powder.



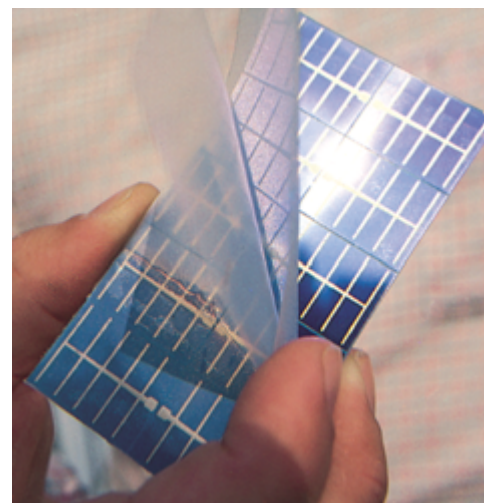
This reaction represents the most popular use of sulfuric acid, the industrial chemical produced in largest quantity.

SILICON

Silicon is a shiny, blue-gray, high-melting, brittle metalloid. It looks like a metal, but it is chemically more like a nonmetal. It is second only to oxygen in abundance in the earth’s crust, about 87% of which is composed of silica (SiO₂) and its derivatives, the silicate minerals. The crust is 26% Si, compared with 49.5% O. Silicon does not occur free in nature. Pure silicon crystallizes with a diamond-type structure, but the Si atoms are less closely packed than C atoms. Its density is 2.4 g/cm³ compared with 3.51 g/cm³ for diamond.



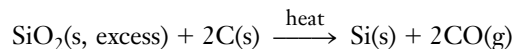
Superphosphate fertilizer.



Pure silicon is used in solar cells to collect energy from the sun.

24-18 SILICON AND THE SILICATES

Elemental silicon is usually prepared by the high-temperature reduction of silica (sand) with coke. Excess SiO_2 prevents the formation of silicon carbide.



Reduction of a mixture of silicon and iron oxides with coke produces an alloy of iron and silicon known as *ferrosilicon*. It is used in the production of acid-resistant steel alloys, such as “duriron,” and in the “deoxidation” of steel. Aluminum alloys for aircraft are strengthened with silicon.

Elemental silicon is used to make silicone polymers. Its semiconducting properties (Section 13-17) are used in transistors and solar cells.

The biggest chemical differences between silicon and carbon are that (1) silicon does not form stable double bonds, (2) it does not form very stable Si—Si bonds unless the silicon atoms are bonded to very electronegative elements, and (3) it has vacant $3d$ orbitals in its valence shell into which it can accept electrons from donor atoms. The Si—O single bond is the strongest of all silicon bonds and accounts for the stability and prominence of silica and the silicates.

Silicon dioxide (silica) exists in two familiar forms in nature: quartz, small chips of which occur in sand; and flint (Latin *silex*), an uncrystallized amorphous type of silica. Silica is properly represented as $(\text{SiO}_2)_n$ because it is a polymeric solid of SiO_4 tetrahedra sharing all oxygens among surrounding tetrahedra (Figure 13-32c). For comparison, solid carbon dioxide (dry ice) consists of discrete $\text{O}=\text{C}=\text{O}$ molecules, as does gaseous CO_2 .

Some gems and semiprecious stones such as amethyst, opal, agate, and jasper are crystals of quartz with colored impurities.

Most of the crust of the earth is made up of silica and silicates. The natural silicates comprise a large variety of compounds. The structures of all these are based on SiO_4 tetrahedra, with metal ions occupying spaces between the tetrahedra. The extreme stability of the silicates is presumably due to the donation of extra electrons from O into vacant $3d$ orbitals of Si. In many common minerals, called aluminosilicates, Al atoms replace some Si atoms with very little structural change. Because an Al atom has one less positive charge in its nucleus than Si does, it is also necessary to introduce a univalent ion, such as K^+ or Na^+ .

The physical characteristics of the silicates are often suggested by the arrangement of the SiO_4 tetrahedra. A single-chain silicate, diopside $[\text{CaMg}(\text{SiO}_3)_2]_n$, and a double-chain silicate, asbestos $[\text{Ca}_2\text{Mg}_5(\text{Si}_4\text{O}_{11})_2(\text{OH}_2)]_n$, occur as fibrous or needle-like crystals. Talc, $[\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2]_n$, a silicate with a sheet-like structure, is flaky. Micas are sheet-like aluminosilicates with about one of every four Si atoms replaced by Al. Muscovite mica is $[\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2]_n$. Micas occur in thin sheets that are easily peeled away from one another.

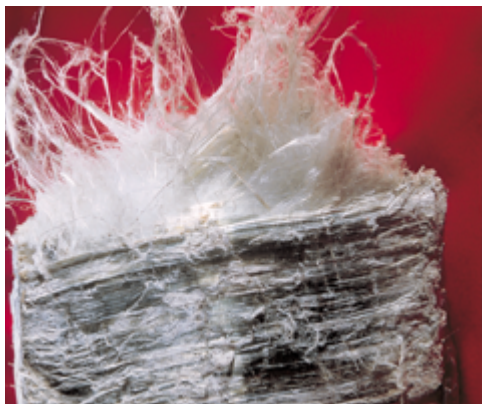
The clay minerals are silicates and aluminosilicates with sheet-like structures. They result from the weathering of granite and other rocks. The layers have enormous “inner surfaces” that can absorb large amounts of H_2O . Clay mixtures often occur as minute platelets with a very large total surface area. When wet, the clays are easily shaped. When heated to high temperatures, they lose H_2O ; when fired in a furnace, they become very rigid.

Fused sodium silicate, Na_2SiO_3 , and calcium silicate, CaSiO_3 , are the major components of the glass used in such things as drinking glasses, bottles, and window panes. **Glass** is a hard, brittle material that has no fixed composition or regular structure. Because it

Si is much larger than C. As a result, Si—Si bonds are too long to permit the effective π bonding that is necessary for multiple bonds.

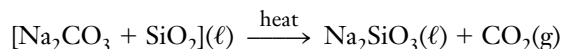
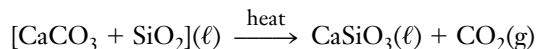


Natural quartz crystals, SiO_2 .



“Asbestos” refers to a group of impure magnesium silicate minerals. As you can see, asbestos is a fibrous material. When inhaled, these fibers are highly toxic and carcinogenic.

has no regular structure, it does not break evenly along crystal planes, but breaks to form rounded surfaces and jagged edges. The basic ingredients are produced by heating a mixture of Na_2CO_3 and CaCO_3 with sand until it melts, at about 700°C .



The resulting “soda–lime” glass is clear and colorless (if all CO_2 bubbles escape and if the amounts of reactants are carefully controlled).

Key Terms

Chain initiation step The first step in a chain reaction; produces reactive species (such as radicals) that then propagate the reaction.

Chain propagation step An intermediate step in a chain reaction; in such a step one or more reactive species is consumed, and another reactive species is produced.

Chain reaction A reaction in which reactive species, such as radicals, are produced in more than one step. Consists of an initiation step, one or more propagation steps, and one or more termination steps.

Chain termination step The combination of reactive species (such as radicals) which terminates the chain reaction.

Contact process An industrial process by which sulfur trioxide and sulfuric acid are produced from sulfur dioxide.

Frasch process A method by which elemental sulfur is mined or extracted. Sulfur is melted with superheated water (at 170°C under high pressure) and forced to the surface of the earth as a slurry.

Haber process An industrial process for the catalyzed production of ammonia from N_2 and H_2 at high temperature and pressure.

Halogens Group VIIA elements; F, Cl, Br, I, and At. The free elements exist as diatomic molecules.

Nitrogen cycle The complex series of reactions by which nitrogen is slowly but continually recycled in the atmosphere, lithosphere, and hydrosphere.

Noble gases Group VIIIA elements; He, Ne, Ar, Kr, Xe, and Rn.

Ostwald process An industrial process for the production of nitrogen oxide and nitric acid from ammonia and oxygen.

PANs Abbreviation for peroxyacyl nitrates, photochemical oxidants in smog.

Particulate matter Finely divided solid particles suspended in polluted air.

Photochemical oxidants Photochemically produced oxidizing agents capable of causing damage to plants and animals.

Photochemical smog A brownish smog occurring in urban areas that receive large amounts of sunlight; caused by photochemical (light-induced) reactions among nitrogen oxides, hydrocarbons, and other components of polluted air that produce photochemical oxidants.

Radical An atom or group of atoms that contains one or more unpaired electrons (usually very reactive species).

Exercises

The Noble Gases

- (a) Write the Lewis dot representations of the noble gases.
(b) Why are the noble gases so unreactive?
- Why were the noble gases among the last elements to be discovered?
- List some of the uses of the noble gases and reasons for the uses.
- Arrange the noble gases in order of increasing (a) atomic radii, (b) melting points, (c) boiling points, (d) densities, and (e) first ionization energies.
- Explain the order of increasing melting and boiling points of the noble gases in terms of polarizabilities of the atoms and forces of attraction between them.

6. What gave Neil Bartlett the idea that compounds of xenon could be synthesized? Which noble gases are known to form compounds? With which elements are the noble gas atoms bonded?

7. Describe the bonding and geometry in XeF_2 , XeF_4 , and XeF_6 .

*8. Xenon(VI) fluoride can be produced by the combination of xenon(IV) fluoride with fluorine. Write a chemical equation for this reaction. What mass of XeF_6 could be produced from 2.75 g of XeF_4 and excess fluorine?

The Halogens

9. Write the electron configuration for each halogen atom. Write the Lewis symbol for a halogen atom, X. What is

the usual oxidation state of the halogens in binary compounds with metals, semiconducting elements, and most nonmetals?

10. Write the Lewis structure of a halogen molecule, X_2 . Describe the bonding in the molecule. What is the trend of bond length and strength going down the family from F_2 to I_2 ?
11. What types of intermolecular forces are found in molecular halogens? What is the trend in these forces going down the group from F_2 to I_2 ? Describe the physical state of each molecular halogen at room temperature and pressure.
12. List the halogens in order of increasing (a) atomic radii, (b) ionic radii, (c) electronegativities, (d) melting points, (e) boiling points, and (f) standard reduction potentials.
13. Write the equations describing the half-reactions and net reaction for the electrolysis of molten KF/HF mixtures. At which electrodes are the products formed? What is the purpose of the HF ?
14. Carl O. Christe's preparation of F_2 did not involve direct chemical oxidation. Explain this statement.
15. Write equations describing general reactions of the free halogens, X_2 , with (a) Group IA (alkali) metals, (b) Group IIA (alkaline earth) metals, and (c) Group IIIA metals. Represent the metals as M .
16. Write balanced equations for any reactions that occur in aqueous mixtures of (a) NaI and Cl_2 , (b) $NaCl$ and Br_2 , (c) NaI and Br_2 , (d) $NaBr$ and Cl_2 , and (e) NaF and I_2 .
- *17. An aqueous solution contains either $NaBr$ or a mixture of $NaBr$ and NaI . Using only aqueous solutions of I_2 , Br_2 , and Cl_2 and a small amount of CH_2Cl_2 , describe how you might determine what is in the unknown solution.
- *18. Write equations illustrating the tendency of F^- to stabilize high oxidation states of cations and the tendency of I^- to stabilize low oxidation states. Why is this the case?
19. Why are the free halogens more soluble in water than most nonpolar molecules?
20. Distinguish between hydrogen bromide and hydrobromic acid.
21. Refer to Figure 13-5. What is the order of decreasing boiling points of the hydrogen halides? Why is the HF "out of line?"
22. Describe the effect of hydrofluoric acid on glass.
23. What is the acid anhydride of perchloric acid?
24. Name the following compounds: (a) $KBrO_3$; (b) $KOBr$; (c) $NaClO_4$; (d) $NaClO_2$; (e) $HOBr$; (f) $HBrO_3$; (g) HIO_3 ; (h) $HClO_4$.
25. Write the Lewis formulas and structures of the four ternary acids of chlorine.
26. Write equations describing reactions by which the following compounds can be prepared: (a) hypohalous acids of Cl , Br , and I (in solution with hydrohalic acids); (b) hypohalite salts; (c) chlorous acid; (d) perchloric acid.
27. What is the order of increasing acid strength of the ternary chlorine acids? Explain the order.

28. Choose the strongest acid from each group: (a) $HOCl$, $HOBr$, HOI ; (b) $HOCl$, $HClO_2$, $HClO_3$, $HClO_4$; (c) HOI , $HBrO_3$, $HClO_4$. Explain your choices.

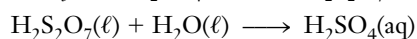
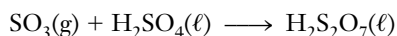
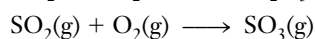
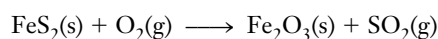
Group IIIA Elements

29. Write abbreviated electron configurations for atomic oxygen, selenium, and polonium.
30. Write out the electron configurations of oxide, sulfide, and selenide ions.
31. Characterize the Group VIA elements with respect to color and physical state under normal conditions.
32. The Group VIA elements, except oxygen, can exhibit oxidation states ranging from -2 to $+6$, but not -3 or $+7$. Why?
33. Sulfur, selenium, and tellurium are all capable of forming six-coordinate compounds such as SF_6 . Give two reasons why oxygen cannot be the central atom in such six-coordinate molecules.
34. For the following species, draw (i) diagrams that show the hybridization of atomic orbitals and (ii) three-dimensional structures that show all hybridized orbitals and outermost electrons. (iii) Determine the oxidation state of the Group VIA element (other than oxygen) in each species. (a) H_2S ; (b) SF_6 ; (c) SF_4 ; (d) SO_2 ; (e) SO_3 .
35. Repeat Exercise 34 for (a) SeF_6 , (b) SO_3^{2-} , (c) SO_4^{2-} , (d) HSO_4^- , and (e) thiosulfate ion, $S_2O_3^{2-}$ (one S is central atom).
36. Write equations for the reactions of (a) S , Se , and Te with excess F_2 ; (b) O_2 , S , Se , and Te with H_2 ; (c) S , Se , and Te with O_2 .
37. Write equations for the reactions of (a) S and Te with HNO_3 ; (b) S and Se with excess Cl_2 ; (c) S and Se with Na , Ca , and Al .
38. Discuss the acidity of the aqueous Group VIA hydrides, including the relative values of acid ionization constants. What is primarily responsible for the order of increasing acidities in this series?
39. Compare the structures of the dioxides of sulfur, selenium, tellurium, and polonium. How do they relate to the metallic or nonmetallic character of these elements?
40. Write equations for reactions of
 - (a) $NaOH$ with sulfuric acid (1:1 mole ratio)
 - (b) $NaOH$ with sulfuric acid (2:1 mole ratio)
 - (c) $NaOH$ with sulfurous acid (1:1 mole ratio)
 - (d) $NaOH$ with sulfurous acid (2:1 mole ratio)
 - (e) $NaOH$ with selenic acid, H_2SeO_4 (1:1 mole ratio)
 - (f) $NaOH$ with selenic acid, (2:1 mole ratio)
 - (g) $NaOH$ with tellurium dioxide (1:1 mole ratio)
 - (h) $NaOH$ with tellurium dioxide (2:1 mole ratio)
- *41. How much sulfur dioxide could be produced from complete combustion of 1.00 ton of coal containing 5.85% sulfur?



Industrial smokestack.

42. What mass of H_2SO_4 could be produced in the following process if 1.00 ton of FeS_2 is used? The *unbalanced* equations for the process are



43. Common copper ores in the western United States contain the mineral chalcopyrite, CuFeS_2 . Assuming that a commercially useful ore contains 0.291 mass % Cu and that all the sulfur ultimately appears in the smelter stack gases as SO_2 , calculate the mass of sulfur dioxide generated by the conversion of 1.00 ton of the ore.
- *44. A gaseous mixture at some temperature in a 1.00-L vessel originally contained 1.00 mol SO_2 and 5.00 mol O_2 . Once equilibrium conditions were attained, 77.8% of the SO_2 had been converted to SO_3 . What is the value of the equilibrium constant (K_c) for this reaction at this temperature?

Nitrogen and Phosphorus

45. Characterize each of the Group VA elements with respect to normal physical state and color.
46. Write out complete electron configurations for the atoms of the Group VA elements; nitride ion, N^{3-} ; and phosphide ion, P^{3-} .
47. Compare and contrast the properties of (a) N_2 and P_4 ; (b) HNO_3 and H_3PO_4 ; (c) N_2O_3 and P_4O_6 .
48. Describe the natural nitrogen cycle.
49. List natural sources of nitrogen and phosphorus and at least two uses for each.
50. Discuss the effects of temperature, pressure, and catalysts on the Haber process for the production of ammonia. (You may wish to consult Section 17-7.)
51. Determine the oxidation states of nitrogen in the following: (a) NO_3^- ; (b) NO_2^- ; (c) N_2H_4 ; (d) NH_3 ; (e) NH_2^- .
52. Determine the oxidation states of nitrogen in the following: (a) N_2 ; (b) NO ; (c) N_2O_4 ; (d) HNO_3 ; (e) HNO_2 .
53. Draw three-dimensional structures showing all outer-shell electrons, describe molecular and ionic geometries, and indicate hybridization (except for N^{3-}) at the central element, for the following species: (a) N_2 , (b) N^{3-} ; (c) NH_3 , (d) NH_4^+ ; (e) NH_2^- , amide ion.
54. Draw three-dimensional structures showing all outer-shell electrons, describe molecular and ionic geometries, and indicate hybridization at the central element for the following species: (a) NH_2Br , bromamine; (b) HN_3 , hydrazoic acid; (c) N_2O_2 ; (d) $\text{NO}_2^+\text{NO}_3^-$, solid nitronium nitrate; (e) HNO_3 ; (f) NO_2^- .
55. Draw three-dimensional structures showing all outer-shell electrons for the following species: (a) P_4 ; (b) P_4O_{10} ; (c) As_4O_6 ; (d) H_3PO_4 ; (e) AsO_4^{3-} .
56. Write formula unit equations for the following: (a) thermal decomposition of potassium azide, KN_3 ; (b) reaction of gaseous ammonia with gaseous HCl ; (c) reaction of aqueous ammonia with aqueous HCl ; (d) thermal decomposition of ammonium nitrate at temperature above 260°C ; (e) reaction of ammonia with oxygen in the presence of red hot platinum catalyst; (f) thermal decomposition of nitrous oxide (dinitrogen oxide), N_2O ; (g) reaction of NO_2 with water.
57. Write the formula unit equation for the preparation of “superphosphate of lime.”
58. Write two equations illustrating the ability of ammonia to function as a Lewis base.
59. In liquid ammonia would sodium amide, NaNH_2 , be acidic, basic, or neutral? Would ammonium chloride, NH_4Cl , be acidic, basic, or neutral? Why?
60. Which of the following molecules have a nonzero dipole moment—that is, are polar molecules? (a) NH_3 ; (b) NH_2Cl ; (c) NO ; (d) NH_2OH ; (e) HNO_3 .
61. Describe with equations the Ostwald process for the production of nitrogen oxide, NO , and nitric acid.
62. Why is NO so reactive?
63. Write a Lewis formula for NO_2 . Would you predict that it is very reactive? How about N_2O_4 (dimerized NO_2)?
64. At room temperature, a sample of NO_2 gas is brown. Explain why this sample loses its color as it is cooled.
65. Discuss the problem of NO_x emissions with respect to air pollution. Use equations to illustrate the important reactions.
66. What are the acid anhydrides of (a) nitric acid, HNO_3 ; (b) nitrous acid, HNO_2 ; (c) phosphoric acid, H_3PO_4 ; and (d) phosphorous acid, H_3PO_3 ?
67. Calcium phosphate (phosphate rock) is not applied directly as a phosphorus fertilizer. Why?
68. Discuss the use of sodium nitrite as a meat preservative.

CONCEPTUAL EXERCISES

69. Not much is known about astatine because it is very rare, is radioactive, and decays very quickly. Would you predict the chemical and physical properties of astatine to be more

like those of a metal or nonmetal? Defend your answer on the basis of astatine's location on the periodic table.

70. Elemental chlorine is obtained by the electrolysis of molten NaCl (Downs cell). Elemental fluorine is obtained by the electrolysis of KHF_2 in a cell made of Monel metal (a stainless steel alloy). Both of these processes are dangerous. Why?
71. Acid rain consists of acids formed by the reaction of acid anhydrides and water. List four acid anhydrides commonly involved in acid rain formation and the sources of each.
72. Sulfur deposits are mined by the Frasch process. Explain why free sulfur is not found on the earth's surface.
73. (a) On the basis of electronic structures, explain why most metal halides are ionic. (b) On the basis of your explanation, predict which halide compounds are likely to be covalent.
74. (a) Which of the halogens is the most active chemically and (b) which of the halogens is most likely to be reduced from the free state? (c) Which of the halogens is most likely to act as an oxidizing agent? (d) Which of the halogens is least likely to be an effective oxidizing agent? (e) Which of the halogens is likely to be a liquid under room conditions? (f) Which of the halogens is found free in nature?
75. The nitrogen cycle indicates that electrical storms (lightning) are a source of nitrogen compounds. (a) What is the function of the lightning? (b) What compounds of nitrogen are produced during electrical storms? (c) What is the effect of these compounds on the rain water?

BUILDING YOUR KNOWLEDGE

- *76. Standard enthalpies of formation are -402 kJ/mol for $\text{XeF}_6(\text{s})$ and -261.5 kJ/mol for $\text{XeF}_4(\text{s})$. Calculate ΔH_{rxn}^0 at 25°C for the preparation of XeF_6 from XeF_4 and $\text{F}_2(\text{g})$.
77. The average atomic mass of N is 14.0067 amu. There are two isotopes which contribute to this average: $^{14}_7\text{N}$ (14.00307 amu) and $^{15}_7\text{N}$ (15.00011 amu). Calculate the percentage of $^{15}_7\text{N}$ atoms in a sample of naturally occurring nitrogen.
78. The $\text{N}\equiv\text{N}$ and the $\text{N}-\text{N}$ bond energies are listed in Tables 15-2 and 15-3. Predict whether four gaseous nitrogen atoms would form two gaseous nitrogen molecules or a gaseous tetrahedral molecule similar to P_4 , basing your prediction on the amount of energy released as the molecules are formed. Repeat the calculations for phosphorus using 485 kJ/mol for $\text{P}\equiv\text{P}$ and 201 kJ/mol for $\text{P}-\text{P}$.
- *79. Commercial concentrated HNO_3 contains 69.5 mass % HNO_3 and has a density of 1.42 g/mL . What is the molarity of this solution? What volume of the concentrated acid should you use to prepare 10.0 L of dilute HNO_3 solution with a concentration of 6.00 M ?
- *80. What is the total mass of silicon in the crust of the earth? Assume that the radius of the earth is 6400 km , the crust is 50 km thick, the density of the crust is 3.5 g/cm^3 , and 25.7 mass \% of the crust is silicon.
- *81. How many grams of xenon oxide tetrafluoride, XeOF_4 , and how many liters of HF at STP could be prepared, assuming complete reaction of 10.5 g of xenon tetrafluoride, XeF_4 , with a stoichiometric quantity of water according to the equation below?
- $$6\text{XeF}_4(\text{s}) + 8\text{H}_2\text{O}(\ell) \longrightarrow 2\text{XeOF}_4(\ell) + 4\text{Xe}(\text{g}) + 16\text{HF}(\text{g}) + 3\text{O}_2(\text{g})$$
- *82. Argon crystallizes at -235°C in a face-centered cubic unit cell with $a = 5.43 \text{ \AA}$. Determine the apparent radius of an argon atom in the solid.
- *83. A reaction mixture contained $100. \text{ g}$ of K_2MnF_6 and 174 g of SbF_5 . Fluorine was produced in 38.3 \% yield. How many grams of F_2 were produced? What volume is this at STP?