

# Elements Handbook

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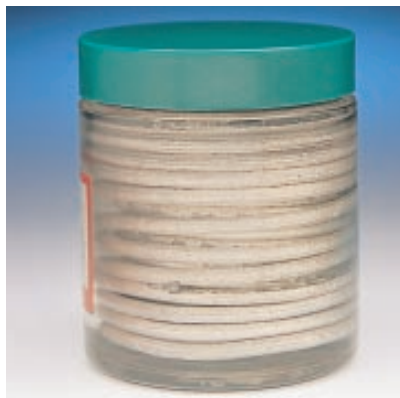
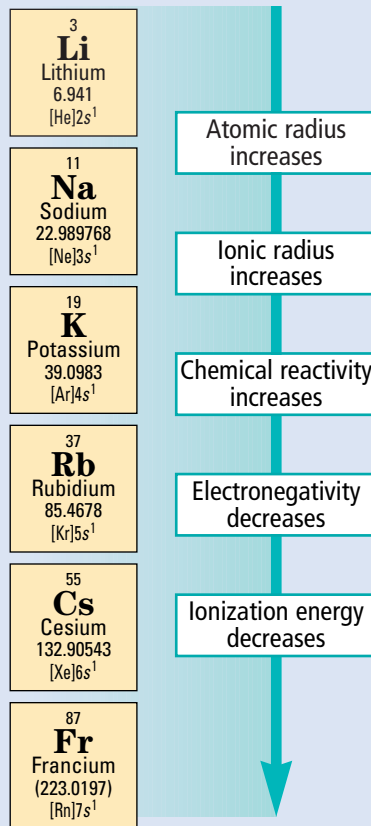
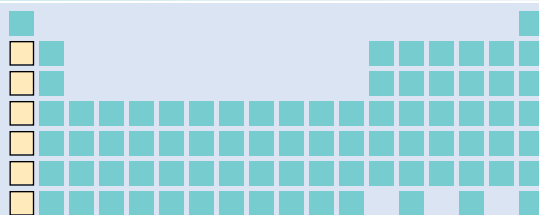
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# GROUP 1 ALKALI METALS

## CHARACTERISTICS

- do not occur in nature as elements
- are reactive metals obtained by reducing the 1+ ions in their natural compounds
- are stored under kerosene or other hydrocarbon solvent because they react with water vapor or oxygen in air
- consist of atoms with one electron in the outermost energy level
- form colorless ions, each with a 1+ charge
- form ionic compounds
- form water-soluble bases
- are strong reducing agents
- consist of atoms that have low ionization energies
- are good conductors of electricity and heat
- are ductile, malleable, and soft enough to be cut with a knife
- have a silvery luster, low density, and low melting point



Lithium was discovered in 1817. It is found in most igneous rocks and is used in batteries as an anode because it has a very low reduction potential. Lithium is soft and is stored in oil or kerosene to prevent it from reacting with the air.



Sodium derives its name from the word soda. It was first isolated in 1807 from the electrolysis of caustic soda, NaOH. Sodium is soft enough to be cut with a knife. It is shiny until it reacts with oxygen, which causes the surface to lose its luster.



Potassium was first isolated in 1807 from the electrolysis of caustic potash, KOH.



## COMMON REACTIONS

**With Water and Acids to Form Bases and Hydrogen Gas**

*Example:*  $2\text{Na}(s) + 2\text{H}_2\text{O}(l) \longrightarrow 2\text{NaOH}(aq) + \text{H}_2(g)$

Li, K, Rb, and Cs also follow this pattern.

*Example:*  $2\text{Na}(s) + 2\text{HCl}(aq) \longrightarrow 2\text{NaCl}(aq) + \text{H}_2(g)$

Li, K, Rb, and Cs also follow this pattern.

**With Halogens to Form Salts**

*Example:*  $2\text{Na}(s) + \text{F}_2(g) \longrightarrow 2\text{NaF}(s)$

Li, K, Rb, and Cs also follow this pattern in reacting with  $\text{F}_2$ ,  $\text{Cl}_2$ ,  $\text{Br}_2$ , and  $\text{I}_2$ .

**With Oxygen to Form Oxides, Peroxides, or Superoxides**

*Lithium forms an oxide.*

$4\text{Li}(s) + \text{O}_2(g) \longrightarrow 2\text{Li}_2\text{O}(s)$

*Sodium forms a peroxide.*

$2\text{Na}(s) + \text{O}_2(g) \longrightarrow \text{Na}_2\text{O}_2(s)$

*Alkali metals with higher molecular masses can form superoxides.*

$\text{K}(s) + \text{O}_2(g) \longrightarrow \text{KO}_2(s)$

Rb and Cs also follow this pattern.

**Alkali-Metal Oxides with Water to Form Bases**

Oxides of Na, K, Rb, and Cs can be prepared indirectly.

These basic anhydrides form hydroxides in water.

*Example:*  $\text{K}_2\text{O}(s) + \text{H}_2\text{O}(l) \longrightarrow 2\text{KOH}(aq)$

Li, Na, Rb, and Cs also follow this pattern.



*A small piece of potassium dropped into water will react explosively, releasing  $\text{H}_2$  to form a strongly basic hydroxide solution. The heat of the reaction ignites the hydrogen gas that is produced.*



*Sodium reacts vigorously with chlorine to produce  $\text{NaCl}$ . Most salts of Group 1 metals are white crystalline compounds.*

## ANALYTICAL TEST

Alkali metals are easily detected by flame tests because each metal imparts a characteristic color to a flame.

When sodium and potassium are both present in a sample, the yellow color of the sodium masks the violet color of the potassium. The violet color can be seen only when the combined sodium-potassium flame is viewed through a cobalt-blue glass. The glass blocks the yellow flame of sodium and makes it possible to see the violet flame of potassium.



Lithium



Sodium



Potassium



Rubidium



Cesium

## PROPERTIES OF THE GROUP 1 ELEMENTS

	<b>Li</b>	<b>Na</b>	<b>K</b>	<b>Rb</b>	<b>Cs</b>	<b>Fr</b>
Melting point (°C)	180.5	97.8	63.25	38.89	28.5	27
Boiling point (°C)	1342	882.9	760	691	668	—
Density (g/cm <sup>3</sup> )	0.534	0.971	0.862	1.53	1.87	—
Ionization energy (kJ/mol)	520	496	419	403	376	—
Atomic radius (pm)	152	186	227	248	265	270
Ionic radius (pm)	76	102	138	152	167	180
Common oxidation number in compounds	+1	+1	+1	+1	+1	—
Crystal structure	bcc*	bcc	bcc	bcc	bcc	—
Hardness (Mohs' scale)	0.6	0.4	0.5	0.3	0.2	—

\*body-centered cubic

APPLICATION *Technology***Sodium Vapor Lighting**

The flame test for sodium shows a bright line between 589.0 and 589.5 nm, which is the yellow range of the emission spectrum. Sodium can be vaporized at high temperatures in a sealed tube and made to give off light using two electrodes connected to a power source. Sodium vapor lighting is often used along highways and in parking lots because it provides good illumination while using less energy than other types of lighting.

Sodium vapor lighting comes in both low-pressure and high-pressure bulbs. Low-pressure lamps reach an internal temperature of 270°C to vaporize the sodium under a pressure of about 1 Pa. High-pressure lamps contain mercury and xenon in addition to sodium. These substances reach an internal temperature of 1100°C under a pressure of about 100 000 Pa. The high-pressure lamp provides a higher light intensity. The design of both types of lamps must take into account the high reactivity of sodium, which increases at high temperatures. Because ordinary glass will react with sodium at 250°C, a special sodium-resistant glass is used for low-pressure lamps. High-pressure lamps use an aluminum oxide material for the column containing the sodium, mercury, and xenon. Both types of lamps contain tungsten electrodes.

The light intensity per watt for sodium vapor lamps far exceeds that of fluorescent lamps, high-pressure mercury vapor lamps, tungsten halogen lamps, and incandescent bulbs.



APPLICATION *Health*

Electrolyte Balance in the Body

The elements of Group 1 are important to a person’s diet and body maintenance because they form ionic compounds, that are present in the body as solutions of the ions. All ions carry an electric charge, so they are electrolyte solutes. Two of the most important electrolyte solutes found in the body are  $K^+$  and  $Na^+$  ions. Both ions facilitate the transmission of nerve impulses and control the amount of water retained by cells.



During situations where the body is losing water rapidly through intense sweating or diarrhea for a prolonged period (more than 5 hours), a sports drink can hydrate the body and restore electrolyte balance.

TABLE 1A Sodium-Potassium Composition of Body Fluids

Cation	Inside cells (mmol/L)	Outside cells or in plasma (mmol/L)
$Na^+$	12	145
$K^+$	140	4

The sodium and potassium ion concentrations of body fluids are shown in Table 1A. Sodium ions are found primarily in the fluid outside cells, while potassium ions are largely found in the fluid inside cells. Anions are present in the fluids to balance the electrical charge of the  $Na^+$  and  $K^+$  cations.

Abnormal electrolyte concentrations in blood serum can indicate the presence of disease. The ion concentrations that vary as a result of disease are  $Na^+$ ,  $K^+$ ,  $Cl^-$ , and  $HCO_3^-$ . Sodium ion concentration is a good indicator of the water balance between blood and tissue cells. Unusual potassium ion levels can indicate kidney or gastrointestinal problems. Chloride ion is the anion that balances the positive charge of the sodium ion in the fluid outside the cells. It also diffuses into a cell to maintain normal electrolyte balance when hydrogen carbonate ions diffuse out of the cell into the blood. Table 1B shows medical conditions associated with electrolyte imbalances.

TABLE 1B Electrolyte Imbalances

Electrolyte	Normal range (mmol/L)	Causes of imbalance	
		Excess	Deficiency
Sodium, $Na^+$	135–145	hypernatremia (increased urine excretion; excess water loss)	hyponatremia (dehydration; diabetes-related low blood pH; vomiting; diarrhea)
Potassium, $K^+$	3.5–5.0	hyperkalemia (renal failure; low blood pH)	hypokalemia (gastrointestinal conditions)
Hydrogen carbonate, $HCO_3^-$	24–30	hypercapnia (high blood pH; hypoventilation)	hypocapnia (low blood pH; hyperventilation; dehydration)
Chloride, $Cl^-$	100–106	hyperchloremia (anemia; heart conditions; dehydration)	hypochloremia (acute infection; burns; hypoventilation)

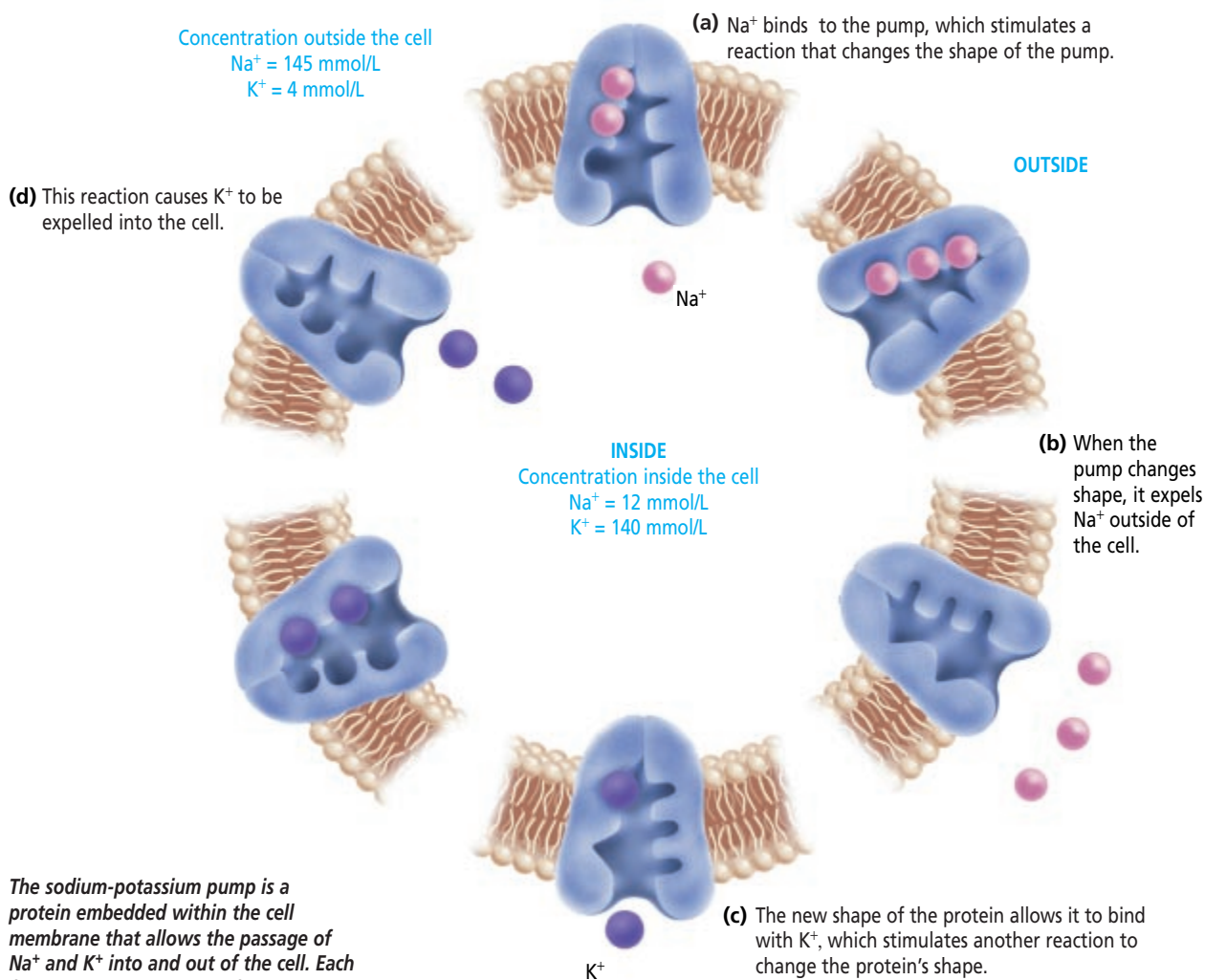
### Sodium-Potassium Pump in the Cell Membrane

The process of active transport allows a cell to maintain its proper electrolyte balance. To keep the ion concentrations at the proper levels shown in Table 1B, a sodium-potassium pump embedded in the cell membrane shuttles sodium ions out of the cell across the cell membrane. A model for the action of the sodium-potassium pump is shown below.

### Nerve Impulses and Ion Concentration

An uneven distribution of  $\text{Na}^+$  and  $\text{K}^+$  ions across nerve cell membranes is essential for the normal

operation of the nervous system. This uneven distribution of ions creates a voltage across nerve cell membranes. When a nerve cell is stimulated, sodium ions diffuse into the cell from the surrounding fluid, raising voltage across the nerve cell membrane from  $-70$  mV to nearly  $+60$  mV. Potassium ions then diffuse out of the cell into the surrounding fluid, restoring the voltage across the nerve cell membrane to  $-70$  mV. This voltage fluctuation initiates the transmission of a nerve impulse. The amount of  $\text{Na}^+$  inside the cell has increased slightly, and the amount of  $\text{K}^+$  outside the cell has decreased. But the sodium-potassium pump will restore these ions to their proper concentrations.



*The sodium-potassium pump is a protein embedded within the cell membrane that allows the passage of  $\text{Na}^+$  and  $\text{K}^+$  into and out of the cell. Each figure depicts the action of a single protein.*



## What's your sodium IQ?

**T**hough sodium is an important mineral in your body, a diet that is high in sodium is one of several factors linked to high blood pressure, also known as hypertension. High  $\text{Na}^+$  levels cause water retention, which results in increased blood pressure. Sodium is not the direct cause of all hypertension, but reducing sodium levels in the diet can affect individuals with a condition known as salt-sensitive hypertension. Therefore, the Dietary Guidelines for Americans recommend consuming salt and sodium in moderation. Test your knowledge about sodium in foods with the questions below.

- Which of the following condiments do you think has the lowest salt content?  
a. mustard      c. catsup      e. vinegar  
b. steak sauce      d. pickles
- One-fourth of a teaspoon of salt contains about \_\_\_\_\_ of sodium.  
a. 10 mg      c. 500 mg      e. 1 kg  
b. 100 g      d. 500 g



- According to FDA regulations for food product labels, a food labeled *salt-free* must contain less than \_\_\_\_\_ mg of sodium ion per serving.  
a. 100      c. 0.001      e. 0.00005  
b. 5      d. 0.005
- The Nutrition Facts label for a particular food reads "Sodium 15 mg." This is the amount of sodium ion per \_\_\_\_\_.  
a. package      c. serving      e. RDA  
b. teaspoon      d. ounce
- The recommended average daily intake of sodium ion for adults is 2400 mg. For a low-sodium diet the intake should be \_\_\_\_\_.  
a. 200 mg      c. 750 mg      e. 150 mg  
b. 2000 mg      d. 500 mg
- Each of the following ingredients can be found in the ingredients lists for some common food products. Which ones indicate that the product contains sodium?  
a. trisodium phosphate      d. sodium sulfate  
b. sodium bicarbonate      e. MSG  
c. sodium benzoate      f. baking soda
- Which of the following spices is NOT a salt substitute?  
a. caraway seeds      d. ginger  
b. dill      e. onion salt  
c. mace
- Most salt in the diet comes from salting foods too heavily at the dinner table.  
a. true      b. false
- Which of the following foods are high in sodium?  
a. potato chips      c. doughnuts      e. figs  
b. pizza      d. banana
- Your body requires about 200 mg of sodium ion, or 500 mg of salt, per day. Why do these numbers differ?

*Answers: 1. e; 2. c; 3. b; 4. c; 5. c; 6. all of them; 7. e; 8. b, processed foods can contain very high levels of sodium; 9. a, b, c; 10. Salt is not pure sodium.*



# GROUP 2 ALKALINE EARTH METALS

## CHARACTERISTICS

- do not occur naturally in their elemental state
- occur most commonly as the carbonates, phosphates, silicates, and sulfates
- occur naturally as compounds that are either insoluble or only slightly soluble in water
- consist of atoms that contain two electrons in their outermost energy level
- consist of atoms that tend to lose two electrons per atom, forming ions with a 2+ charge
- are less reactive than alkali metals
- form ionic compounds primarily
- react with water to form bases and hydrogen gas
- are good conductors of heat and electricity
- are ductile and malleable
- have a silvery luster
- include the naturally radioactive element radium

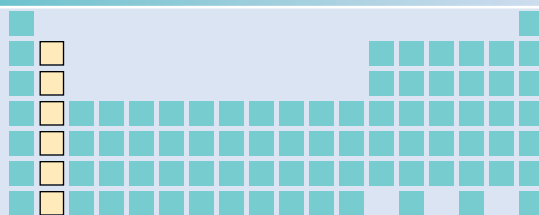
*Calcium carbonate is a major component of marble.*



*The mineral dolomite,  $\text{CaCO}_3 \cdot \text{MgCO}_3$ , is a natural source of both calcium and magnesium.*



*Beryllium is found in the mineral compound beryl. Beryl crystals include the dark green emerald and the blue-green aquamarine. The colors of these gems come from other metal impurities.*



4  
**Be**  
Beryllium  
9.012182  
[He]2s<sup>2</sup>

12  
**Mg**  
Magnesium  
24.3050  
[Ne]3s<sup>2</sup>

20  
**Ca**  
Calcium  
40.078  
[Ar]4s<sup>2</sup>

38  
**Sr**  
Strontium  
87.62  
[Kr]5s<sup>2</sup>

56  
**Ba**  
Barium  
137.327  
[Xe]6s<sup>2</sup>

88  
**Ra**  
Radium  
(226.0254)  
[Rn]7s<sup>2</sup>

Atomic radius  
increases

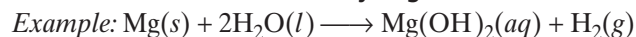
Ionic radius  
increases

Chemical reactivity  
increases

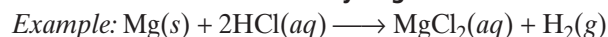
Electronegativity  
decreases

Ionization energy  
decreases

## COMMON REACTIONS

**With Water to Form Bases and Hydrogen Gas**

Ca, Sr, and Ba also follow this pattern.

**With Acids to Form Salts and Hydrogen Gas**

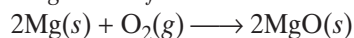
Be, Ca, Sr, and Ba also follow this pattern.

**With Halogens to Form Salts**

Ca, Sr, and Ba also follow this pattern in reacting with  $\text{F}_2$ ,  $\text{Cl}_2$ ,  $\text{Br}_2$ , and  $\text{I}_2$ .

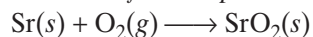
**With Oxygen to Form Oxides or Peroxides**

*Magnesium forms an oxide.*



Be and Ca also follow this pattern.

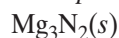
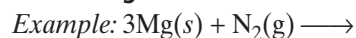
*Strontium forms a peroxide.*



Ba also reacts in this way.

**With Hydrogen to Form Hydrides**

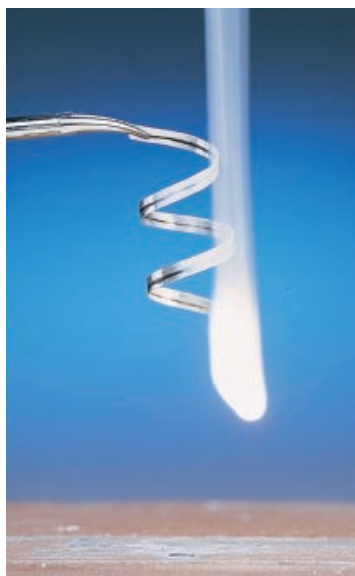
Ca, Sr, and Ba also follow this pattern.

**With Nitrogen to Form Nitrides**

Be and Ca also follow this pattern.



Calcium reacts with water to form hydrogen gas.



Magnesium burns in air to form  $\text{MgO}$  and  $\text{Mg}_3\text{N}_2$ .



Magnesium reacts with  $\text{HCl}$  to produce  $\text{MgCl}_2(aq)$ .

## ANALYTICAL TEST

Flame tests can be used to identify three of the alkaline earth elements. The colors of both calcium and strontium can be masked by the presence of barium, which produces a green flame.



Calcium



Strontium



Barium

## PROPERTIES OF THE GROUP 2 ELEMENTS

	Be	Mg	Ca	Sr	Ba	Ra
Melting point (°C)	1287 ± 5	649	839 ± 2	769	725	700
Boiling point (°C)	2467	1107	1484	1384	1640	1737
Density (g/cm <sup>3</sup> )	1.85	1.74	1.54	2.6	3.51	—
Ionization energy (kJ/mol)	900	738	590	550	503	509
Atomic radius (pm)	112	160	197	215	222	220
Ionic radius (pm)	45	72	100	118	136	148
Common oxidation number in compounds	+2	+2	+2	+2	+2	+2
Crystal structure	hcp*	hcp	fcc**	fcc	bcc	bcc
Hardness (Mohs' scale)	4.0	2.0	1.5	1.8	1.5	—

\*hexagonal close-packed

\*\*face-centered cubic

APPLICATION *Technology*

## Fireworks

Fireworks are made from pyrotechnics—chemical substances that produce light and smoke when they are ignited. Pyrotechnics are also used in flares, smoke bombs, explosives, and matches. An aerial fireworks device is a rocket made of a cylinder, chemicals inside the cylinder, and fuses attached to the cylinder. The illustration on the right shows how the device works. The lift charge at the bottom of the cylinder consists of a small amount of black gunpowder. When the side fuse ignites the gunpowder, it explodes like a small bomb. The gunpowder consists of potassium nitrate, charcoal, and sulfur. When these three chemicals react with one another, they produce gases. In this case, the gases produced are carbon monoxide, carbon dioxide, sulfur dioxide, and nitrogen monoxide. These hot gases expand very rapidly, providing the thrust that lifts the rocket into the sky.

About the time the shell reaches its maximum altitude and minimum speed, the time fuse ignites the chemicals contained in the cylinder. The chemicals inside the cylinder determine the color of the burst.



*The cylinder of a multiple-burst rocket contains separate reaction chambers connected by fuses. A common fuse ignites the propellant and the time-delay fuse in the first reaction chamber.*



### Chemical Composition and Color

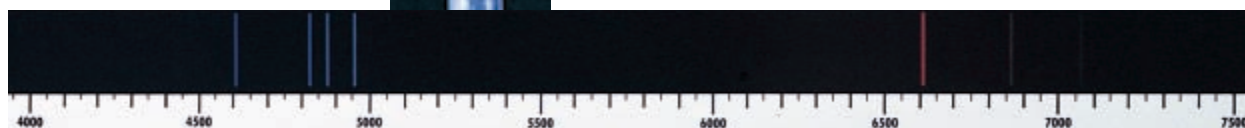
One of the characteristics of fireworks that we enjoy most is their variety of rich colors. These colors are created in much the same way as the colors produced during a flame test. In a fireworks device, the chloride salt is heated to a high temperature, causing the excited atoms to give off a burst of light. The color of light produced depends on the metal used. The decomposition of barium chloride,  $\text{BaCl}_2$ , for example, produces a burst of green light, whereas strontium chloride,  $\text{SrCl}_2$ , releases red light.

People who design fireworks combine artistry with a technical knowledge of chemical properties. They have found ways to combine different colors within a single cylinder and to make parts of the cylinder explode at different times. Fireworks designers have a technical knowledge of projectile motion that is used to determine the height, direction, and angle at which a fireworks device will explode to produce a fan, fountain, flower, stream, comet, spider, star, or other shape.

### Strontium and the Visible Spectrum

When heated, some metallic elements and their compounds emit light at specific wavelengths that are characteristic of the element or compound. Visible light includes wavelengths between about 400 and 700 nanometers. The figure below shows the emission spectrum for strontium. When heated, strontium gives off the maximum amount of visible light at about 700 nanometers, which falls in the red-light region of the visible spectrum.

*The emission spectrum for strontium shows strong bands in the red region of the visible light spectrum.*



### Flares

Flares operate on a chemical principle that is different from that of fireworks. A typical flare consists of finely divided magnesium metal and an oxidizing agent. When the flare is ignited, the oxidizing agent reacts with the magnesium metal to produce magnesium oxide. This reaction releases so much energy that it produces a glow like that of the filaments in a light bulb. The brilliant white light produced by the flare is caused by billions of tiny particles of magnesium that glow when they react. If slightly larger particles of magnesium metal are used in the flare, the system glows for a longer period of time because the particles' reaction with the oxidizing agent is slower.

A colored flare can be thought of as a combination of a white flare and a chemical that produces colored light when burned.

For example, a red flare can be made from magnesium metal, an oxidizing agent, and a compound of strontium. When the flare is ignited, the oxidizing agent and magnesium metal react, heating the magnesium to white-hot temperatures. The heat from this reaction causes the strontium compound to give off its characteristic red color.



*A flare is made up of billions of reacting magnesium particles.*

For safety reasons, some fireworks manufacturers store their products in metal sheds separated by sand banks. Also, people who work with fireworks are advised to wear cotton clothing because cotton is less likely than other fabrics to develop a static charge, which can cause a spark and accidentally ignite fireworks.

**APPLICATION** *Health***Calcium: An Essential Mineral in the Diet**

Calcium is the most abundant mineral in the body. It is the mineral that makes up a good portion of the teeth and the bone mass of the body. A small percentage of calcium in the body is used in the reactions by which cells communicate and in the regulation of certain body processes. Calcium is so important to normal body functioning that if the calcium level of the blood falls far below normal, hormones signal the release of calcium from bone and signal the gastrointestinal tract to absorb more calcium during the digestion process.

A prolonged diet that is low in calcium is linked to a disease characterized by a decrease in bone mass, a condition called osteoporosis. Reduced bone mass results in brittle bones that fracture easily. Osteoporosis generally occurs later in life and is more prevalent in females. However, because you achieve peak bone mass during the late teens or early twenties, it is critical that your diet meet the recommended requirements to increase your peak bone mass. The recommended dietary intake for calcium is 1000 mg per day. Maintaining that level in the diet along with regular exercise through adulthood are thought to reduce the rate of bone loss later in life. Excess calcium in the diet (consuming more than 2500 mg daily) can interfere with the absorption of other minerals.



*Dairy products are generally good sources of calcium.*

**Magnesium: An Essential Mineral in the Diet**

Though magnesium has several functions in the body, one of the more important functions is its role in the absorption of calcium by cells. Magnesium, like sodium and potassium, is involved in the transmission of nerve impulses. Like calcium, magnesium is a component of bone.

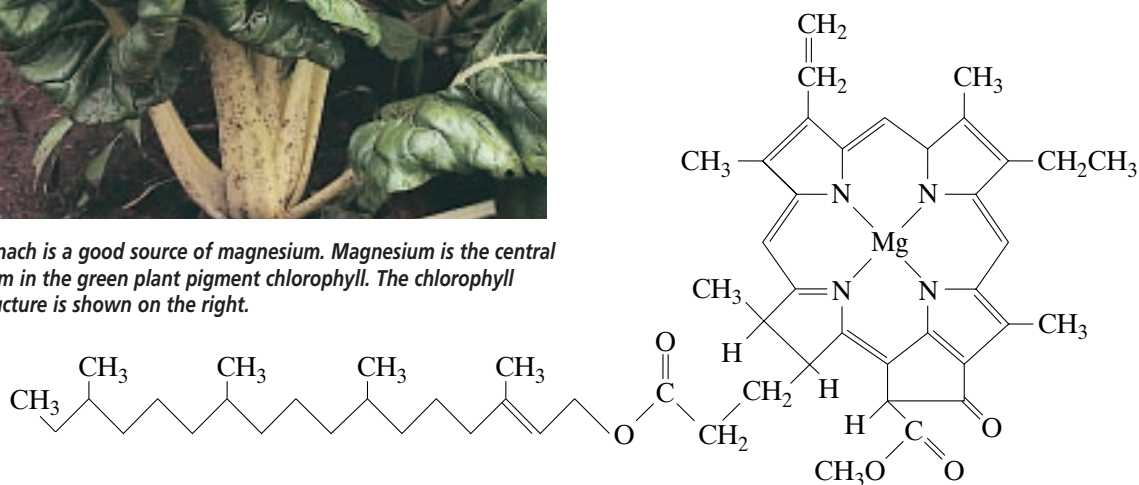
A major source of magnesium in the diet is plants. Magnesium is the central atom in the green plant pigment chlorophyll. The structure of chlorophyll in plants is somewhat similar to the structure of heme—the oxygen-carrying molecule in animals. (See page 758 for the heme structure.)

**TABLE 2A** Good Sources of Calcium in the Diet

Food	Serving size	Calcium present (mg)
Broccoli	6.3 oz	82
Cheddar cheese	1 oz	204
Cheese pizza, frozen	pizza for one	375
Milk, low-fat 1%	8 oz	300
Tofu, regular	4 oz	130
Vegetable pizza, frozen	pizza for one	500
Yogurt, low-fat	8 oz	415
Yogurt, plain whole milk	8 oz	274



Spinach is a good source of magnesium. Magnesium is the central atom in the green plant pigment chlorophyll. The chlorophyll structure is shown on the right.



The recommended dietary intake of magnesium is 400 mg per day. This is equivalent to just 4 oz of bran cereal. Because magnesium levels are easily maintained by a normal diet, it is unusual for anyone to have a magnesium deficiency. Most magnesium deficiencies are the result of factors that decrease magnesium absorption. People with gastrointestinal disorders, alcohol abusers, and the critically ill are most likely to have these types of absorption problems.

Excess magnesium in the diet is excreted by the kidneys, so there are no cumulative toxic effects.

**TABLE 2B** Good Sources of Magnesium in the Diet

Food	Serving size	Magnesium present (mg)
Barley, raw	1 cup	244
Beef, broiled sirloin	4 oz	36
Cabbage, raw	1 med. head	134
Cashews, dry-roasted	1 oz	74
Chicken, roasted breast	4 oz	31
Lima beans, boiled	1/2 cup	63
Oatmeal	1 oz	39
Potato, baked	7.1 oz	115
Prunes, dried	4 oz	51
Rice bran	8 oz	648
Salmon, canned	4 oz	39
Spinach, raw	10 oz	161

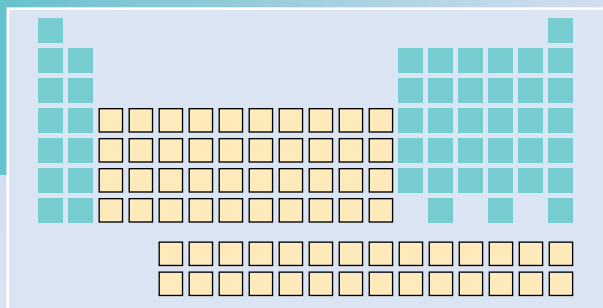


# GROUPS 3–12

## TRANSITION METALS

### CHARACTERISTICS

- consist of metals in Groups 3 through 12
- contain one or two electrons in their outermost energy level
- are usually harder and more brittle than metals in Groups 1 and 2
- have higher melting and boiling points than metals in Groups 1 and 2
- are good conductors of heat and electricity
- are malleable and ductile
- have a silvery luster, except copper and gold
- include radioactive elements with numbers 89 through 112
- include mercury, the only liquid metal at room temperature
- have chemical properties that differ from each other
- tend to have two or more common oxidation states
- often form colored compounds
- may form complex ions



*Iron ore is obtained from surface mines. Hematite,  $\text{Fe}_2\text{O}_3$ , is the most common iron ore.*



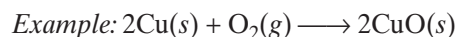
*Copper ores are also obtained from surface mines. Copper ore is shown here.*



*Gold, silver, platinum, palladium, iridium, rhodium, ruthenium, and osmium are sometimes referred to as the noble metals because they are not very reactive. These inert metals are found in coins, jewelry, and metal sculptures.*

## COMMON REACTIONS

Because this region of the periodic table is so large, you would expect great variety in the types of reaction characteristics of transition metals. For example, copper oxidizes in air to form the green patina you see on the Statue of Liberty. Copper reacts with concentrated  $\text{HNO}_3$  but not with dilute  $\text{HNO}_3$ . Zinc, on the other hand, reacts readily with dilute  $\text{HCl}$ . Iron oxidizes in air to form rust, but chromium is generally unreactive in air. Some common reactions for transition elements are shown by the following.

**May form two or more different ions****May react with oxygen to form oxides****May react with halogens to form halides****May form complex ions**

See examples in the lower right.



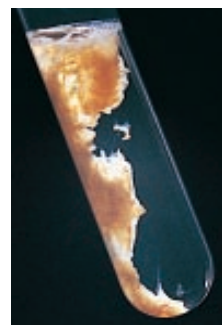
Copper reacts with oxygen in air.



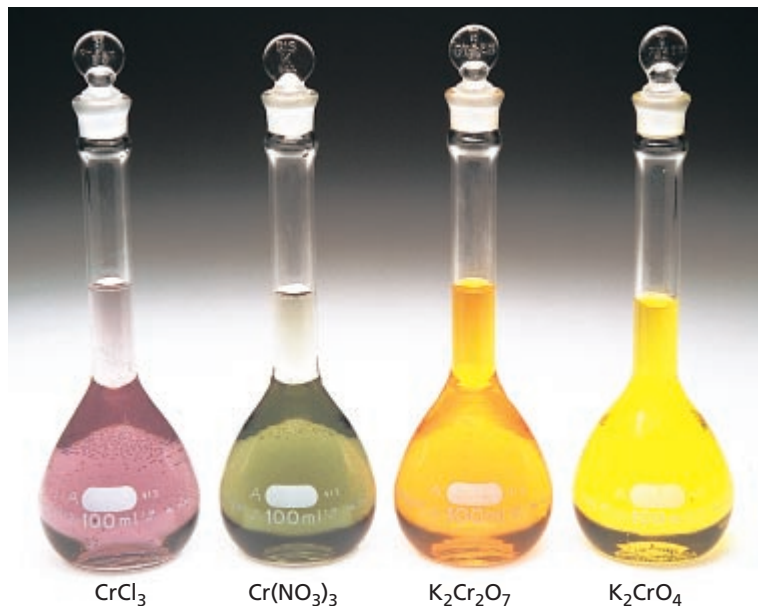
Copper reacts with concentrated nitric acid.



Zinc reacts with dilute hydrochloric acid.



Soluble iron(III) salts form insoluble  $\text{Fe}(\text{OH})_3$  when they are reacted with a hydroxide base.



Chromium has several common oxidation states, represented here by aqueous solutions of its compounds. The violet and green solutions contain chromium in the +3 state, and the yellow and orange solutions contain chromium in the +6 oxidation state.

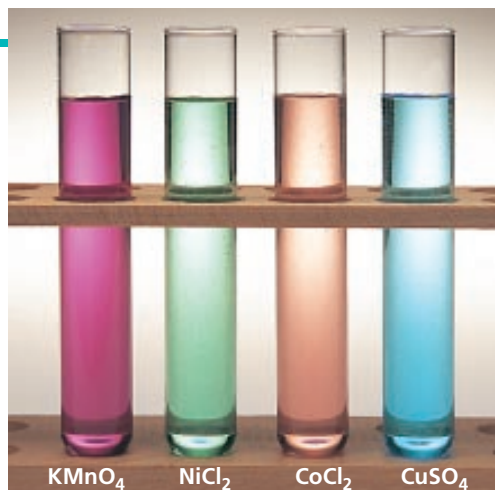


Complex ions belong to a class of compounds called coordination compounds. Coordination compounds show great variety in colors. Several transition-metal coordination compounds are shown.



## ANALYTICAL TEST

Flame tests are not commonly used to identify transition metals. The presence of a certain transition-metal ion in a solution is sometimes obvious from the solution's color. Some transition-metal ions can be more accurately identified using a procedure called qualitative analysis. **Qualitative analysis** is the identification of ions by their characteristic reactions. The transition-metal ions most often identified through qualitative analysis include copper, nickel, zinc, chromium, iron cobalt, cadmium, manganese, and tin. Most tests to identify the presence of an ion in a mixture involve causing the ion to precipitate out of solution. Some of the more dramatic precipitation reactions for transition metals are shown.



Some transition metal ions can be identified by characteristic colors of their salt solutions.



Copper (formation of  $[\text{Cu}(\text{NH}_3)_4](\text{OH})_2$ )



Cadmium (formation of  $\text{CdS}$ )



Zinc (formation of  $\text{ZnS}$ )



Chromium (formation of  $\text{PbCrO}_4$ )



Iron (formation of  $[\text{Fe}(\text{SCN})]^{2+}$ )



Manganese (formation of  $\text{MnO}_2$ )



Nickel (formation of a nickel dimethylglyoxime complex)



## PROPERTIES OF SOME TRANSITION METALS

	Cr	Fe	Co	Ni	Cu	Zn	Ag	Au	Hg
Melting point (°C)	1857 ± 20	1535	1495	1455	1083	420	962	1064	−38.8
Boiling point (°C)	2672	2750	2870	2732	2567	907	2212	2808 ± 2	356.6
Density (g/cm <sup>3</sup> )	7.20	7.86	8.9	8.92	8.96	7.14	10.5	19.3	13.5
Ionization energy (kJ/mol)	653	762	760	737	46	906	731	890	1007
Atomic radius (pm)	128	126	125	124	128	134	144	144	151
Common oxidation numbers	+2, +3, +6	+2, +3	+2, +3	+2	+1, +2	+2	+1	+1, +3	+1, +2

APPLICATION *Geology***Gemstones and Color**

A gemstone is a mineral that can be cut and polished to make gems for an ornament or piece of jewelry. At one time, all gemstones were naturally occurring minerals mined from the Earth's crust. Today, however, chemists can duplicate natural processes to produce artificial gemstones. Amethyst, emerald, jade, opal, ruby, sapphire, and topaz occur naturally and can also be produced synthetically.

The color of a gemstone is determined by the presence of small amounts of one or more transition metals. For example, aluminum oxide,  $\text{Al}_2\text{O}_3$ , often occurs naturally as corundum—a clear, colorless mineral. However, if as few as 1 to 2% of the aluminum ions,  $\text{Al}^{3+}$ , are replaced by chromium ions,  $\text{Cr}^{3+}$ , the corundum takes on a reddish color and is known as ruby. If a small fraction of aluminum ions in corundum are replaced by  $\text{Fe}^{3+}$  and  $\text{Ti}^{3+}$ , the corundum has

a greenish color and is known as emerald. In another variation, if vanadium ions,  $\text{V}^{3+}$ , replace a few  $\text{Al}^{3+}$  ions in corundum, the result is a gemstone known as alexandrite. This gemstone appears green in reflected natural light and red in transmitted or artificial light.

Table 3A lists transition metals that are responsible for the colors of various gemstones. The table provides only a general overview, however, as most naturally occurring gemstones occur in a range of hues, depending on the exact composition of the stone.

**Artificial Gemstones**

In 1902, the French chemist Auguste Verneuil found a way to melt a mixture of aluminum oxide and chromium salts and then cool the mixture very slowly to produce large crystals of reddish aluminum oxide—rubies.

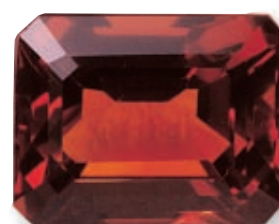
*Sapphire**Ruby**Peridot**Garnet*

TABLE 3A Transition Metals and Gemstone Colors

Gemstone	Color	Element
Amethyst	purple	iron
Aquamarine	blue	iron
Emerald	green	iron/titanium
Garnet	red	iron
Peridot	yellow-green	iron
Ruby	red	chromium
Sapphire	blue	iron/titanium
Spinel	colorless to red to black	varies
Turquoise	blue	copper

Verneuil's method, although somewhat modified, is still the one most widely used today for the manufacture of colored gemstones. When magnesium oxide is substituted for aluminum oxide, a colorless spinel-like product is formed. The addition of various transition metals then adds a tint to the spinel that results in the formation of synthetic emerald, aquamarine, tourmaline, or other gemstones. Synthetic gems look very much like their natural counterparts.



Synthetic sapphire



Synthetic ruby

## APPLICATION Technology

### Alloys

An alloy is a mixture of a metal and one or more other elements. In most cases, the second component of the mixture is also a metal.

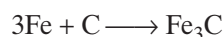
Alloys are desirable because mixtures of elements usually have properties different from and often superior to the properties of individual metals. For example, many alloys that contain iron are harder, stronger, and more resistant to oxidation than iron itself.

*Amalgams are alloys that contain mercury. They are soft and pliable when first produced, but later become solid and hard. Dental fillings were once made of an amalgam of mercury and silver. Concerns about the possible toxicity of mercury led to the development of other filling materials.*



**Cast Iron and Steel**

The term *steel* applies to any alloy consisting of iron and less than 1.5% carbon, and often other elements. When iron ore is treated with carbon in the form of coke to extract pure iron metal, some of the carbon also reacts with the iron to produce a form of iron carbide known as cementite. The reaction can be represented by the following equation.



Cast iron is a mixture that consists of some pure iron, known as ferrite, some cementite, and some carbon atoms trapped within the crystalline structure of the iron and cementite. The rate at which cast iron is cooled changes the proportion of these three components. If the cast iron is cooled slowly, the ferrite and cementite tend to separate from each other, forming

a banded product that is tough but not very hard. However, if the cast iron is cooled quickly, the components of the original mixture cannot separate from each other, forming a product that is both tough and hard.

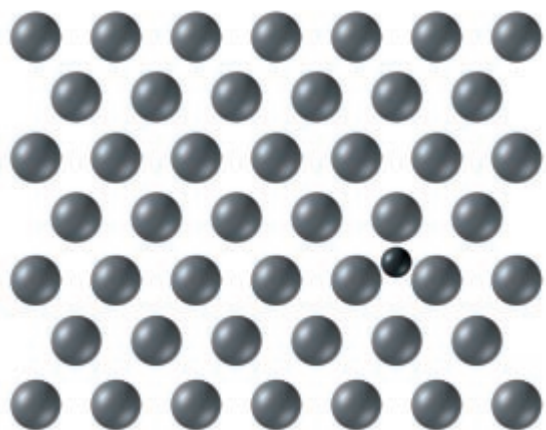


*Stainless steel, which is hard and resists corrosion, is made of iron and chromium (12–30%). The properties of stainless steel make it a suitable alloy for making cutlery and utensils.*

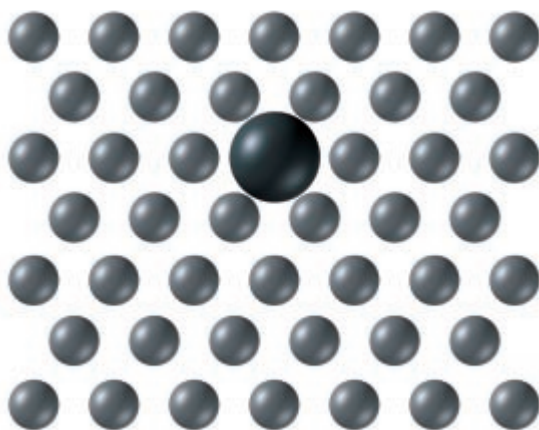
**TABLE 3B** Composition and Uses of Some Alloys

Name of alloy	Composition	Uses
Brass	copper with up to 50% zinc	inexpensive jewelry; hose nozzles and couplings; piping; stamping dies
Bronze	copper with up to 12% tin	coins and medals; heavy gears; tools; electrical hardware
Coin metal	copper: 75% nickel: 25%	United States coins
Duralumin	aluminum: 95% copper: 4% magnesium: 0.5% manganese: <1%	aircraft, boats, railroad cars, and machinery because of its high strength and resistance to corrosion
Nichrome	nickel: 80–85% chromium: 15–20%	heating elements in toasters, electric heaters, etc.
Phosphor bronze	bronze with a small amount of phosphorus	springs, electrical springs, boat propellers
Solder	lead: 50%, tin: 50% or tin: 98%, silver: 2%	joining two metals to each other  joining copper pipes
Sterling silver	silver: 92.5% copper: 7.5%	jewelry, art objects, flatware
Type metal	lead: 75–95% antimony: 2–18% tin: trace	used to make type for printing because it expands as it cools



**Interstitial crystal**

*A smaller atom or ion fits into a small space between particles in the array.*

**Substitutional crystal**

*A larger atom or ion is substituted for a particle in the array.*

**Structures and Preparation of Alloys**

Alloys generally crystallize in one of two ways, depending on relative sizes of atoms. If the atoms of one of the metals present are small enough to fit into the spaces between the atoms of the second metal, they form an alloy with an interstitial structure (*inter* means “between,” and *stitial* means “spaces”). If atoms of the two metals are of similar size or if one is larger, the atoms of one metal can substitute for the atoms of the second metal in its crystalline structure. Such alloys are substitutional alloys. Models for both types of crystals are shown above.

Techniques for making alloys depend on the metals used in the mixture. In some cases, the two metals can simply be melted together to form a mixture. The composition of the mixture often varies within a range, evidence that the final product is indeed a mixture and not a compound. In other cases, one metal may be melted first and the second dissolved in it. Brass is prepared in this way. If copper and zinc were heated together to a high temperature, zinc (bp  $907^{\circ}\text{C}$ ) would evaporate before copper (mp  $1084^{\circ}\text{C}$ ) melted. Therefore, the copper is melted first, and the zinc is added to it.



*Brass has a high luster and resembles gold when cleaned and polished. A brass object can be coated with a varnish to prevent reactions of the alloy with air and water.*



*Sterling silver is more widely used than pure silver because it is stronger and more durable.*

**APPLICATION** *The Environment***Mercury Poisoning**

Mercury is the only metal that is liquid at room temperature. It has a very high density compared with most other common transition metals and has a very high surface tension and high vapor pressure. Mercury and many of its compounds must be handled with extreme care because they are highly toxic. Mercury spills are especially hazardous because the droplets scatter easily and are often undetected during cleanup. These droplets release toxic vapors into the air.

Overexposure to mercury vapor or its compounds can occur by absorption through the skin, respiratory tract, or digestive tract. Mercury is a cumulative poison, which means that its concentration in the body increases as exposure increases.

Mercury that enters the body damages the kidneys, heart, and brain. The action of mercury on the brain affects the nervous system. Symptoms of mercury poisoning include numbness, tunnel vision, garbled speech, bleeding and inflammation of the gums, muscle spasms, anemia, and emotional disorders, such as depression, irritability, and personality changes. The saying “mad as a hatter” probably came about because of mercury poisoning. Mercury salts were once routinely used to process the felt used in hats.

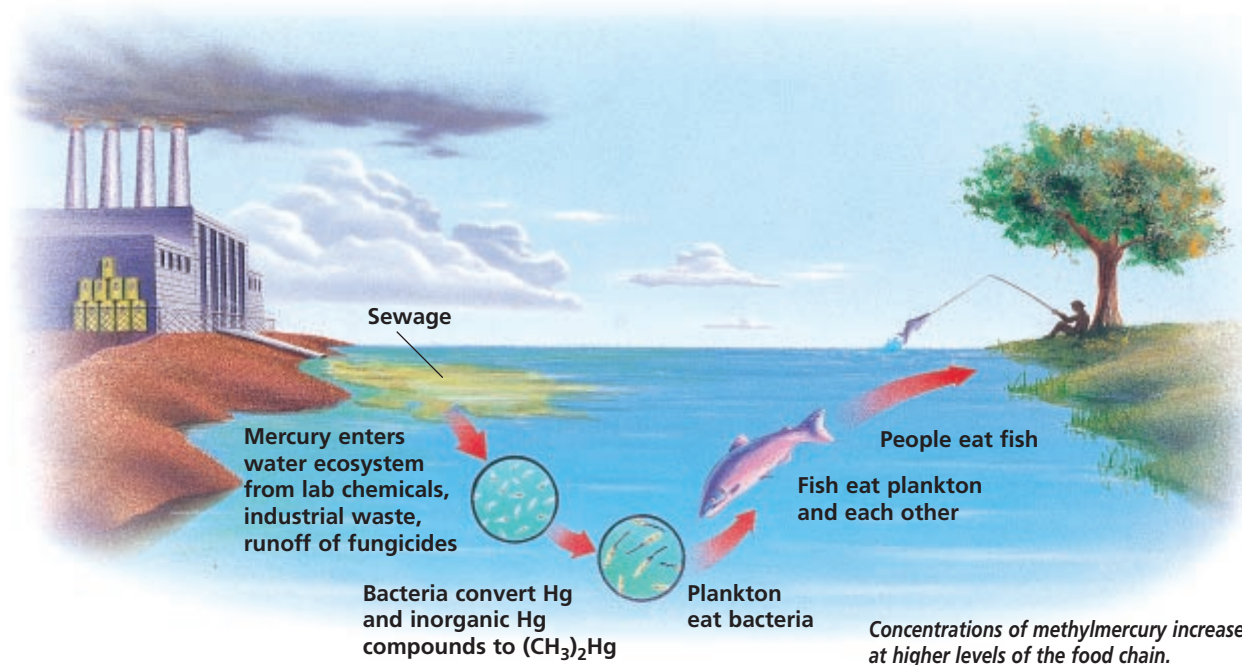
Hatters often displayed the nerve and mental impairments associated with overexposure to mercury.

**Methylmercury in Freshwater Ecosystems**

Mercury, Hg, can be found in our environment and in our food supply. Fortunately, the body has some protective mechanisms to deal with trace amounts of mercury. However, levels of mercury and of an organic mercury compound, methylmercury ( $\text{CH}_3$ )<sub>2</sub>Hg, are increasing in the environment due to mercury mining operations and runoff from the application of pesticides and fungicides.

Mercury is easily converted to methylmercury by bacteria. Methylmercury is more readily absorbed by cells than mercury itself. As a result, methylmercury accumulates in the food chain as shown in the diagram below. A serious incident of methylmercury poisoning occurred in Japan in the 1950s. People living in Minamata, Japan, were exposed to high levels of methylmercury from eating shellfish.

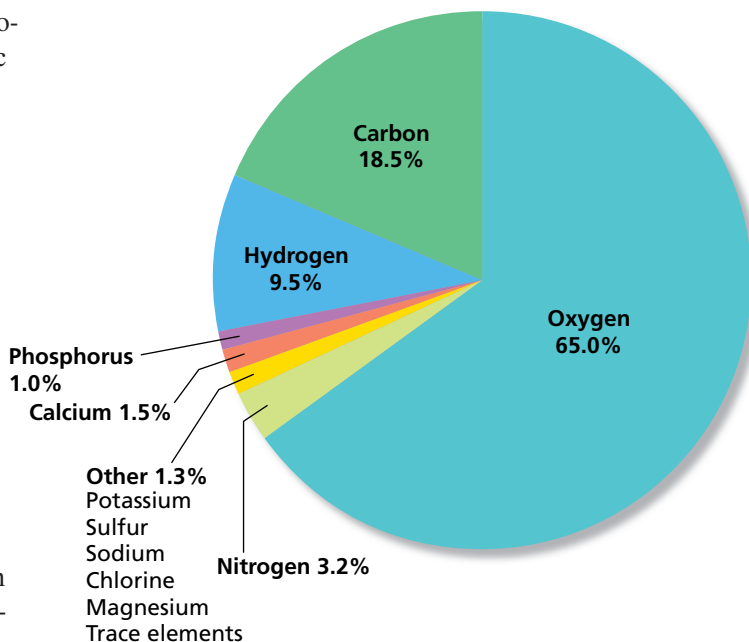
In the United States there is concern about mercury levels in fish from some freshwater lakes. Though environmental regulations have reduced the level of lake pollutants, it takes time to see a reduction in the concentration of an accumulated poison.



**APPLICATION** *Health***Elements in the Body**

The four most abundant elements in the body (oxygen, carbon, hydrogen, and nitrogen) are the major components of organic biomolecules, such as carbohydrates, proteins, fats, and nucleic acids. Other elements compose a dietary category of compounds called minerals. Minerals are considered the inorganic elements of the body. Minerals fall into two categories—the major minerals and the trace minerals, or trace elements, as they are sometimes called. Notice in the periodic table below that most elements in the trace elements category of minerals are transition metals.

Trace elements are minerals with dietary daily requirements of 100 mg or less. They are found in foods derived from both plants and animals. Though these elements are present in very small quantities, they perform a variety of essential functions in the body, as shown in Table 3C on the next page.

**Abundance of Elements in the Body (by mass)**

1 H																		2 He																	
Group 1		Group 2																Group 18																	
3 Li		4 Be																10 Ne																	
11 Na		12 Mg																18 Ar																	
19 K		20 Ca		21 Sc		22 Ti		23 V		24 Cr		25 Mn		26 Fe		27 Co		28 Ni		29 Cu		30 Zn		31 Ga		32 Ge		33 As		34 Se		35 Br		36 Kr	
37 Rb		38 Sr		39 Y		40 Zr		41 Nb		42 Mo		43 Tc		44 Ru		45 Rh		46 Pd		47 Ag		48 Cd		49 In		50 Sn		51 Sb		52 Te		53 I		54 Xe	
55 Cs		56 Ba		57 La		72 Hf		73 Ta		74 W		75 Re		76 Os		77 Ir		78 Pt		79 Au		80 Hg		81 Tl		82 Pb		83 Bi		84 Po		85 At		86 Rn	
87 Fr		88 Ra		89 Ac																															

Elements in organic matter

Major minerals

Trace elements



**TABLE 3C Transition Metal Trace Elements**

Transition metal	Function
Vanadium, Cadmium	function not fully determined, but linked to a reduced growth rate and impaired reproduction
Chromium	needed for glucose transport to cells
Manganese	used in the enzyme reactions that synthesize cholesterol and metabolize carbohydrates
Iron	central atom in the heme molecule—a component of hemoglobin, which binds oxygen in the blood for transport to cells
Cobalt	a component of vitamin B <sub>12</sub>
Nickel	enzyme cofactor in the metabolism of fatty acids and amino acids
Copper	a major component of an enzyme that functions to protect cells from damage
Zinc	needed for tissue growth and repair and as an enzyme cofactor
Molybdenum	enzyme cofactor in the production of uric acid

### Role of Iron

Most iron in the body is in hemoglobin.  $\text{Fe}^{3+}$  is the central ion in the heme molecule, which is a component of the proteins hemoglobin and myoglobin. Hemoglobin in red blood cells transports oxygen to cells and picks up carbon dioxide as waste. Myoglobin is a protein that stores oxygen to be used in muscle contraction. Iron is also in the proteins of the electron transport system and the immune system.

Mechanisms of the body control the rate of iron absorption from food in the diet. When iron reserves are low, chemical signals stimulate cells of the intestines to absorb more iron during digestion. If the diet is low in iron, causing a deficiency, hemoglobin production stops and a condition called iron-deficiency anemia results. The blood cells produced during this state are stunted and unable to deliver adequate oxygen to cells. As a result, a person with iron-deficiency anemia feels tired and weak and has difficulty maintaining normal body temperature. The recommended daily intake of iron is 15 mg. The recommended level doubles for pregnant women. Iron supplements are for people who do not get enough iron in their daily diets. Table 3D lists some foods that are good sources of iron in the diet. Too much iron can be toxic because the body stores iron once it is absorbed. Abusing iron supplements can cause severe liver and heart damage.

**TABLE 3D Sources of Iron in Foods**

Food	Serving size	Iron present (mg)
Beef roast (lean cut)	4 oz	3.55
Beef, T-bone steak (lean cut)	4 oz	3.40
Beef, ground (hamburger)	4 oz	2.78
Broccoli	6.3 oz	1.50
Chicken, breast	4 oz	1.35
Chicken, giblets	4 oz	7.30
Oatmeal, instant enriched	1 pkg	8.35
Pita bread, white enriched	6 1/2 in. diameter	1.40
Pork roast	4 oz	1.15
Prunes	4 oz	2.00
Raisins	4 oz	1.88

# GROUP 13 BORON FAMILY

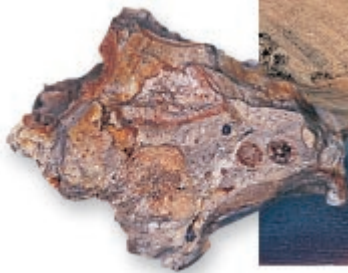
## CHARACTERISTICS

- do not occur naturally in element form
- are scarce in nature (except aluminum, which is the most abundant metallic element)
- consist of atoms that have three electrons in their outer energy level
- are metallic solids (except boron, which is a solid metalloid)
- are soft and have low melting points (except boron, which is hard and has a high melting point)
- are chemically reactive at moderate temperatures (except boron)

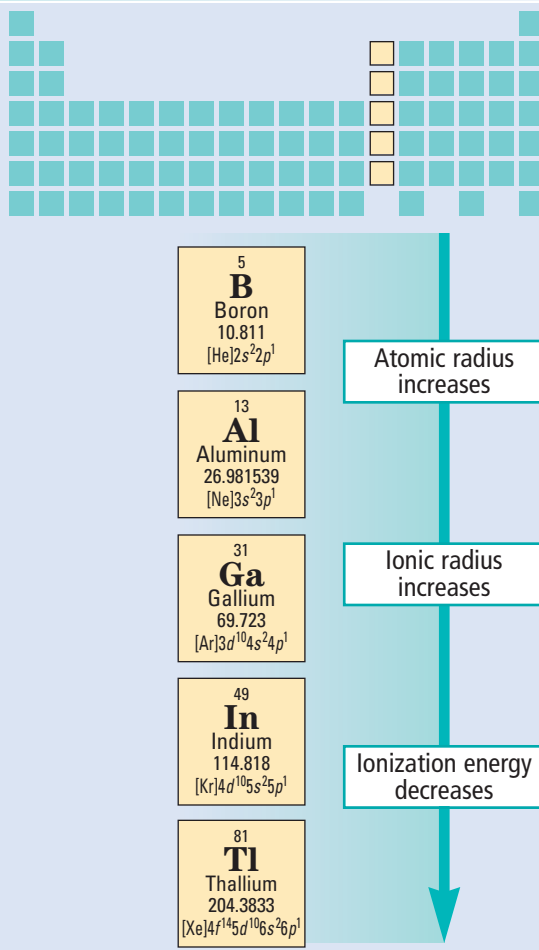
*Boron is a covalent solid. Other members of the family are metallic solids.*



*The warmth of a person's hand will melt gallium. Gallium metal has the lowest melting point (29.77°C) of any metal except mercury.*

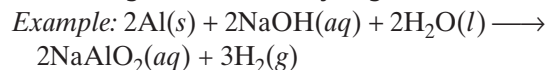


*Aluminum is the most abundant metal in Earth's crust. It exists in nature as an ore called bauxite.*

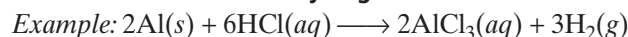


## COMMON REACTIONS

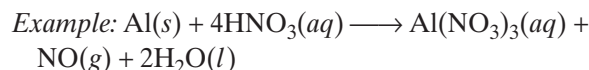
The reaction chemistry of boron differs greatly from that of the other members of this family. Pure boron is a covalent network solid, whereas the other members of the family are metallic crystals in pure form. Boron resembles silicon more closely than it resembles the other members of its family.

**With Strong Bases to Form Hydrogen Gas and a Salt**

Ga also follows this pattern.

**With Dilute Acids to Form Hydrogen Gas and a Salt**

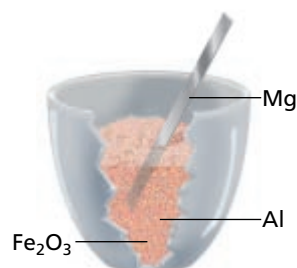
Ga, In, and Tl follow this pattern in reacting with dilute HF, HCl, HBr, and HI.

**With Halogens to Form Halides**

B, Al, Ga, In, and Tl also follow this pattern in reacting with  $\text{F}_2$ ,  $\text{Cl}_2$ ,  $\text{Br}_2$ , and  $\text{I}_2$  (except  $\text{BF}_3$ ).

**With Oxygen to Form Oxides**

Ga, In, and Tl also follow this pattern.



A mixture of powdered aluminum and iron(III) oxide is called thermite. Al reacts with  $\text{Fe}_2\text{O}_3$  using Mg ribbon as a fuse to provide activation energy. The energy produced by the thermite reaction is sufficient to produce molten iron as a product.



## ANALYTICAL TEST

Other than atomic absorption spectroscopy, there is no simple analytical test for all the members of the boron family.

*The confirmatory test for the presence of aluminum in qualitative analysis is the formation of  $\text{Al}(\text{OH})_3$ , which may be hard to detect in solution. The precipitate is made visible by the addition of a red dye called aluminum reagent.*



Aluminum forms a thin layer of  $\text{Al}_2\text{O}_3$ , which protects the metal from oxidation and makes it suitable for outdoor use.



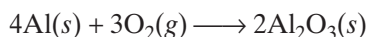
## PROPERTIES OF THE GROUP 13 ELEMENTS

	B	Al	Ga	In	Tl
Melting point (°C)	2300	660.37	29.77	156.61	303.5
Boiling point (°C)	2550	2467	2203	2080	1457
Density (g/cm <sup>3</sup> )	2.34	2.702	5.904	7.31	11.85
Ionization energy (kJ/mol)	801	578	579	558	589
Atomic radius (pm)	85	143	135	167	170
Ionic radius (pm)	—	54	62	80	89
Common oxidation number in compounds	+3	+3	+1, +3	+1, +3	+1, +3
Crystal structure	monoclinic	fcc	orthorhombic	fcc	hcp
Hardness (Mohs' scale)	9.3	2.75	1.5	1.2	1.2

## APPLICATION

*Technology***Aluminum**

Chemically, aluminum is much more active than copper, and it belongs to the category of *self-protecting metals*. These metals are oxidized when exposed to oxygen in the air and form a hard, protective metal oxide on the surface. The oxidation of aluminum is shown by the following reaction.



This oxide coating protects the underlying metal from further reaction with oxygen or other substances. Self-protecting metals are valuable in themselves or when used to coat iron and steel to keep them from corroding.

Aluminum is a very good conductor of electric current. Many years ago, most high-voltage electric power lines were made of copper. Although copper is a better conductor of electricity than aluminum, copper is heavier and more expensive. Today more than 90% of high-voltage transmission lines are made of relatively pure aluminum. The aluminum wire does not have to be self-supporting because steel cable is incorporated to bear the weight of the wire in the long spans between towers.

In the 1960s, aluminum electric wiring was used in many houses and other buildings. Over time, however,



*These high-voltage transmission lines are made of aluminum supported with steel cables.*

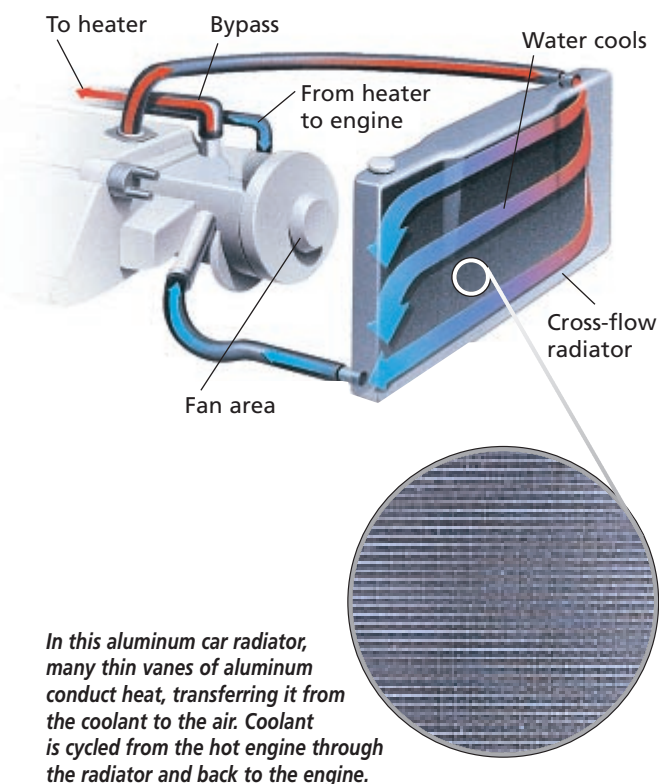
because the aluminum oxidized,  $\text{Al}_2\text{O}_3$  built up and increased electric resistance at points where wires connected to outlets, switches, and other metals. As current flowed through the extra resistance, enough heat was generated to cause a fire. Though some homes have been rewired, aluminum wiring is still prevalent in many homes.

## Aluminum Alloys

Because aluminum has a low density and is inexpensive, it is used to construct aircraft, boats, sports equipment, and other lightweight, high-strength objects. The pure metal is not strong, so it is mixed with small quantities of other metals—usually manganese, copper, magnesium, zinc, or silicon—to produce strong low-density alloys. Typically, 80% of a modern aircraft frame consists of aluminum alloy.

Aluminum and its alloys are good conductors of heat. An alloy of aluminum and manganese is used to make cookware. High-quality pots and pans made of stainless steel may have a plate of aluminum on the bottom to help conduct heat quickly to the interior.

Automobile radiators made of aluminum conduct heat as hot coolant from the engine enters the bottom of the radiator. The coolant is deflected into several channels. These channels are covered by thin vanes of aluminum, which conduct heat away from the coolant and transfer it to the cooler air rushing past. By the time the coolant reaches the top of the radiator, its temperature has dropped so that when it flows back into the engine it can absorb more heat. To keep the process efficient, the outside of a radiator should be kept unobstructed and free of dirt buildup.



*In this aluminum car radiator, many thin vanes of aluminum conduct heat, transferring it from the coolant to the air. Coolant is cycled from the hot engine through the radiator and back to the engine.*

**TABLE 4A** Alloys of Aluminum and Their Uses

Principal alloying element(s)*	Characteristics	Application examples
Manganese	moderately strong, easily worked	cookware, roofing, storage tanks, lawn furniture
Copper	strong, easily formed	aircraft structural parts; large, thin structural panels
Magnesium	strong, resists corrosion, easy to weld	parts for boats and ships, outdoor decorative objects, tall poles
Zinc and magnesium	very strong, resists corrosion	aircraft structural parts, vehicle parts, anything that needs high strength and low weight
Silicon	expands little on heating and cooling	aluminum castings
Magnesium and silicon	resists corrosion, easily formed	exposed parts of buildings, bridges

\* All these alloys have small amounts of other elements.

# GROUP 14 CARBON FAMILY

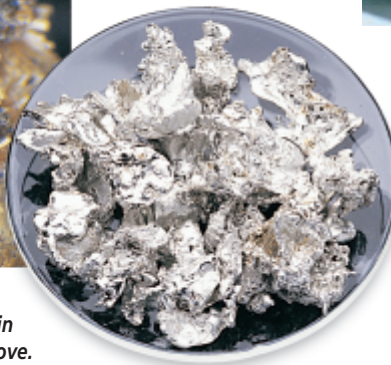
## CHARACTERISTICS

- include a nonmetal (carbon), two metalloids (silicon and germanium), and two metals (tin and lead)
- vary greatly in both physical and chemical properties
- occur in nature in both combined and elemental forms
- consist of atoms that contain four electrons in the outermost energy level
- are relatively unreactive
- tend to form covalent compounds (tin and lead also form ionic compounds)

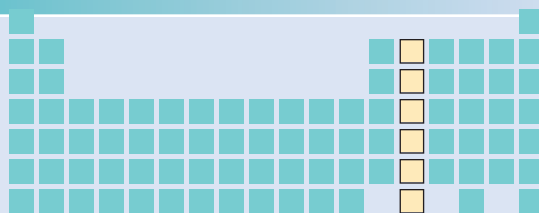
*Lead has a low reactivity and is resistant to corrosion. It is very soft, highly ductile, and malleable. Lead is toxic and, like mercury, it is a cumulative poison.*



*Tin, which is shown on the right, is a self-protecting metal like lead, but unlike lead it has a high luster. Tin occurs in nature in cassiterite ore, which is shown above.*



*Silicon has a luster but does not exhibit metallic properties. Most silicon in nature is a silicon oxide, which occurs in sand and quartz, which is shown here.*



6  
**C**  
Carbon  
12.011  
[He]2s<sup>2</sup>2p<sup>2</sup>

14  
**Si**  
Silicon  
28.0855  
[Ne]3s<sup>2</sup>3p<sup>2</sup>

32  
**Ge**  
Germanium  
72.61  
[Ar]3d<sup>10</sup>4s<sup>2</sup>4p<sup>2</sup>

50  
**Sn**  
Tin  
118.710  
[Kr]4d<sup>10</sup>5s<sup>2</sup>5p<sup>2</sup>

82  
**Pb**  
Lead  
207.2  
[Xe]4f<sup>14</sup>5d<sup>10</sup>6s<sup>2</sup>6p<sup>2</sup>

Atomic radius  
increases

Ionization energy  
decreases





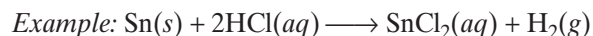
## COMMON REACTIONS

**With Oxygen to Form Oxides**

Pb follows this pattern, as do C, Si, and Ge at high temperatures.

**With Acids to Form Salts and Hydrogen Gas**

Only the metallic elements of this group react slowly with aqueous acids.



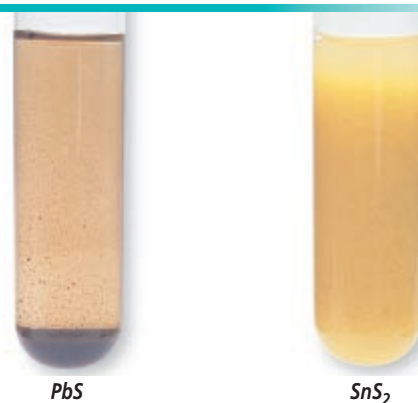
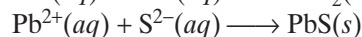
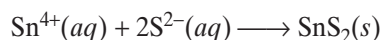
Both Sn and Pb can also react to form tin(IV) and lead(IV) salts, respectively.

**With Halogens to Form Halides**

Si, Ge, and Pb follow this pattern, reacting with  $\text{F}_2$ ,  $\text{Cl}_2$ ,  $\text{Br}_2$ , and  $\text{I}_2$ .

## ANALYTICAL TEST

The only way to identify all the elements of this group is by atomic absorption spectroscopy. Ionic compounds of tin and lead can be identified in aqueous solutions by adding a solution containing sulfide ions. The formation of a yellow precipitate indicates the presence of  $\text{Sn}^{4+}$ , and the formation of a black precipitate indicates the presence of  $\text{Pb}^{2+}$ .



## PROPERTIES OF THE GROUP 14 ELEMENTS

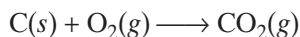
	C	Si	Ge	Sn	Pb
Melting point (°C)	3500/3652*	1410	937.4	231.88	327.502
Boiling point (°C)	3930	2355	2830	2260	1740
Density (g/cm <sup>3</sup> )	3.51/2.25*	2.33 ± 0.01	5.323	7.28	11.343
Ionization energy (kJ/mol)	1086	787	762	709	716
Atomic radius (pm)	77	118	122	140	175
Ionic radius (pm)	260 ( $\text{C}^{4-}$ ion)	—	—	118 ( $\text{Sn}^{2+}$ ion)	119 ( $\text{Pb}^{2+}$ ion)
Common oxidation number in compounds	+4, -4	+4	+2, +4	+2, +4	+2, +4
Crystal structure	cubic/hexagonal*	cubic	cubic	tetragonal	fcc
Hardness (Mohs' scale)	10/0.5*	6.5	6.0	1.5	1.5

\*The data are for two allotropic forms: diamond/graphite.

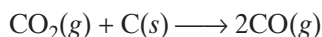
**APPLICATION** *Chemical Industry***Carbon and the Reduction of Iron Ore**

Some metals, especially iron, are separated from their ores through reduction reactions in a blast furnace. The blast furnace gets its name from the fact that air or pure oxygen is blown into the furnace, where it oxidizes carbon to form carbon monoxide, CO. Carbon and its compounds are important reactants in this process.

What happens inside the blast furnace to recover the iron from its ore? The actual chemical changes that occur are complex. A simplified explanation begins with the reaction of oxygen in hot air with coke, a form of carbon. Some of the coke burns to form carbon dioxide.



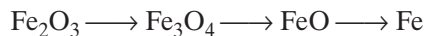
As the concentration of oxygen is increased, the carbon dioxide comes in contact with pieces of hot coke and is reduced to carbon monoxide.



The carbon monoxide now acts as a reducing agent to reduce the iron oxides in the ore to metallic iron.



The reduction is thought to occur in steps as the temperature in the furnace increases. The following are some of the possible steps.



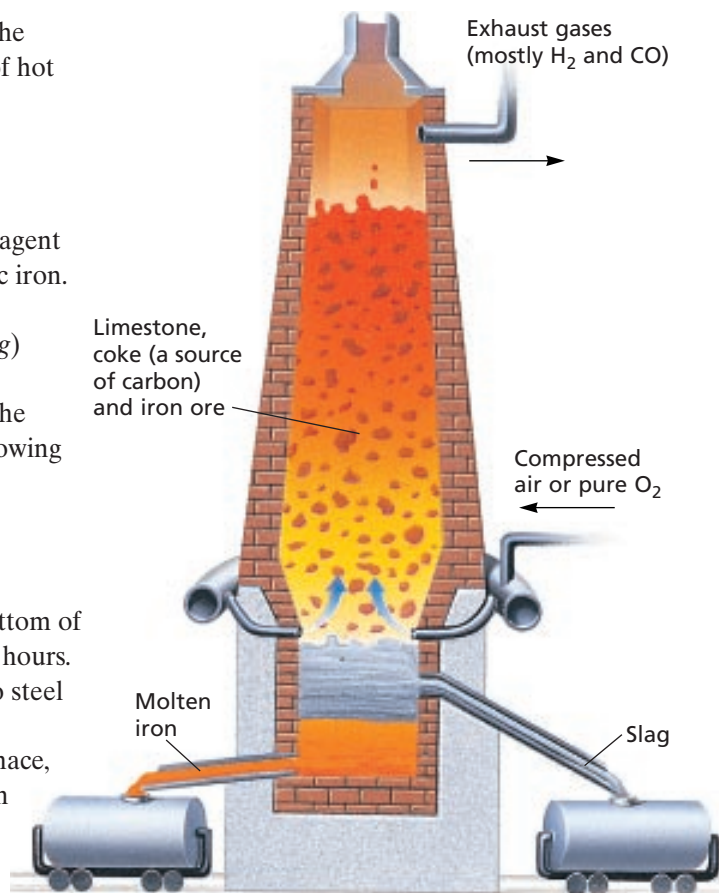
The white-hot liquid iron collects in the bottom of the furnace and is removed every four or five hours. The iron may be cast in molds or converted to steel in another process.

Limestone, present in the center of the furnace, decomposes to form calcium oxide and carbon dioxide.



The calcium oxide then combines with silica, a silicon compound, to form calcium silicate slag.

The relatively high carbon content of iron produced in a blast furnace makes the metal hard but brittle. It also has other impurities, like sulfur and phosphorus, that cause the recovered iron to be brittle. The conversion of iron to steel is essentially a purification process in which impurities are removed by oxidation. This purification process is carried out in another kind of furnace at very high temperatures. All steel contains 0.02 to 1.5% carbon. In fact, steels are graded by their carbon content. Low-carbon steels typically contain 0.02 to 0.3% carbon. Medium-carbon steels typically contain 0.03 to 0.7% carbon. High-carbon steels contain 0.7 to 1.5% carbon.



*Molten iron flowing from the bottom of a blast furnace has been reduced from its ore through a series of reactions at high temperatures in different regions of the furnace.*

## Carbon Dioxide

Carbon dioxide is a colorless gas with a faintly irritating odor and a slightly sour taste. The sour taste is the result of the formation of carbonic acid when  $\text{CO}_2$  dissolves in the water in saliva. It is a stable gas that does not burn or support combustion. At temperatures lower than  $31^\circ\text{C}$  and at pressures higher than 72.9 atm,  $\text{CO}_2$  condenses to the liquid form. A phase diagram for  $\text{CO}_2$  is found in the chapter review section of Chapter 12. At normal atmospheric pressure, solid  $\text{CO}_2$  (dry ice) sublimates at  $-78.5^\circ\text{C}$ . The linear arrangement of carbon dioxide molecules makes them nonpolar.

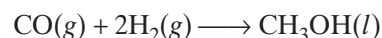
$\text{CO}_2$  is produced by the burning of organic fuels and from respiration processes in most living things. Most  $\text{CO}_2$  released into the atmosphere is used by plants during photosynthesis. Recall that photosynthesis is the process by which green plants and some forms of algae and bacteria make food. During photosynthesis,  $\text{CO}_2$  reacts with  $\text{H}_2\text{O}$ , using the energy from sunlight. The relationships among the various processes on Earth that convert carbon to

carbon dioxide are summarized in the diagram of the carbon cycle, which is pictured below.

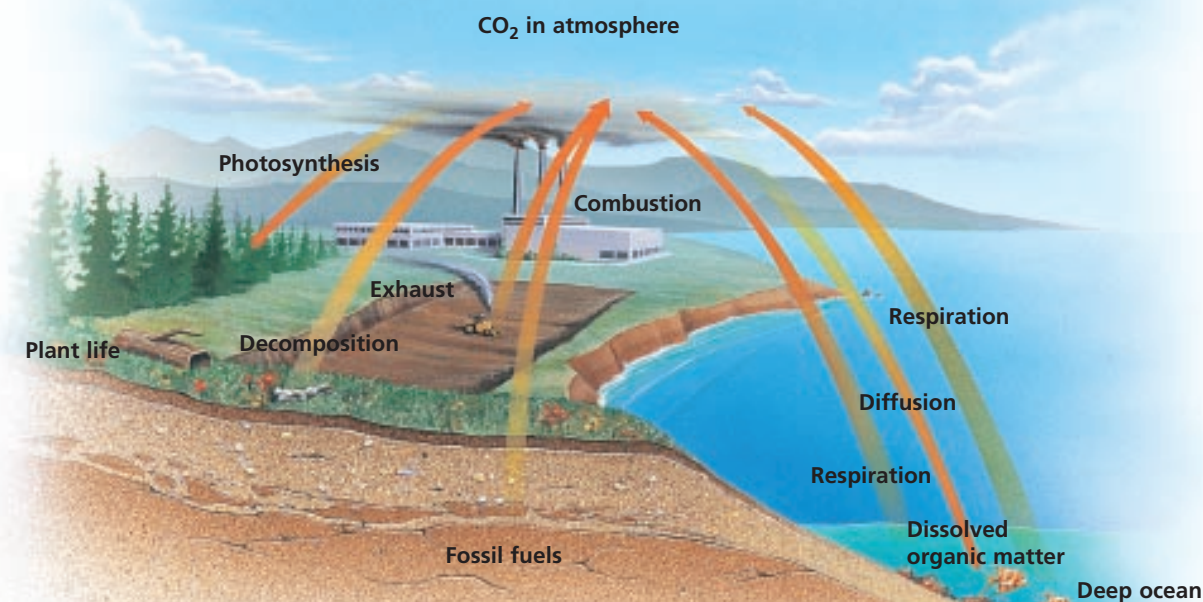
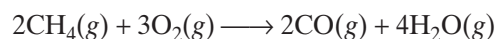
## Carbon Monoxide

Carbon monoxide is a poisonous gas produced naturally by decaying plants, certain types of algae, volcanic eruptions, and the oxidation of methane in the atmosphere.

Because  $\text{CO}$  is colorless, odorless, and tasteless, it is difficult to detect. It is slightly less dense than air and slightly soluble in water. Its main chemical uses are in the reduction of iron, described on page 756, and the production of organic compounds, such as methanol.



Carbon monoxide is also produced during the incomplete combustion of organic fuels. Incomplete combustion of methane occurs when the supply of oxygen is limited.



*The processes that recycle  $\text{CO}_2$  are collectively called the carbon cycle.*

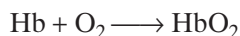


APPLICATION *Biochemistry***Carbon Dioxide and Respiration**

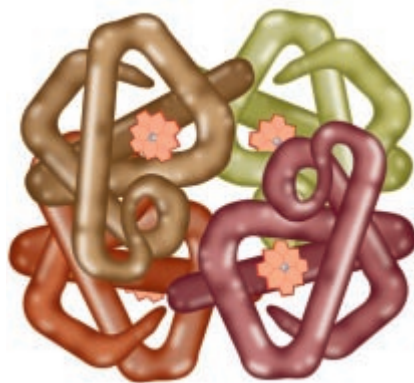
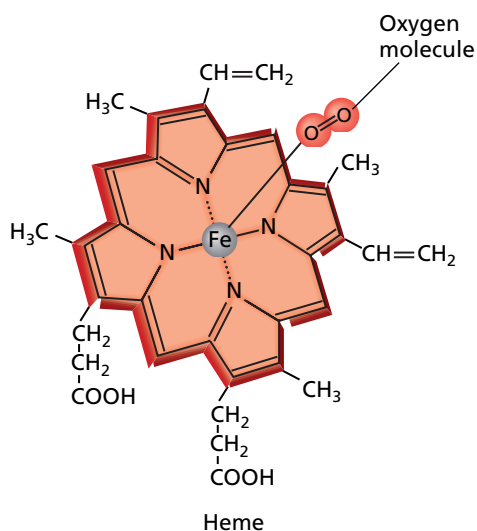
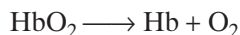
Many organisms, including humans, carry out cellular respiration. In this process, cells break down food molecules and release the energy used to build those molecules during photosynthesis. Glucose,  $C_6H_{12}O_6$ , is a common substance broken down in respiration. The following chemical equation expresses this process.



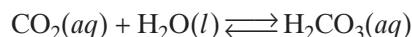
In humans and most other vertebrate animals, the oxygen needed for this reaction is delivered to cells by hemoglobin found in red blood cells. Oxygen binds with hemoglobin as blood passes through capillaries in the lungs, as represented by the following reaction.



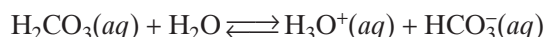
Hb represents the hemoglobin molecule, and  $HbO_2$  represents oxyhemoglobin, which is hemoglobin with bound oxygen. When the red blood cells pass through capillaries near cells that have depleted their oxygen supply through respiration, the reaction reverses and oxyhemoglobin gives up its oxygen.



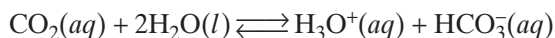
Carbon dioxide produced during respiration is a waste product that must be expelled from an organism. Various things happen when  $CO_2$  enters the blood. Seven percent dissolves in the plasma, about 23% binds loosely to hemoglobin, and the remaining 70% reacts reversibly with water in plasma to form hydrogen carbonate,  $HCO_3^-$  ions. To form  $HCO_3^-$  ions,  $CO_2$  first combines with  $H_2O$  to form carbonic acid,  $H_2CO_3$ , in a reversible reaction.



The dissolved carbonic acid ionizes to  $HCO_3^-$  ions and aqueous  $H^+$  ions in the form of  $H_3O^+$ .



The combined equilibrium reaction follows.



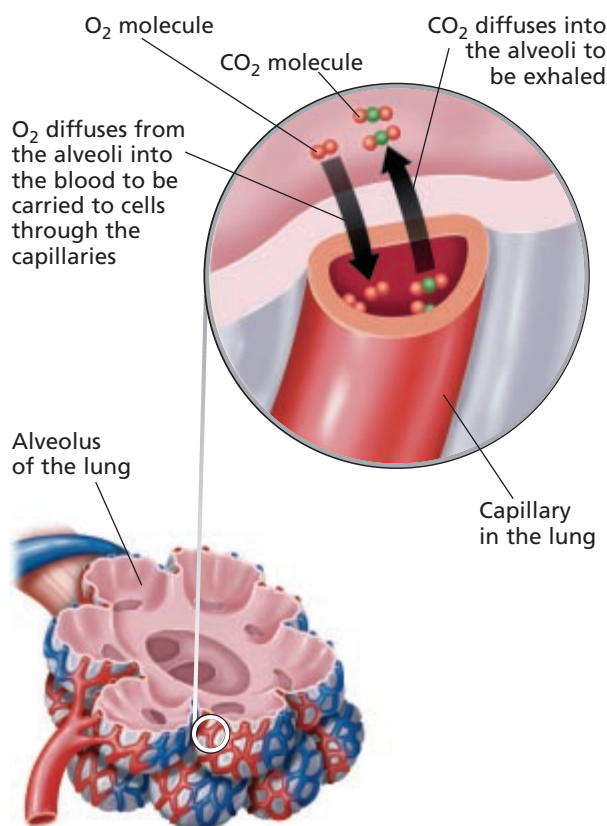
When the blood reaches the lungs, the reaction reverses and the blood releases  $CO_2$ , which is then exhaled to the surroundings.

*The oxygen carrier molecule, heme, is a component of the more-complex protein hemoglobin. Note that each hemoglobin molecule has four heme subunits. Hemoglobin is a component of red blood cells.*

### Exchange of CO<sub>2</sub> and O<sub>2</sub> in the Lungs

Why does CO<sub>2</sub> leave the blood as it passes through the lung's capillaries, and why does O<sub>2</sub> enter the blood? The exchange is caused by the difference in concentrations of CO<sub>2</sub> and O<sub>2</sub> in the blood and in the atmosphere. Oxygen is 21% of the atmosphere. Although the amount of CO<sub>2</sub> varies from place to place, it averages about 0.033% of the atmosphere. Thus, O<sub>2</sub> is about 640 times more concentrated in the atmosphere than is CO<sub>2</sub>.

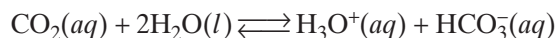
Substances tend to diffuse from regions of higher concentration toward regions of lower concentration. Thus, when blood reaches the capillaries of the lung, O<sub>2</sub> from the air diffuses into the blood, where its pressure is only 40 mm Hg, while CO<sub>2</sub> diffuses out of the blood, where its pressure is 45 mm Hg, and into the air. The diagram below summarizes the process.



*The pressure of O<sub>2</sub> in the blood entering the lung is much lower than it is in the atmosphere. As a result, O<sub>2</sub> diffuses into the blood. The opposite situation exists for CO<sub>2</sub>, so it diffuses from the blood into the air. Note that blood leaving the lung still contains a significant concentration of CO<sub>2</sub>.*

### Acidosis and Alkalosis

In humans, blood is maintained between pH 7.3 and 7.5. The pH of blood is dependent on the concentration of CO<sub>2</sub> in the blood. Look again at this equilibrium system.



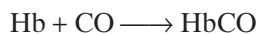
Notice that the right side of the equation contains the H<sub>3</sub>O<sup>+</sup> ion, which determines the pH of the blood. If excess H<sub>3</sub>O<sup>+</sup> enters the blood from tissues, the reverse reaction is favored. Excess H<sub>3</sub>O<sup>+</sup> combines with HCO<sub>3</sub><sup>-</sup> to produce more CO<sub>2</sub> and H<sub>2</sub>O. If the H<sub>3</sub>O<sup>+</sup> concentration begins to fall, the forward reaction is favored, producing additional H<sub>3</sub>O<sup>+</sup> and HCO<sub>3</sub><sup>-</sup>. To keep H<sub>3</sub>O<sup>+</sup> in balance, adequate amounts of both CO<sub>2</sub> and HCO<sub>3</sub><sup>-</sup> must be present. If something occurs that changes these conditions, a person can become very ill and can even die.

Hyperventilation occurs when a person breathes too rapidly for an extended time. Too much CO<sub>2</sub> is eliminated, causing the reverse reaction to be favored, and H<sub>3</sub>O<sup>+</sup> and HCO<sub>3</sub><sup>-</sup> are used up. As a result, the person develops a condition known as alkalosis because the pH of the blood rises to an abnormal alkaline level. The person begins to feel lightheaded and faint, and, unless treatment is provided, he or she may fall into a coma. Alkalosis is treated by having the victim breathe air that is rich in CO<sub>2</sub>. One way to accomplish this is to have the person breathe with a bag held tightly over the nose and mouth. Alkalosis is also caused by fever, infection, intoxication, hysteria, and prolonged vomiting.

The reverse of alkalosis is a condition known as acidosis. This condition is often caused by a depletion of HCO<sub>3</sub><sup>-</sup> ions from the blood, which can occur as a result of kidney dysfunction. The kidney controls the excretion of HCO<sub>3</sub><sup>-</sup> ions. If there are too few HCO<sub>3</sub><sup>-</sup> ions in solution, the forward reaction is favored and H<sub>3</sub>O<sup>+</sup> ions accumulate, which lowers the blood's pH. Acidosis can also result from the body's inability to expel CO<sub>2</sub>, which can occur during pneumonia, emphysema, and other respiratory disorders. Perhaps the single most common cause of acidosis is uncontrolled diabetes, in which acids normally excreted in the urinary system are instead retained by the body.

**APPLICATION** *The Environment***Carbon Monoxide Poisoning**

Standing on a street corner in any major city exposes a person to above-normal concentrations of carbon monoxide from automobile exhaust. Carbon monoxide also reacts with hemoglobin. The following reaction takes place in the capillaries of the lung.



Unlike  $\text{CO}_2$  or  $\text{O}_2$ , CO binds strongly to hemoglobin. Carboxyhemoglobin,  $\text{HbCO}$ , is 200 times more stable than oxyhemoglobin,  $\text{HbO}_2$ . So as blood circulates, more and more CO molecules bind to hemoglobin, reducing the amount of  $\text{O}_2$  bond sites available for transport. Eventually, CO occupies so many hemoglobin binding sites that cells die from lack of oxygen. Symptoms of carbon monoxide poisoning include headache, mental confusion, dizziness, weakness, nausea, loss of muscular control, and decreased heart rate and respiratory rate. The victim loses consciousness and will die without treatment.

If the condition is caught in time, a victim of carbon monoxide poisoning can be revived by breathing pure oxygen. This treatment causes carboxyhemoglobin to be converted slowly to oxyhemoglobin according to the following chemical equation.



Mild carbon monoxide poisoning usually does not have long-term effects. In severe cases, cells are destroyed. Damage to brain cells is irreversible.

The level of danger posed by carbon monoxide depends on two factors: the concentration of the gas in the air and the amount of time that a person is exposed to the gas. Table 5A shows the effects of increasing levels of carbon monoxide in the bloodstream. These effects vary considerably depending on a person's activity level and metabolic rate.



*Carbon monoxide detectors are now available to reduce the risk of poisoning from defective home heating systems. The Consumer Products Safety Commission recommends that all homes have a CO detector with a UL label.*

**TABLE 5A** Symptoms of CO Poisoning at Increasing Levels of CO Exposure and Concentration

Concentration of CO in air (ppm)*	Hemoglobin molecules as HbCO	Visible effects
100 for 1 hour or less	10% or less	no visible symptoms
500 for 1 hour or less	20%	mild to throbbing headache, some dizziness, impaired perception
500 for an extended period of time	30–50%	headache, confusion, nausea, dizziness, muscular weakness, fainting
1000 for 1 hour or less	50–80%	coma, convulsions, respiratory failure, death

\* ppm is parts per million



APPLICATION *Biochemistry***Macromolecules**

Large organic polymers are called macromolecules (the prefix *macro* means “large”). Macromolecules play important roles in living systems. Most macromolecules essential to life belong to four main classes, three of which we know as nutrients in food:

- 1. Proteins** Hair, tendons, ligaments, and silk are made of protein. Other proteins act as hormones, transport substances throughout the body, and fight infections. Enzymes are proteins that control the body's chemical reactions. Proteins provide energy, yielding 17 kJ/g.
- 2. Carbohydrates** Sugars, starches, and cellulose are carbohydrates. Carbohydrates are sources of energy, yielding 17 kJ/g.
- 3. Lipids** Fats, oils, waxes, and steroids are lipids, nonpolar substances that do not dissolve in water. Fats are sources of energy, yielding 38 kJ/g.
- 4. Nucleic acids** The nucleic acids are DNA and RNA. In most organisms, DNA is used to store hereditary information and RNA helps to assemble proteins.

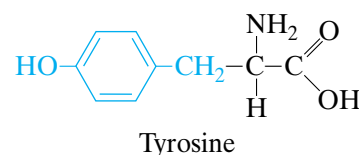
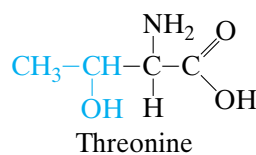
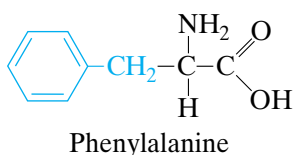
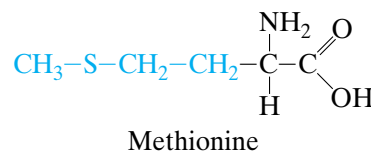
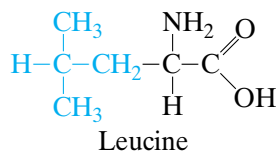
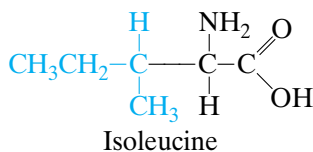
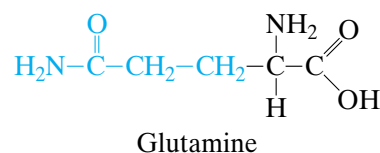
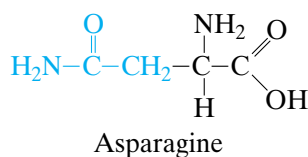
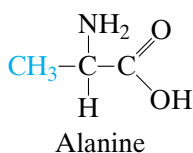
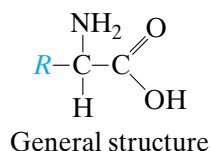
**Proteins**

Proteins are macromolecules formed by condensation reactions between amino acid monomers. Proteins contain carbon, oxygen, hydrogen, nitrogen, and usually some sulfur.

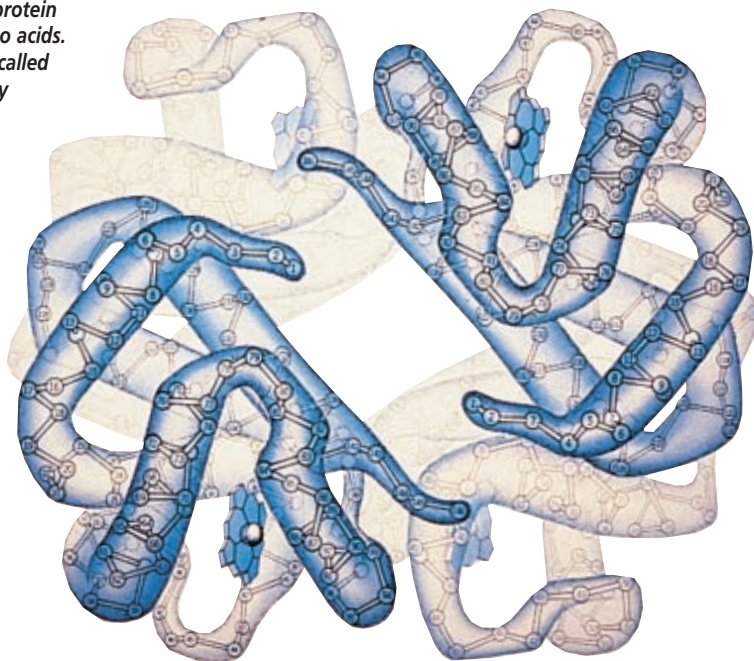
All amino acids have a carboxyl group,  $\text{—COOH}$ , and an amino group,  $\text{—NH}_2$ , attached to a central carbon atom, which is also attached to hydrogen,  $\text{—H}$ . Amino acids differ from one another at the fourth bond site of the central carbon, which is attached to a group of atoms (called an *R* group). *R* groups differ from one amino acid to another, as shown in the structures for several amino acids below. The proteins of all organisms contain a set of 20 common amino acids. The reaction that links amino acids is a condensation reaction, which is described in Chapter 21.

Each protein has its own unique sequence of amino acids. A complex organism has at least several thousand different proteins, each with a special structure and function. For instance, *insulin*, a hormone that helps the body regulate the level of sugar in the blood, is made up of two linked chains.

*Amino acids have the same general structure. These examples show some of the variations within this class of compounds.*



Hemoglobin is a complex protein made of hundreds of amino acids. Its 3-dimensional shape is called a tertiary structure. Tertiary structures break down when a protein is denatured.



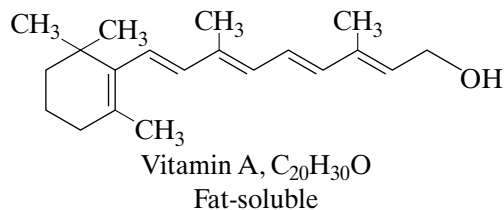
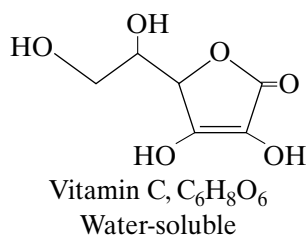
The chains are held together by S—S bonds between sulfur atoms in two cysteine amino acids. Insulin is one of the smaller proteins, containing only 51 amino acids. In contrast, hemoglobin, which carries oxygen in the blood, is a large protein consisting of four long chains with the complicated three-dimensional structures shown above. Proteins can lose their shape with increases in temperature or changes in the chemical composition of their environment. When they are returned to normal surroundings, they may fold or coil up again and re-form their original structure.

Changing even one amino acid can change a protein's structure and function. For example, the difference between normal hemoglobin and the hemoglobin that causes sickle cell anemia is just two amino acids.

### Enzymes

You learned how enzymes alter reaction rates in Chapter 17. Some enzymes cannot bind to their substrates without the help of additional molecules. These may be *minerals*, such as calcium or iron ions, or helper molecules called *coenzymes* that play accessory roles in enzyme-catalyzed reactions. Many vitamins are coenzymes or parts of coenzymes.

*Vitamins* are organic molecules that we cannot manufacture and hence need to eat in small amounts.



You can see why we need vitamins and minerals in our diet—to enable our enzymes to work. You can also see why we need only small amounts of them. Minerals and coenzymes are not destroyed in biochemical reactions. Like enzymes, coenzymes and minerals can be used over and over again.

Temperature and pH have the most significant effects on the rates of reactions catalyzed by enzymes. Most enzymes work best in a solution of approximately neutral pH. Most body cells have a pH of 7.4. However, some enzymes function only in acidic or basic environments. For example, pepsin, the collective



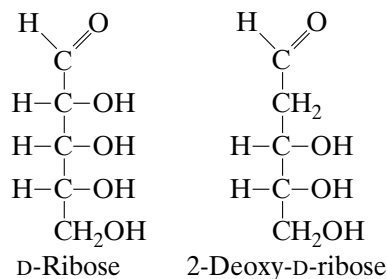
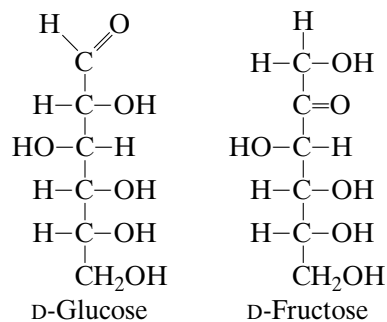
*The protein in fish is denatured by the low pH of lime juice. Notice that the flesh shown with the limes has turned white compared with the flesh at normal pH.*

term for the digestive enzymes found in the human stomach, works best at a very acidic pH of about 1.5. Cells that line the stomach secrete hydrochloric acid to produce this low pH environment. When food travels down the digestive tract, it carries these enzymes out of the stomach into the intestine. In the intestine, stomach enzymes stop working because sodium bicarbonate in the intestine raises the pH to about 8. Digestive enzymes in the intestine are formed by the pancreas and work best at pH 8.

Most chemical reactions, including enzyme reactions, speed up with increases in temperature. However, high temperatures (above about 60°C) destroy, or denature, protein by breaking up the three-dimensional structure. For example, the protein in an egg or a piece of meat denatures when the egg or meat is cooked. Proteins in the egg white become opaque when denatured. Heating can preserve food by denaturing the enzymes of organisms that cause decay. In milk pasteurization, the milk is heated to denature enzymes that would turn it sour. Refrigeration and freezing also help preserve food by slowing the enzyme reactions that cause decay.

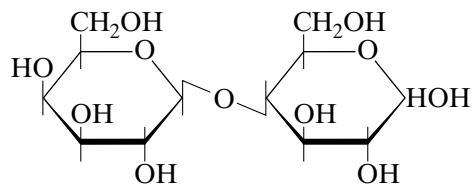
### Carbohydrates

Carbohydrates are sugars, starches, and related compounds. The monomers of carbohydrates are monosaccharides, or simple sugars, such as fructose and glucose. A monosaccharide contains carbon, hydrogen, and oxygen in about a 1:2:1 ratio, which is an empirical formula of  $\text{CH}_2\text{O}$ .

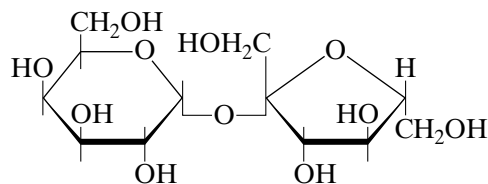


### Monosaccharides chain representation

Two monosaccharides may be joined together to form a disaccharide. Sucrose, shown below, is a disaccharide. A disaccharide can be hydrolyzed to produce the monosaccharides that formed it. By a series of condensation reactions, many monosaccharides can be joined to form a polymer called a polysaccharide (commonly known as a complex carbohydrate).

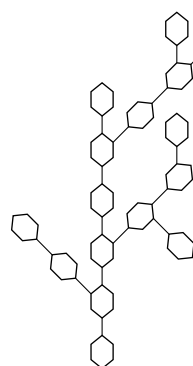
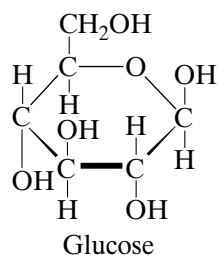


*Lactose—made from glucose and galactose*



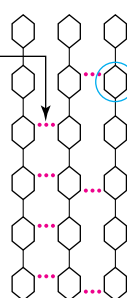
*Sucrose—made from glucose and fructose*





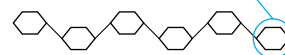
Glycogen

Cellulose chains  
linked by  
hydrogen bonds



Cellulose

Glucose monomers



Starch

Glucose is the structural unit for glycogen, cellulose, and starch. Notice that these three polymers differ in the arrangement of glucose monomers.

Three important polysaccharides made of glucose monomers are glycogen, starch, and cellulose. Animals store energy in glycogen. The liver and muscles remove glucose from the blood and condense it into glycogen, which can later be hydrolyzed back into glucose and used to supply energy as needed.

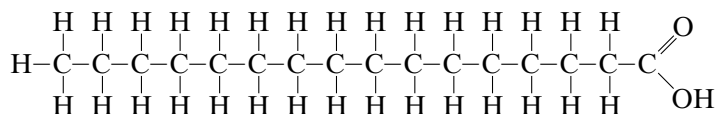
Starch consists of two kinds of glucose polymers. It is hydrolyzed in plants to form glucose for energy and for building material to produce more cells. The structural polysaccharide cellulose is probably the most common organic compound on Earth. Glucose monomers link cellulose chains together at the hydroxyl groups to form cellulose fibers. Cotton fibers consist almost entirely of cellulose.

### Lipids

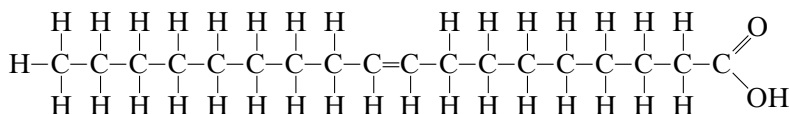
Lipids are a varied group of organic compounds that share one property: they are not very soluble in water. Lipids contain a high proportion of C—H bonds, and they dissolve in nonpolar organic solvents, such as ether, chloroform, and benzene.

Fatty acids are the simplest lipids. A fatty acid consists of an unbranched chain of carbon and hydrogen atoms with a carboxyl group at one end. Bonding within the carbon chain gives both saturated and unsaturated fatty acids, just as the simple hydrocarbons (see Chapter 20) can be saturated or unsaturated.

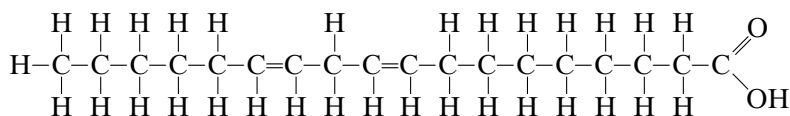
The bonds in a carboxyl group are polar, and so the carboxyl end of a fatty acid attracts water



Palmitic acid — saturated



Oleic acid — monounsaturated

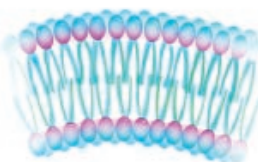


Linoleic acid — polyunsaturated

These examples of common fatty acids show the differences in saturation level.

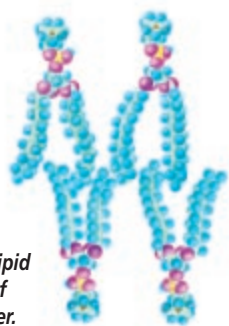


*This phospholipid molecule contains two fatty-acid chains.*

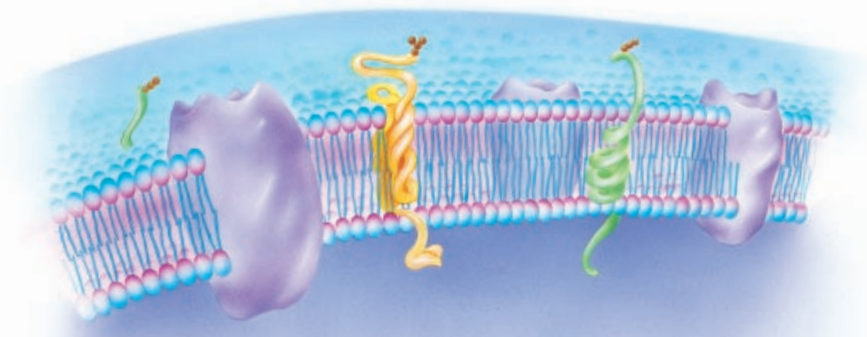


*The lipid bilayer is the framework of the cell membrane.*

*The fatty acids are oriented toward the interior of the bilayer because they have a low attraction for water.*



*This phospholipid chain is part of the lipid bilayer.*



molecules. The carbon-hydrogen bonds of a lipid's hydrocarbon chain are nonpolar, however. The polar end will dissolve in water, and the other end will dissolve in nonpolar organic compounds. This behavior enables fatty acids to form membranes when they are dropped into water. It also gives soaps and detergents their cleaning power.

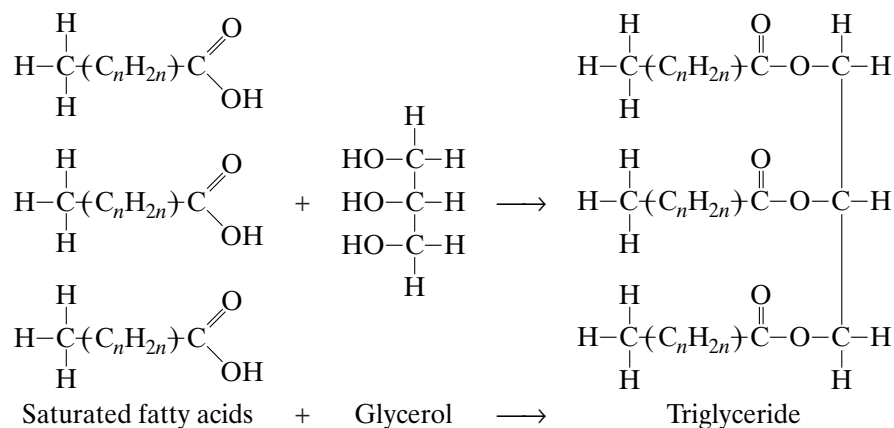
Lipids are the main compounds in biological membranes, such as the cell membrane. Because lipids are insoluble, the lipid bilayer of a cell membrane is adapted to keep the contents of the cell inside separated from the outer environment of the cell.

The structural component of a cell membrane is a phospholipid. The "head" of the phospholipid is polar,

and the fatty acid tails are nonpolar, as shown in the model above.

Most fatty acids found in foods and soaps belong to a class of compounds called triglycerides. The fat content shown on a nutrition label for packaged food represents a mixture of the triglycerides in the food. Triglycerides have the general structure shown below.

Fatty acids are usually combined with other molecules to form classes of biomolecules called glycolipids (made from a carbohydrate and a lipid) or lipoproteins (made from a lipid and a protein). These compounds are also parts of more-complex lipids found in the body.

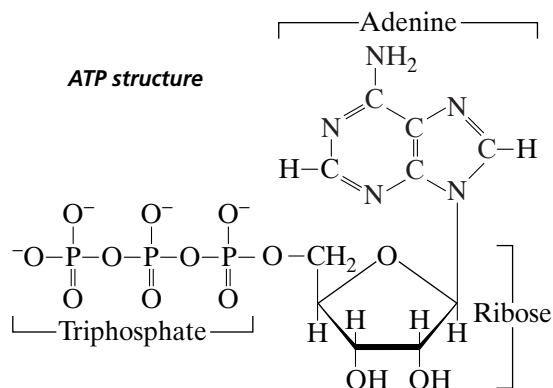


*Triglycerides are made from three long-chain fatty acids bonded to a glycerol backbone.*

## Nucleic Acids

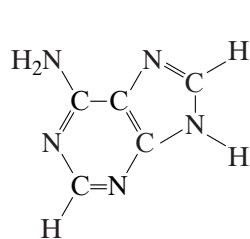
Nucleic acids are macromolecules that transmit genetic information. Deoxyribonucleic acid (DNA) is the material that contains the genetic information that all organisms pass on to their offspring during reproduction. This information includes instructions for making proteins as well as for making the other nucleic acid, ribonucleic acid (RNA). Ribonucleic acid (RNA) assists in protein synthesis by helping to coordinate the process of protein assembly.

Nucleotides are the monomers of nucleic acids. A nucleotide has three parts: one or more phosphate groups, a sugar containing five carbon atoms, and a ring-shaped nitrogen base, as shown below. RNA nucleotides contain the simple sugar ribose. DNA nucleotides contain deoxyribose (ribose stripped of one oxygen atom). Structures for both of these sugars are shown on page 763. Cells contain nucleotides with one, two, or three phosphate groups attached. Besides being the monomers of nucleic acids, several nucleotides play other roles. For example, adenosine triphosphate (ATP) is the

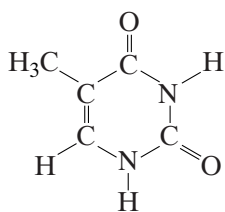


nucleotide that supplies the energy for many metabolic reactions.

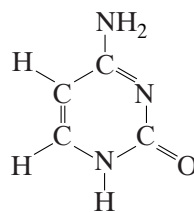
The bases in nucleic acids attract each other in pairs, a phenomenon known as base-pairing. DNA is made of four different nucleotides—those containing the bases adenine (A), thymine (T), guanine (G), and cytosine (C). The attraction between base pairs is hydrogen bonding. Adenine forms hydrogen bonds with thymine. Similarly, cytosine bonds to guanine. This base-pairing holds strands of DNA together.



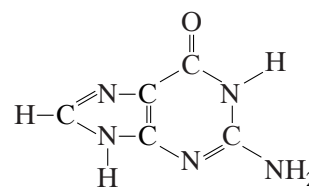
Adenine



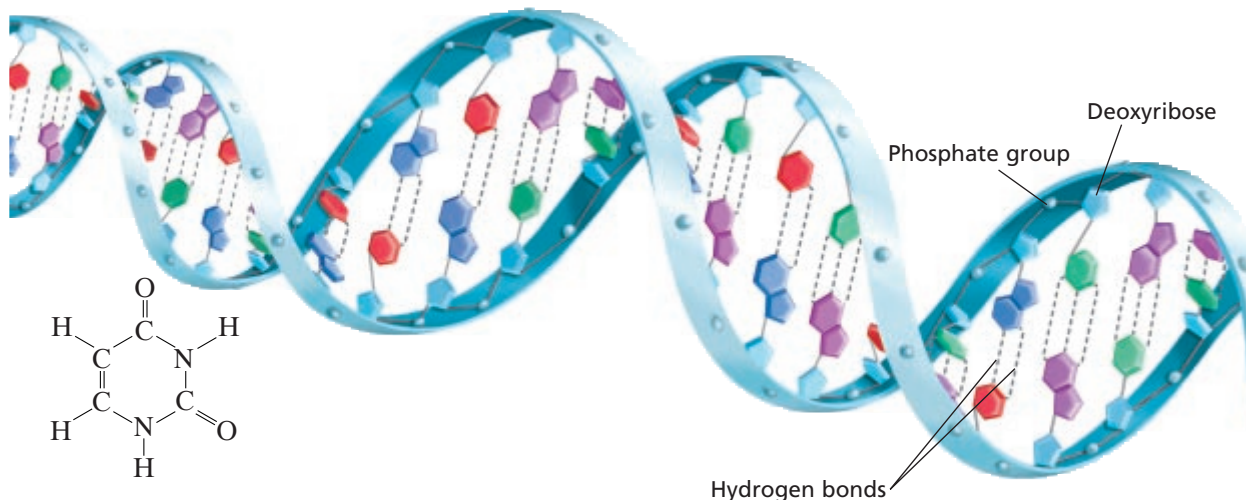
Thymine



Cytosine



Guanine



Uracil, RNA only



## APPLICATION *Chemical Industry*

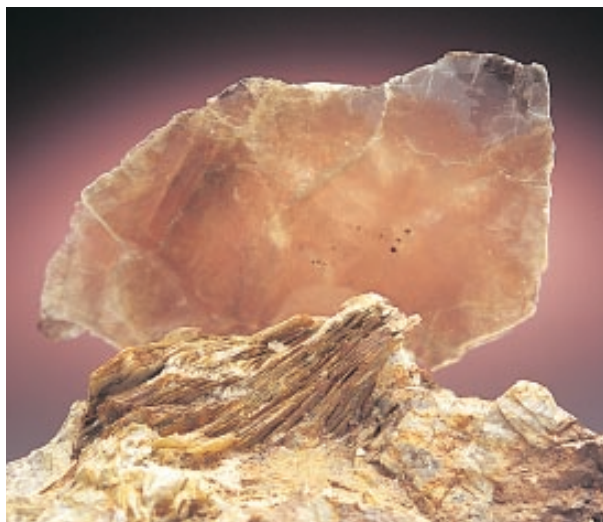
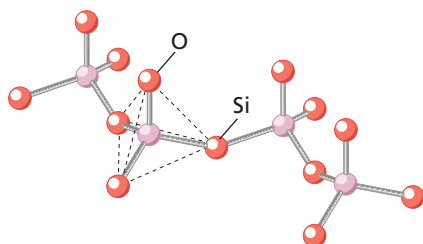
### Silicon and Silicates

Silicon is as important in the mineral world as carbon is in living systems. Silicon dioxide and silicates make up about 87% of the Earth's crust. Silicates are a class of compounds containing silicon, oxygen, one or more metals, and possibly hydrogen. Many mineral compounds are silicates. Sand is probably the most familiar silicate.

Glasses consist of 75% silicate. Borosilicate glass is the special heat-resistant glass used in making laboratory beakers and flasks. The addition of 5% boron oxide to the glass increases the softening temperature of the glass. Because boron and silicon atoms have roughly similar radii, these atoms can be substituted for one another to make borosilicate glass.

Asbestos is the name given to a class of fibrous magnesium silicate minerals. Asbestos is very strong and flexible, and it does not burn, so it was widely used as a heat-insulating material.

*Silicon has the ability to form long chain compounds by bonding with oxygen. The  $\text{SiO}_4$  subunit in this silicate is tetrahedral.*



*Silicates exist in a variety of mineral forms, including mica.*

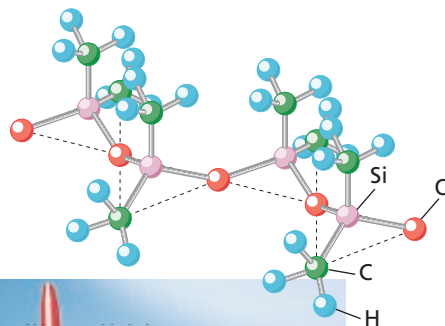
It is now known that asbestos is a carcinogen. When handled, asbestos releases dust particles that are easily inhaled and can cause lung cancer. Asbestos materials found in older homes and buildings should be removed by firms licensed by the Environmental Protection Agency (EPA).

### Silicones

Silicones are a class of organic silicon polymers composed of silicon, carbon, oxygen, and hydrogen. The silicon chain is held together by bonding with the oxygen atoms. Each silicon atom is also bonded to different hydrocarbon groups to create a variety of silicone structures.

Silicones are widely used for their adhesive and protective properties. They have good electric insulating properties and are water-repellent. Some silicones have the character of oils or greases, so they are used as lubricants. Silicones are also used in automobile and furniture polishes as protective agents.

*Silicones also have a tetrahedral structure. How does this structure differ from that of a silicate?*



*Because of their protective properties, silicones are used in a number of consumer products, from cosmetics to caulking.*

**APPLICATION** *Technology***Semiconductors**

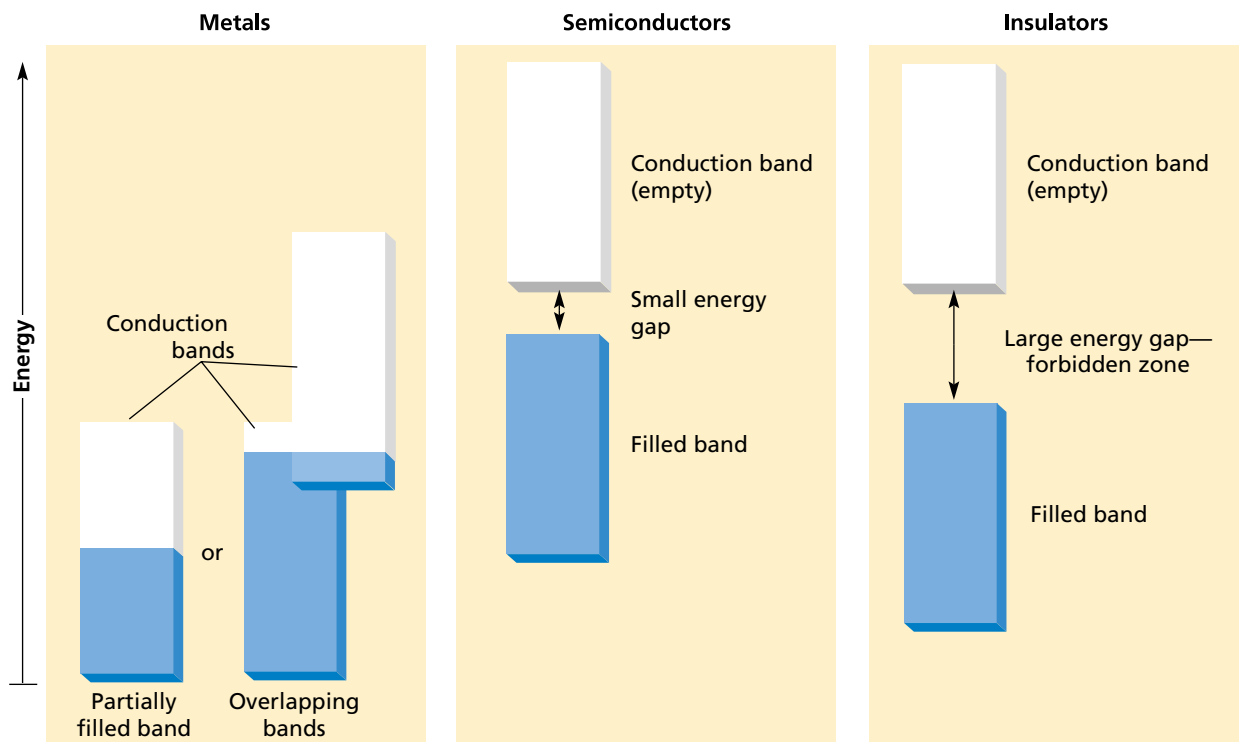
When electrons can move freely through a material, the material is a conductor. The electrons in metals are loosely held and require little additional energy to move from one vacant orbital to the next. A set of overlapping orbitals is called a *conduction band*. Because electrons can easily jump to the conduction band, metals conduct electricity when only a very small voltage is applied.

Semiconductors conduct a current if the voltage applied is large enough to excite the outer-level electrons of their atoms into the higher energy levels. With semiconductors, more energy, and thus a higher voltage, is required to cause conduction. By contrast, nonmetals are insulators because they do not conduct at ordinary voltages. Too much energy is needed to raise their outer electrons into conduction bands.

Semiconductor devices include transistors; diodes, including light-emitting diodes (LEDs); some lasers;

and photovoltaic cells (“solar” cells). Though silicon is the basis of most semiconductor devices in the computer industry, pure silicon has little use as a semiconductor. Instead, small amounts of impurities are added to increase its conductive properties. Adding impurities to silicon is called *doping*, and the substances added are *dopants*. The dopant is usually incorporated into just the surface layer of a silicon chip. Typical dopants include the Group 15 elements phosphorus and arsenic and the Group 13 elements boron, aluminum, gallium, and indium.

A silicon atom has four electrons in its outer energy level whereas Group 13 atoms have three and Group 15 atoms have five. Adding boron to silicon creates a mix of atoms having four valence electrons and atoms having three valence electrons. Boron atoms form only three bonds with silicon, whereas silicon forms four bonds with other silicon atoms. The unbonded spot between a silicon atom



*This model shows the difference in the levels of energy required to excite electrons into the conduction band in metals, semiconductors, and insulators. The forbidden zone is too great an energy gap in insulators for these elements to function as conductors. The energy gap for semiconductors is small enough that it can be crossed under certain conditions.*

																		Group 18																	
1 H																		2 He																	
Group 1		Group 2																Group 13		Group 14		Group 15		Group 16		Group 17									
3 Li		4 Be																5 B		6 C		7 N		8 O		9 F		10 Ne							
11 Na		12 Mg																13 Al		14 Si		15 P		16 S		17 Cl		18 Ar							
19 K		20 Ca		Group 3		Group 4		Group 5		Group 6		Group 7		Group 8		Group 9		Group 10		Group 11		Group 12		31 Ga		32 Ge		33 As		34 Se		35 Br		36 Kr	
37 Rb		38 Sr		39 Y		40 Zr		41 Nb		42 Mo		43 Tc		44 Ru		45 Rh		46 Pd		47 Ag		48 Cd		49 In		50 Sn		51 Sb		52 Te		53 I		54 Xe	
55 Cs		56 Ba		57 La		72 Hf		73 Ta		74 W		75 Re		76 Os		77 Ir		78 Pt		79 Au		80 Hg		81 Tl		82 Pb		83 Bi		84 Po		85 At		86 Rn	
87 Fr		88 Ra		89 Ac																															

Dopants

Semiconductor elements

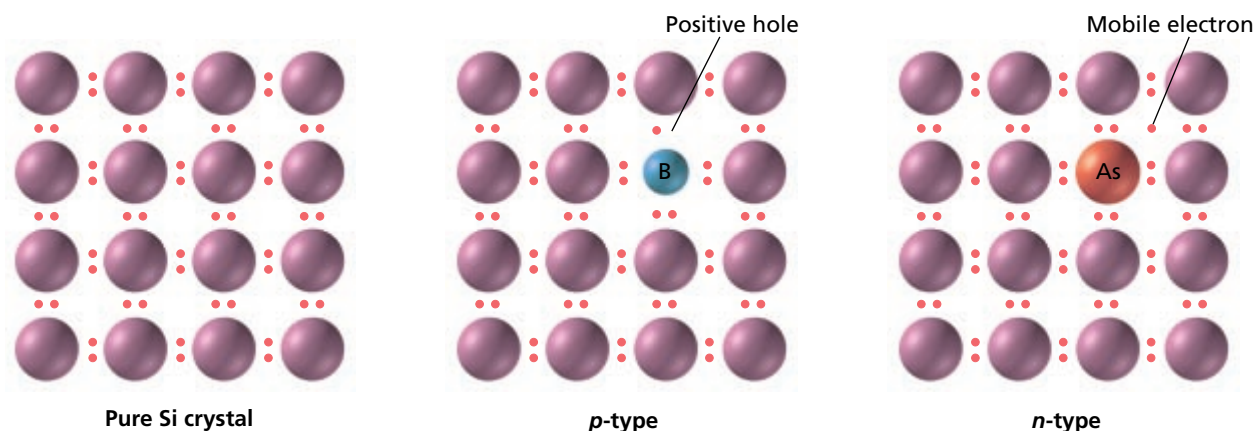
Forms semiconductor compounds

■ Dopants  
■ Semiconductor elements  
■ Forms semiconductor compounds

Semiconductor elements and dopants fall in the metalloid region of the periodic table. Semiconductor compounds often contain metals.

and a boron atom is a hole that a free electron can occupy. Because this hole “attracts” an electron, it is viewed as if it were positively charged. Semiconductors that are doped with boron, aluminum, or gallium are *p-type semiconductors*, the *p* standing for “positive.” P-type semiconductors conduct electricity better than pure silicon because they provide spaces that moving electrons can occupy as they flow through the material.

Doping silicon with phosphorus or arsenic produces the opposite effect. When phosphorus is added to silicon, it forms four bonds to silicon atoms and has a nonbonding electron left over. This extra electron is free to move through the material when a voltage is applied, thus increasing its conductivity compared with pure silicon. These extra electrons have a negative charge. Therefore, the material is an *n-type semiconductor*. Compare these two types of semiconductors in the models below.



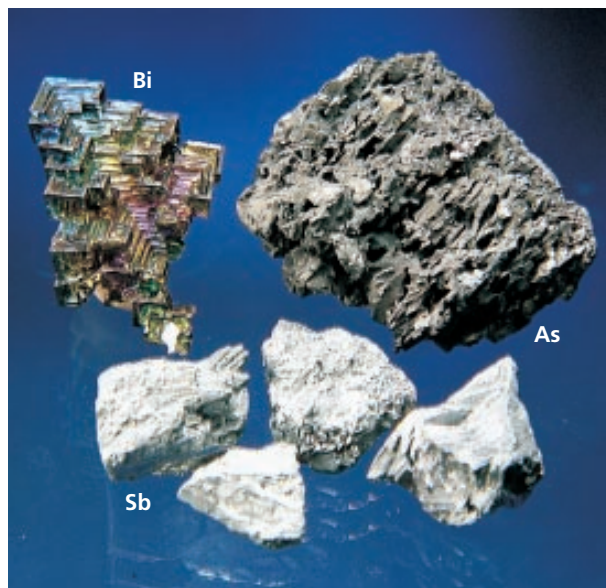
Each silicon atom in the pure crystal is surrounded by four pairs of electrons. The p-type semiconductor model contains an atom of boron with a hole that an electron can occupy. The n-type semiconductor model contains an atom of arsenic, which provides the extra electron that can move through the crystal.



# GROUP 15 NITROGEN FAMILY

## CHARACTERISTICS

- consist of two nonmetals (nitrogen and phosphorus), two metalloids (arsenic and antimony), and one metal (bismuth)
- Nitrogen is most commonly found as atmospheric  $N_2$ ; phosphorus as phosphate rock; and arsenic, antimony, and bismuth as sulfides or oxides. Antimony and bismuth are also found as elements.
- range from very abundant elements (nitrogen and phosphorus) to relatively rare elements (arsenic, antimony, and bismuth)
- consist of atoms that contain five electrons in their outermost energy level
- tend to form covalent compounds, most commonly with oxidation numbers of +3 or +5
- exist in two or more allotropic forms, except nitrogen and bismuth
- are solids at room temperature, except nitrogen



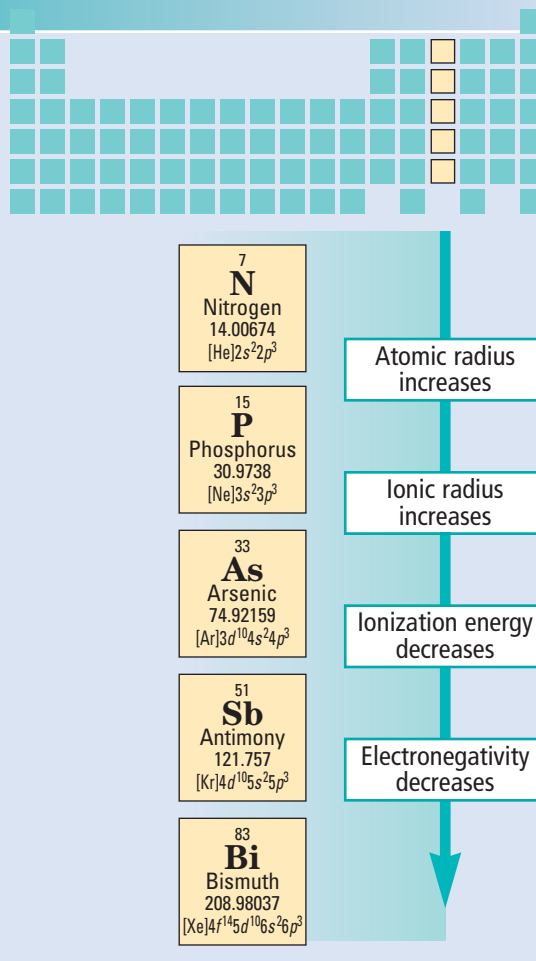
You can see the contrast in physical properties among the elements of this family. Arsenic, antimony, and bismuth are shown.



Some matches contain phosphorus compounds in the match head. Safety matches contain phosphorus in the striking strip on the matchbox.



Phosphorus exists in three allotropic forms. White phosphorus must be kept underwater because it catches on fire when exposed to air. The red and black forms are stable in air.



## COMMON REACTIONS

## With Oxygen to Form Oxides



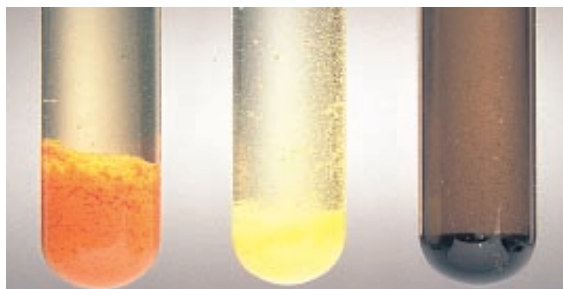
As, Sb, and Bi follow this reaction pattern, but as monatomic elements. N reacts as  $\text{N}_2$  to form  $\text{N}_2\text{O}_3$  and  $\text{N}_2\text{O}_5$ .

## With Metals to Form Binary Compounds



## ANALYTICAL TEST

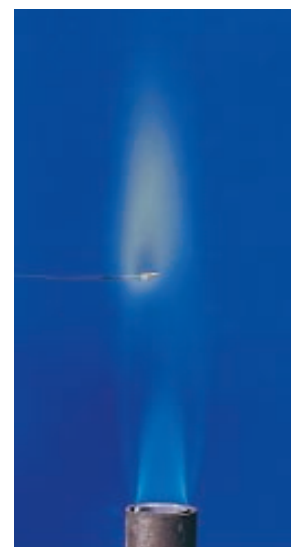
Other than atomic absorption spectroscopy, there are no simple analytical tests for the presence of nitrogen or phosphorus compounds in a sample. Antimony produces a pale green color in a flame test, and arsenic produces a light blue color. Arsenic, antimony, and bismuth are recognized in qualitative analyses by their characteristic sulfide colors.



Formation of sulfides is the confirmatory qualitative analysis test for the presence of bismuth, antimony, and arsenic.



Arsenic flame test



Antimony flame test

## PROPERTIES OF THE GROUP 15 ELEMENTS

	N	P*	As	Sb	Bi
Melting point (°C)	-209.86	44.1	817 (28 atm)	630.5	271.3
Boiling point (°C)	-195.8	280	613 (sublimes)	1750	1560 ± 5
Density (g/cm <sup>3</sup> )	1.25 × 10 <sup>-3</sup>	1.82	5.727	6.684	9.80
Ionization energy (kJ/mol)	1402	1012	947	834	703
Atomic radius (pm)	75	110	122	143	151
Ionic radius (pm)	146 (N <sup>3-</sup> )	212 (P <sup>3-</sup> )	—	76 (Sb <sup>3+</sup> )	103 (Bi <sup>3+</sup> )
Common oxidation number in compounds	-3, +3, +5	-3, +3, +5	+3, +5	+3, +5	+3
Crystal structure†	cubic (as a solid)	cubic	rhombohedral	hcp	rhombohedral
Hardness (Mohs' scale)	none (gas)	—	3.5	3.0	2.25

\* Data given apply to white phosphorus.

† Crystal structures are for the most common allotropes.

**APPLICATION** *Biology***Plants and Nitrogen**

All organisms, including plants, require certain elements to survive and grow. These elements include carbon, hydrogen, oxygen, nitrogen, phosphorus, potassium, sulfur, and several other elements needed in small amounts. An organism needs nitrogen to synthesize structural proteins, enzymes, and the nucleic acids DNA and RNA.

Carbon, hydrogen, and oxygen are available to plants from carbon dioxide in the air and from water in both the air and the soil. Nitrogen is necessary for plants' survival. Although nitrogen gas,  $N_2$ , makes up 78% of air, plants cannot take nitrogen out of the air and incorporate it into their cells, because the strong triple covalent bond in  $N_2$  is not easily broken. Plants need nitrogen in the form of a compound that they can take in and use. The process of using atmospheric

$N_2$  to make  $NH_3$  is called *nitrogen fixation*. Several kinds of nitrogen-fixing bacteria live in the soil and in the root nodules of plants called legumes. Legumes obtain the nitrogen they need through a symbiotic relationship with nitrogen-fixing bacteria. Legumes include peas, beans, clover, alfalfa, and locust trees. The bacteria convert nitrogen into ammonia,  $NH_3$ , which is then absorbed by the host plants.

Because wheat, rice, corn, and potatoes cannot perform the same feat as legumes, these plants depend on nitrogen-fixing bacteria in the soil. Soil bacteria convert  $NH_3$  into nitrate ions,  $NO_3^-$ , the form of nitrogen that can be absorbed and used by plants. These plants also often need nitrogen fertilizers to supplement the work of the bacteria. Besides supplying nitrogen, fertilizers are manufactured to contain phosphorus, potassium, and trace minerals.



*Nitrogen-fixing bacteria, Rhizobium, live in these small nodules that grow on the roots of soybeans.*



*Soybeans are legumes that live in a symbiotic relationship with nitrogen-fixing bacteria.*



APPLICATION *Chemical Industry*

Fertilizers

Fertilizers can supply nitrogen to plants in the form of ammonium sulfate, ammonium nitrate, and urea, all of which are made from  $\text{NH}_3$ . Now you know why there is such a demand for ammonia. Though some soils contain sufficient concentrations of phosphorus and potassium, most soils need additional nitrogen for adequate plant growth. Ammonia, ammonium nitrate, or urea can fill that need.

Most fertilizers contain all three major plant nutrients N, P, and K, and are called *complete fertilizers*. A typical complete fertilizer might contain ammonium nitrate or sodium nitrate to provide nitrogen. Calcium dihydrogen phosphate,  $\text{Ca}(\text{H}_2\text{PO}_4)_2$ , or the anhydrous form of phosphoric acid,  $\text{P}_2\text{O}_5$ , can provide phosphorus. Potassium chloride, KCl, contains sufficient  $\text{K}_2\text{O}$  impurities to provide potassium.

The proportion of each major nutrient in a fertilizer is indicated by a set of three numbers printed on

the container. These numbers are the N-P-K formula of the fertilizer and indicate the percentage of N, P, and K, respectively. A fertilizer graded as 6-12-6, for example, contains 6% nitrogen, 12% phosphorus, and 6% potassium by weight and all in the form of compounds.

Nitrogen stimulates overall plant growth. Phosphorus promotes root growth and flowering. Potassium regulates the structures in leaves that allow  $\text{CO}_2$  to enter the leaf and  $\text{O}_2$  and  $\text{H}_2\text{O}$  to exit. Fertilizers are available in N-P-K formulas best suited for their intended use. For example, plants that produce large amounts of carbohydrates (sugars) need more potassium than most other types of plants. Grain crops need higher concentrations of phosphorus. Lawn fertilizers applied in the spring are generally high in nitrogen to stimulate shoot growth in grasses. Lawn fertilizers applied in the fall of the year should have a higher phosphorus content to stimulate root growth during the winter.

TABLE 6A    Some Commercial Fertilizers and Uses

Fertilizer composition (N-P-K)	Uses
<b>1-2-1 ratio</b> 10-20-10   15-30-15	early-spring application for trees and shrubs with flowers and fruit; general-purpose feedings of the following: cucumbers, peppers, tomatoes
<b>3-1-2 ratio</b> 12-4-8    15-5-10   21-7-4   16-4-8 20-5-10	lawns and general-purpose feedings of the following: trees, shrubs, most berries, apple trees, grapes, vines, walnut trees, broccoli, cabbage, carrots, onions
<b>High nitrogen</b> 33-0-0    21-0-0    40-4-4   36-6-6	pecan trees, lawns, early feedings of corn
<b>Balanced</b> 13-13-13	general purpose feeding of the following: broccoli, cabbage, melons, potatoes
<b>Special purpose: acid-loving flowering shrubs</b> 12-10-4	azaleas, rhododendrons, camellias, gardenias
<b>Special purpose</b> 18-24-16	roses
<b>Special purpose: flowering</b> 12-55-6	flowering plants and shrubs (annuals and perennials)
<b>Special purpose: root growth</b> 5-20-10	starter fertilizer for transplants

## GROUP 16 OXYGEN FAMILY

## CHARACTERISTICS

- occur naturally as elements and in combined states
- consist of three nonmetals (oxygen, sulfur, and selenium), one metalloid (tellurium), and one metal (polonium)
- consist of atoms that have six electrons in their outermost energy level
- tend to form covalent compounds with other elements
- exist in several allotropic forms
- tend to exist as diatomic and polyatomic molecules, such as  $O_2$ ,  $O_3$ ,  $S_6$ ,  $S_8$ , and  $Se_8$
- commonly exist in compounds with the  $-2$  oxidation state but often exhibit other oxidation states

*Sulfur is found naturally in underground deposits and in the steam vents near volcanoes.*



*Sulfur exists in combined forms in many minerals. Iron pyrite,  $\text{FeS}_2$ , black galena,  $\text{PbS}$ , and yellow orpiment,  $\text{As}_2\text{S}_3$ , are shown.*

8  
**O**  
Oxygen  
15.9994  
[He]2s<sup>2</sup>2p<sup>4</sup>

16  
**S**  
Sulfur  
32.066  
[Ne]3s<sup>2</sup>3p<sup>4</sup>

34  
**Se**  
Selenium  
78.96  
[Ar]3d<sup>10</sup>4s<sup>2</sup>4p<sup>4</sup>

52  
**Te**  
Tellurium  
127.60  
[Kr]4d<sup>10</sup>5s<sup>2</sup>5p<sup>4</sup>

84	<b>Po</b>	Polonium (208.9824)	$[Xe]4f^{14}5d^{10}6s^26p$
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Atomic radius increases

ionic radius increases

Ionization energy decreases

Electronegativity decreases



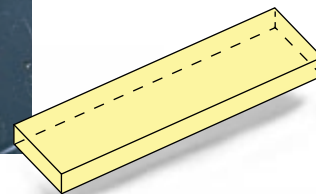
### Orthorhombic



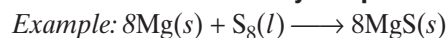
Two allotropic forms of sulfur are orthorhombic and monoclinic. Each has a different crystal structure.



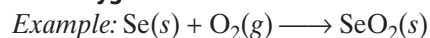
**Monoclinic**



## COMMON REACTIONS

**With Metals to Form Binary Compounds**

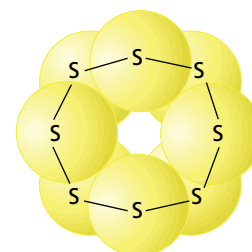
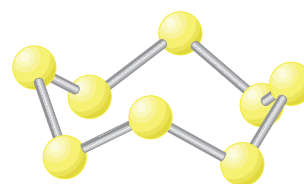
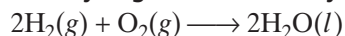
O<sub>2</sub>, Se, and Te follow this pattern in reacting with Na, K, Ca, Mg, and Al.

**With Oxygen to Form Oxides**

S, Te, and Po follow this pattern. S, Se, and Te can form SO<sub>3</sub>, SeO<sub>3</sub>, and TeO<sub>3</sub>.

**With Halogens to Form Binary Compounds**

O, Se, Te, and Po follow this pattern in reacting with F<sub>2</sub>, Cl<sub>2</sub>, Br<sub>2</sub>, and I<sub>2</sub>.

**With Hydrogen to Form Binary Compounds**

Sulfur exists as S<sub>8</sub> molecules in which the atoms are bonded in a ring, as shown by the ball-and-stick and space-filling models.

## ANALYTICAL TEST

Other than atomic absorption spectroscopy, there is no simple analytical test to identify all elements of this family. Selenium and tellurium can be identified by flame tests. A light blue flame is characteristic of selenium, and a green flame is characteristic of tellurium. Oxygen can be identified by the splint test,

in which a glowing splint bursts into flame when thrust into oxygen. Elemental sulfur is typically identified by its physical characteristics, especially its color and its properties when heated. It melts to form a viscous brown liquid and burns with a blue flame.



A glowing splint thrust into oxygen bursts into a bright flame.



Sulfur burns with a characteristically deep blue flame.



Molten sulfur returns to its orthorhombic form upon cooling.



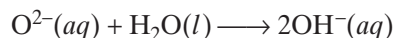
## PROPERTIES OF THE GROUP 16 ELEMENTS

	O	S	Se	Te	Po
Melting point (°C)	-218.4	119.0	217	449.8	254
Boiling point (°C)	-182.962	444.674	685	989.9	962
Density (g/cm <sup>3</sup> )	$1.429 \times 10^{-3}$	1.96	4.82	6.24	9.4
Ionization energy (kJ/mol)	1314	1000	941	869	812
Atomic radius (pm)	73	103	119	142	168
Ionic radius (pm)	140	184	198	221	—
Common oxidation number in compounds	-2	-2, +4, +6	-2, +2, +4, +6	-2, +2, +4, +6	-2, +2, +4, +6
Crystal structure*	orthorhombic, rhombohedral, cubic (when solid)	orthorhombic, monoclinic	hexagonal	hexagonal	cubic, rhombohedral
Hardness (Mohs' scale)	none (gas)	2.0	2.0	2.3	—

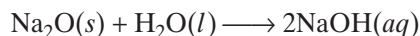
\* Most elements of this family can have more than one crystal structure.

APPLICATION *Chemical Industry***Oxides**

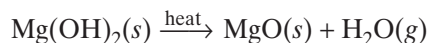
Oxides of the reactive metals are ionic compounds. The oxide ion from any soluble oxide reacts immediately with water to form hydroxide ions as represented by the following equation.



The reactive metal oxides of Groups 1 and 2 react vigorously with water and release a large amount of heat. The product of the reaction is a metal hydroxide. The following equation is an example of this reaction.



A basic oxide can be thought of as the dehydrated form of a hydroxide base. Oxides of the less reactive metals, such as magnesium, can be prepared by using thermal decomposition to drive off the water.



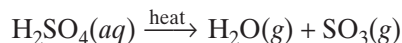
Hydroxides of the reactive metals of Group 1 are too stable to decompose in this manner.

If a hydroxide formed by a metal oxide is water-soluble, it dissolves to form a basic solution. An oxide that reacts with water to form a basic solution is called a basic oxide or a basic anhydride. Table 7A on the next page lists oxides that form basic solutions with water.

**Molecular Oxides**

Nonmetals, located on the right side of the periodic table, form molecular oxides. For example, sulfur forms two gaseous oxides: sulfur dioxide,  $\text{SO}_2$ , and sulfur trioxide,  $\text{SO}_3$ . In reactions typical of nonmetal oxides, each of the sulfur oxides reacts with water to form an oxyacid.

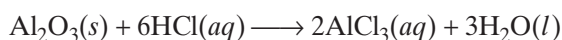
An oxide that reacts with water to form an acid is called an acidic oxide or an acid anhydride. As with the basic anhydrides, each acid anhydride can be thought of as the dehydrated form of the appropriate oxyacid. For example, when sulfuric acid decomposes, the loss of  $\text{H}_2\text{O}$  leaves the oxide  $\text{SO}_3$ , which is an anhydride.



### Amphoteric Oxides

Table 7A lists some common oxides of main-group elements. You can see that the active metal oxides are basic and that the nonmetal oxides are acidic. Between these lies a group of oxides, the *amphoteric oxides*. The bonding in amphoteric oxides is intermediate between ionic and covalent bonding. As a result, oxides of this type show behavior intermediate between that of acidic oxides and basic oxides, and react as both acids and bases.

Aluminum oxide,  $\text{Al}_2\text{O}_3$ , is a typical amphoteric oxide. With hydrochloric acid, aluminum oxide acts as a base. The reaction produces a salt and water.

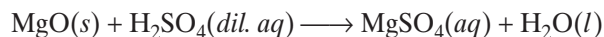


With aqueous sodium hydroxide, aluminum oxide acts as an acid. The reaction forms a soluble ionic compound and water. That compound contains aluminate ions,  $\text{AlO}_2^-$ . (The  $\text{AlO}_2^-$  formula is used here rather than the more precise hydrated aluminate formula,  $\text{Al}(\text{OH})_4^-$ .)

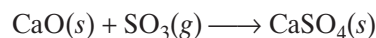
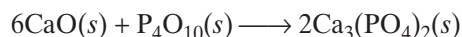
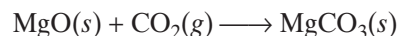


### Reactions of Oxides

In the reaction between an acid and a metal oxide, the products are a salt and water—the same as the products in a neutralization reaction. For example, when magnesium oxide reacts with dilute sulfuric acid, magnesium sulfate and water are produced.



The reaction between a basic metal oxide, such as  $\text{MgO}$ , and an acidic nonmetal oxide, such as  $\text{CO}_2$ , tends to produce an oxygen-containing salt. The dry oxides are mixed and heated without water. Salts such as metal carbonates, phosphates, and sulfates can be made by this synthesis reaction.

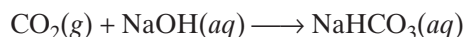


### Reactions of Hydroxides with Nonmetal Oxides

Nonmetal oxides tend to be acid anhydrides. The reaction of a hydroxide base with a nonmetal oxide is an acid-base reaction. The product is either a salt or a salt and water, depending on the identities and relative quantities of reactants. For example, 2 mol of the hydroxide base sodium hydroxide and 1 mol of the nonmetal oxide carbon dioxide form sodium carbonate, which is a salt, and water.



However, if sodium hydroxide is limited, only sodium hydrogen carbonate is produced.

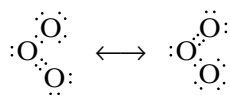


**TABLE 7A Periodicity of Acidic and Basic Oxides of Main-Group Elements**

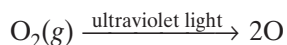
Group Number						
1	2	13	14	15	16	17
$\text{Li}_2\text{O}$ basic	$\text{BeO}$ amphoteric	$\text{B}_2\text{O}_3$ acidic	$\text{CO}_2$ acidic	$\text{N}_2\text{O}_5$ acidic		
$\text{Na}_2\text{O}$ basic	$\text{MgO}$ basic	$\text{Al}_2\text{O}_3$ amphoteric	$\text{SiO}_2$ acidic	$\text{P}_4\text{O}_{10}$ acidic	$\text{SO}_3$ acidic	$\text{Cl}_2\text{O}$ acidic
$\text{K}_2\text{O}$ basic	$\text{CaO}$ basic	$\text{Ga}_2\text{O}_3$ amphoteric	$\text{GeO}_2$ amphoteric	$\text{As}_4\text{O}_6$ amphoteric	$\text{SeO}_3$ acidic	
$\text{Rb}_2\text{O}$ basic	$\text{SrO}$ basic	$\text{In}_2\text{O}_3$ basic	$\text{SnO}_2$ amphoteric	$\text{Sb}_4\text{O}_6$ amphoteric	$\text{TeO}_3$ acidic	$\text{I}_2\text{O}_5$ acidic
$\text{Cs}_2\text{O}$ basic	$\text{BaO}$ basic	$\text{Tl}_2\text{O}_3$ basic	$\text{PbO}_2$ amphoteric	$\text{Bi}_2\text{O}_3$ basic		

APPLICATION *The Environment***Ozone**

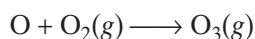
Ozone,  $O_3$ , is an allotrope of oxygen that is important for life on Earth. Like  $O_2$ ,  $O_3$  is a gas at room temperature. However, unlike  $O_2$ ,  $O_3$  is a poisonous bluish gas with an irritating odor at high concentrations. The triatomic ozone molecule is angular (bent) with a bond angle of about  $116.5^\circ$ . The  $O-O$  bonds in ozone are shorter and stronger than a single bond, but longer and weaker than a double bond. The ozone molecule is best represented by two resonance hybrid structures.



Ozone forms naturally in Earth's atmosphere more than 24 km above the Earth's surface in a layer called the stratosphere. There,  $O_2$  molecules absorb energy from ultraviolet light and split into free oxygen atoms.



A free oxygen atom has an unpaired electron and is highly reactive. A chemical species that has one or more unpaired or unshared electrons is referred to as a *free radical*. A free radical is a short-lived fragment of a molecule. The oxygen free radical can react with a molecule of  $O_2$  to produce an ozone molecule.



A molecule of  $O_3$  can then absorb ultraviolet light and split to produce  $O_2$  and a free oxygen atom.



The production and breakdown of ozone in the stratosphere are examples of *photochemical* processes, in which light causes a chemical reaction.

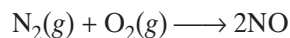
In this way,  $O_3$  is constantly formed and destroyed in the stratosphere, and its concentration is determined by the balance among these reactions. The breakdown of ozone absorbs the sun's intense ultraviolet light in the range of wavelengths between 290 nm and 320 nm. Light of these wavelengths damages and kills living cells, so if these wavelengths were

to reach Earth's surface in large amounts, life would be impossible. Even now, the normal amount of ultraviolet light reaching Earth's surface is a major cause of skin cancer and the damage to DNA molecules that causes mutations. One life-form that is very sensitive to ultraviolet radiation is the phytoplankton in the oceans. These organisms carry out photosynthesis and are the first level of oceanic food webs.

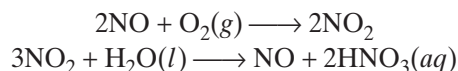
**Ozone and Air Pollution**

Ozone in the lower atmosphere is a harmful pollutant. Ozone is highly reactive and can oxidize organic compounds. The products of these reactions are harmful substances that, when mixed with air, water vapor, and dust, make up *photochemical smog*. This mixture is the smog typically found in cities.

Typically, ozone is produced in a complex series of reactions involving unburned hydrocarbons and nitrogen oxides given off from engines in the form of exhaust and from fuel-burning power plants. When fuel burns explosively in the cylinder of an internal-combustion engine, some of the nitrogen in the cylinder also combines with oxygen to form  $NO$ , a very reactive nitrogen-oxygen free radical.



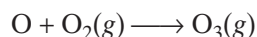
When the free radical reaches the air, it reacts with oxygen to produce  $NO_2$  radicals, which react with water in the air to produce  $HNO_3$ .



In sunlight, nitrogen dioxide decomposes to give nitric oxide and an atom of oxygen. Note that the  $NO$  produced is free to undergo the previous reaction once more.



Just as it is in the stratosphere, a free oxygen atom in the lower atmosphere is highly reactive and reacts with a molecule of diatomic oxygen to form ozone.

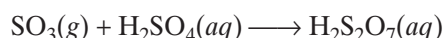




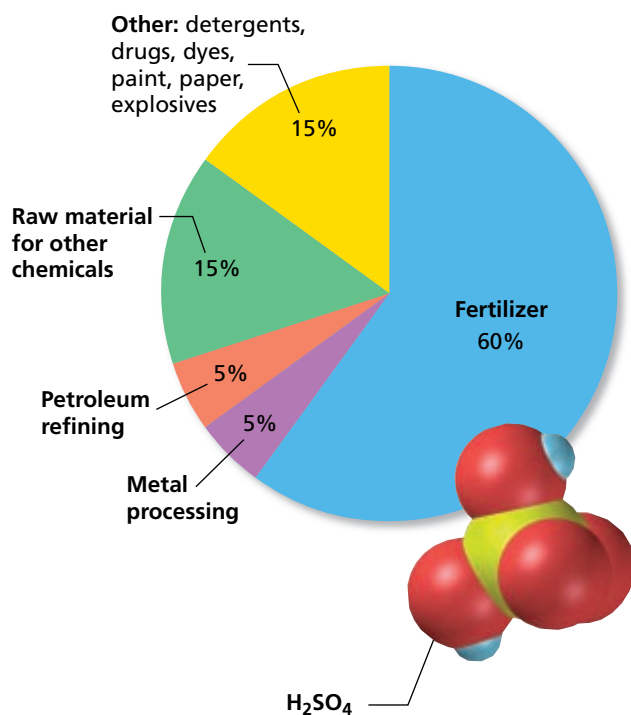
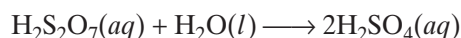
## APPLICATION *Chemical Industry*

### Sulfuric Acid

Sulfuric acid is the so-called “king of chemicals” because it is produced in the largest volume in the United States. It is produced by the contact process. This process starts with the production of  $\text{SO}_2$  by burning sulfur or roasting iron pyrite,  $\text{FeS}_2$ . The purified sulfur dioxide is mixed with air and passed through hot iron pipes containing a catalyst. The contact between the catalyst,  $\text{SO}_2$ , and  $\text{O}_2$  produces sulfur trioxide,  $\text{SO}_3$ , and gives the contact process its name.  $\text{SO}_3$  is dissolved in concentrated  $\text{H}_2\text{SO}_4$  to produce pyrosulfuric acid,  $\text{H}_2\text{S}_2\text{O}_7$ .



The pyrosulfuric acid is then diluted with water to produce sulfuric acid.

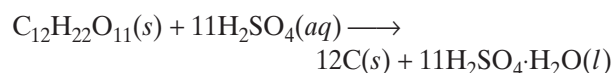


Important uses of the U.S. supply of sulfuric acid

### Properties and Uses of Sulfuric Acid

Concentrated sulfuric acid is a good oxidizing agent. During the oxidation process, sulfur is reduced from +6 to +4 or -2. The change in oxidation state for a reaction depends on the concentration of the acid and on the nature of the reducing agent used in the reaction.

Sulfuric acid is also an important dehydrating agent. Gases that do not react with  $\text{H}_2\text{SO}_4$  can be dried by being bubbled through concentrated sulfuric acid. Organic compounds, like sucrose, are dehydrated to leave carbon, as shown by the following reaction.



The decomposition of sucrose proceeds rapidly, as shown in Figure 21-9 on page 684.

About 60% of the sulfuric acid produced in this country is used to make superphosphate, which is a mixture of phosphate compounds used in fertilizers.

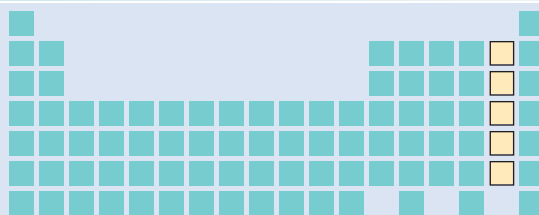
**TABLE 7B** Top Ten Chemicals Produced in the U.S.

Rank	Chemical	Physical state	Formula
1	sulfuric acid	<i>l</i>	$\text{H}_2\text{SO}_4$
2	nitrogen	<i>g</i>	$\text{N}_2$
3	oxygen	<i>g</i>	$\text{O}_2$
4	ethylene	<i>g</i>	$\text{C}_2\text{H}_4$
5	calcium oxide (lime)	<i>s</i>	$\text{CaO}$
6	ammonia	<i>g</i>	$\text{NH}_3$
7	phosphoric acid	<i>l</i>	$\text{H}_3\text{PO}_4$
8	sodium hydroxide	<i>s</i>	$\text{NaOH}$
9	propylene	<i>g</i>	$\text{C}_3\text{H}_6$
10	chlorine	<i>g</i>	$\text{Cl}_2$

# GROUP 17 HALOGEN FAMILY

## CHARACTERISTICS

- are all nonmetals and occur in combined form in nature, mainly as metal halides
- are found in the rocks of Earth's crust and dissolved in sea water
- range from fluorine, the 13th most abundant element, to astatine, which is one of the rarest elements
- exist at room temperature as a gas ( $F_2$  and  $Cl_2$ ), a liquid ( $Br_2$ ), and a solid ( $I_2$  and  $At$ )
- consist of atoms that have seven electrons in their outermost energy level
- tend to gain one electron to form a halide,  $X^-$  ion, but also share electrons and have positive oxidation states
- are reactive, with fluorine being the most reactive of all nonmetals



9  
**F**  
Fluorine  
18.9984032  
[He] $2s^2 2p^5$

17  
**Cl**  
Chlorine  
35.4527  
[Ne] $3s^2 3p^5$

35  
**Br**  
Bromine  
79.904  
[Ar] $3d^{10} 4s^2 4p^5$

53  
**I**  
Iodine  
126.904  
[Kr] $4d^{10} 5s^2 5p^5$

85  
**At**  
Astatine  
(209.9871)  
[Xe] $4f^{14} 5d^{10} 6s^2 6p^5$

Atomic radius  
increases

Ionic radius  
increases

Ionization energy  
decreases

Electronegativity  
decreases



Halogens are the only family that contains elements representing all three states of matter at room temperature. Chlorine is a yellowish green gas; bromine is a reddish brown liquid; and iodine is a purple-black solid.

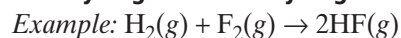


Iodine sublimes to produce a violet vapor that recrystallizes on the bottom of the evaporating dish filled with ice.

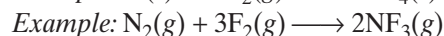
## COMMON REACTIONS\*

**With Metals to Form Halides**

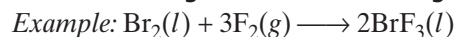
The halide formula depends on the oxidation state of the metal.

**With Hydrogen to Form Hydrogen Halides**

$\text{Cl}_2$ ,  $\text{Br}_2$ , and  $\text{I}_2$  also follow this pattern.

**With Nonmetals and Metalloids to Form Halides**

The formula of the halide depends on the oxidation state of the metalloid or nonmetal.

**With Other Halogens to Form Interhalogen Compounds**

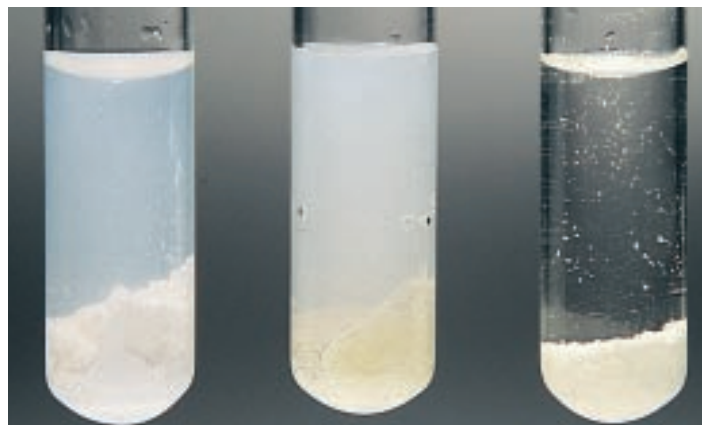
\* Chemists assume that astatine undergoes similar reactions, but few chemical tests have been made.



Chlorine combines readily with iron wool, which ignites in chlorine gas to form  $\text{FeCl}_3$ .



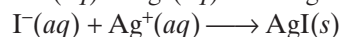
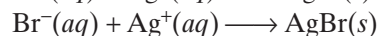
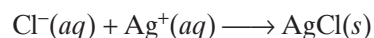
Hydrofluoric acid is used to etch patterns into glass.



Shown here from left to right are precipitates of  $\text{AgCl}$ ,  $\text{AgBr}$ , and  $\text{AgI}$ .

## ANALYTICAL TEST

As with most elements, the presence of each of the halogens can be determined by atomic absorption spectroscopy. Fluorides react with concentrated sulfuric acid,  $\text{H}_2\text{SO}_4$ , to release hydrogen fluoride gas. Three of the halide ions can be identified in solution by their reactions with silver nitrate.





## PROPERTIES OF THE GROUP 17 ELEMENTS

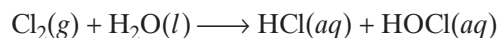
	F	Cl	Br	I	At
Melting point (°C)	-219.62	-100.98	-7.2	113.5	575.2
Boiling point (°C)	-188.14	-34.6	58.78	184.35	610
Density (g/cm <sup>3</sup> )	$1.69 \times 10^{-3}$	$3.214 \times 10^{-3}$	3.119	4.93	not known
Ionization energy (kJ/mol)	1681	1251	1140	1008	—
Atomic radius (pm)	72	100	114	133	140
Ionic radius (pm)	133	181	196	220	—
Common oxidation number in compounds	-1	-1, +1, +3, +5, +7	-1, +1, +3, +5, +7	-1, +1, +3, +5, +7	-1, +5
Crystal structure	cubic	orthorhombic	orthorhombic	orthorhombic	not known

APPLICATION *The Environment*

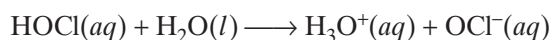
## Chlorine in Water Treatment

For more than a century, communities have treated their water to reduce the amount of toxic substances in the water and to prevent disease. A treatment process widely used in the United States is chlorination. All halogens kill bacteria and other microorganisms. Chlorine, however, is the only halogen acceptable for large-scale treatment of public water supplies.

When chlorine is added to water, the following reaction produces HCl and hypochlorous acid, HOCl.



Hypochlorous acid is a weak acid that ionizes to give hydrogen ions and hypochlorite ions,  $\text{OCl}^-$ .



NaHClO

$\text{CaCl}_2\text{O}_2$

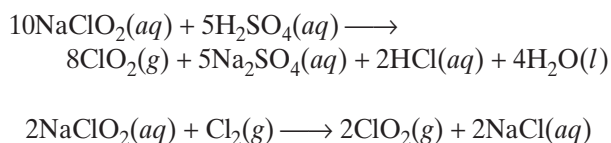
Swimming pools are routinely tested to be sure the chlorine level is safe.

The "chlorine" used in swimming pools is really the compounds shown above and not chlorine at all.

The  $\text{OCl}^-$  ions are strong oxidizing agents that can destroy microorganisms.

In some water-treatment plants, calcium hypochlorite,  $\text{Ca}(\text{ClO})_2$ , a salt of hypochlorous acid, is added to water to provide  $\text{OCl}^-$  ions. Similar treatments are used in swimming pools.

Nearly a hundred cities in the United States and thousands of communities in Europe use chlorine in the form of chlorine dioxide,  $\text{ClO}_2$ , as their primary means of disinfecting water. The main drawback to the use of  $\text{ClO}_2$  is that it is unstable and cannot be stored. Instead,  $\text{ClO}_2$  must be prepared on location by one of the following reactions involving sodium chlorite,  $\text{NaClO}_2$ .



The expense of using  $\text{ClO}_2$  makes it less desirable than  $\text{Cl}_2$  in water-treatment systems unless there are other considerations. For example, the use of  $\text{ClO}_2$  is likely to result in purified water with less of the aftertaste and odor associated with water purified by  $\text{Cl}_2$ .

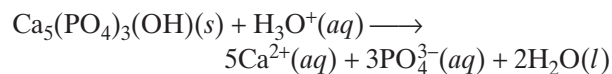
### Fluoride and Tooth Decay

In the 1940s, scientists noticed that people living in communities that have natural water supplies with high concentrations of fluoride ions,  $\text{F}^-$ , have significantly lower rates of dental caries (tooth decay) than most of the population.

In June 1944, a study on the effects of water fluoridation began in two Michigan cities, Muskegon and Grand Rapids, where the natural level of fluoride in drinking water was low (about 0.05 ppm). In Grand Rapids, sodium fluoride,  $\text{NaF}$ , was added to the drinking water to raise levels to 1.0 ppm. In Muskegon, no fluoride was added. Also included in the study was

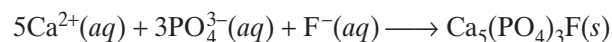
Aurora, Illinois, a city that was similar to Grand Rapids and Muskegon, except that it had a natural  $\text{F}^-$  concentration of 1.2 ppm in the water supply. After 10 years, the rate of tooth decay in Grand Rapids had dropped far below that in Muskegon and was about the same as it was in Aurora.

Tooth enamel is made of a strong, rocklike material consisting mostly of calcium hydroxyphosphate,  $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ , also known as apatite. Apatite is an insoluble and very hard compound—ideal for tooth enamel. Sometimes, however, saliva becomes more acidic, particularly after a person eats a high-sugar meal. Acids ionize to produce hydronium ions, which react with the hydroxide ion,  $\text{OH}^-$ , in the apatite to form water. The loss of  $\text{OH}^-$  causes the apatite to dissolve.



Saliva supplies more  $\text{OH}^-$  ions, and new apatite is formed, but slowly.

If fluoride ions are present in saliva, some fluorapatite,  $\text{Ca}_5(\text{PO}_4)_3\text{F}$ , also forms.



Fluorapatite resists attack by acids, so the tooth enamel resists decay better than enamel containing no fluoride.

When the beneficial effect of fluoride had been established, public health authorities proposed that fluoride compounds be added to water supplies in low-fluoride communities. Fluoridation started in the 1950s, and by 1965, nearly every medical and dental association in the United States had endorsed fluoridation of water supplies. In the past decade, however, that trend slowed as opposition to fluoridation grew.