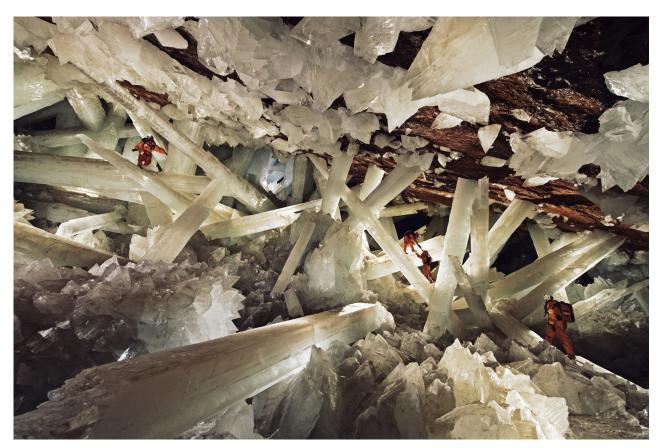
INTERCHAPTER I

The Main-Group Metals



Large deposits of the calcium-containing mineral gypsum, $CaSO_4 \cdot 2H_2O(s)$, are found in many areas. Shown here are the largest known crystals of gypsum discovered in a cavern below the Chihuahuan Desert in Mexico. Several of these giant crystals exceed 10 meters in length!

The metals that occur in Groups 1, 2, and 13–15 in the periodic table are called the main-group metals. The chemical reactivities of these metals vary greatly, from the very reactive alkali metals, which combine spontaneously with the oxygen and water vapor in the air, to the relatively unreactive Group 14 metals tin and lead. We discussed the alkali metals in Interchapter D, and here we discuss the other main-group metals. As usual, we recommend the periodic table website, Periodic Table Live! You can find a link to the website at www.McQuarrieGeneralChemistry.com.

I-I. The Alkaline-Earth Metals Form Ionic Compounds Consisting of M²⁺ Ions

The alkaline-earth metals—beryllium, magnesium, calcium, strontium, barium, and radium—occur in Group 2 in the periodic table (Figure I.1). Beryllium is a relatively rare element but occurs as localized surface deposits in the mineral beryl (Figure I.2). Essentially unlimited quantities of magnesium are readily available in seawater, where Mg²⁺(aq) occurs at an appreciable concentration. Calcium, strontium, and barium rank 5th, 18th, and 19th in abundance in the earth's crust, occurring primarily as carbonates and sulfates. All isotopes of radium are radioactive. Some of the physical properties of the alkaline-earth metals are given in Table I.1.

The chemistry of the Group 2 metals involves primarily the metals and their +2 ions. With few exceptions, the reactivity of the Group 2 metals increases from beryllium to barium. As in all families of the main-group elements, the first member of the family differs in several respects from the other members of the family. The anomalous properties of beryllium are attributed to the small ionic radius of the Be²⁺ ion.



Figure 1.1 The Group 2 elements. Top row: beryllium, magnesium, and calcium. Bottom row: strontium and barium.



Figure I.2 The mineral beryl, $Be_3Al_2Si_6O_{18}(s)$, is the chief source of beryllium and is used as a gem.

The alkaline-earth metals are too reactive to occur as the free metals in nature. They are prepared by high-temperature electrolysis (see Chapter 25) of the appropriate molten chloride; for example,

$$\operatorname{CaCl}_2(l) \xrightarrow{\begin{array}{c} \operatorname{electrolysis} \\ \operatorname{high} T \end{array}} \operatorname{Ca}(l) + \operatorname{Cl}_2(g)$$

The metals Mg(s), Ca(s), Sr(s), and Ba(s) are silvery-white when freshly cut, but they tarnish rapidly

TABLE I.I	Physical properties of the alkaline-earth metals
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Element	Symbol	Atomic number	Atomic mass	Metal radius/pm	Ionic radius of M ²⁺ /pm	Melting point/°C	Boiling point/°C	Density at 25°C/g·cm ⁻³
beryllium	Be	4	9.012182	105	31	1287	2471	1.85
magnesium	Mg	12	24.3050	150	65	650	1090	1.74
calcium	Ca	20	40.078	180	99	842	1484	1.54
strontium	Sr	38	87.62	200	113	777	1382	2.64
barium	Ba	56	137.327	215	135	727	1897	3.62
radium	Ra	88	(226)	215	148	696	~1740	5

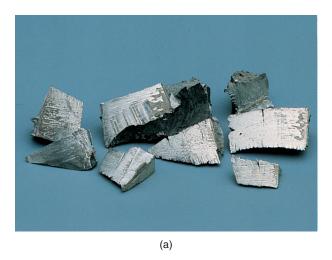




Figure 1.3 Calcium is a very reactive metal and reacts with the oxygen and water vapor in the air. Consequently, fresh calcium turnings, shown in (a), corrode rapidly when exposed to air, as seen in (b).

in air to form metal oxides, MO(s) (Figure I.3). Beryllium and magnesium react slowly with water at ordinary temperatures, although hot magnesium reacts violently with water. The other alkaline-earth metals react more rapidly with water, but the rates of these reactions are still much slower than those for the alkali metals.

The alkaline-earth metals burn in oxygen to form MO(s) oxides, which are ionic solids. Magnesium is used as an incendiary in warfare because of its vigorous reaction with oxygen. It burns even more rapidly



Figure 1.4 Magnesium metal burns vigorously in oxygen with a bright, white flame. The light given off is very intense and can damage the retina if viewed directly.

when sprayed with water and reacts with carbon dioxide at elevated temperatures according to

$$2 \operatorname{Mg}(s) + \operatorname{CO}_2(g) \xrightarrow{\operatorname{high T}} 2 \operatorname{MgO}(s) + \operatorname{C}(s)$$

Covering burning magnesium with sand slows the combustion, but the molten magnesium reacts with the silicon dioxide (the principal component of sand) to form magnesium oxide:

$$2 \operatorname{Mg}(l) + \operatorname{SiO}_{\circ}(s) \rightarrow 2 \operatorname{MgO}(s) + \operatorname{Si}(s)$$

Because magnesium burns with an intense white light, it is used in flares, fireworks, flashbulbs, and as an emergency firelighter by campers (Figure I.4). Magnesium is strong and light and so is used in the construction of aircraft and missiles and in the manufacture of engine blocks and other parts for high-performance vehicles. Due to its light weight and good electrical properties, magnesium is also used in various electronic devices, such as laptop computers.

Like the alkali metals, the alkaline-earth metals show an increasing tendency to form peroxides with increasing size. Strontium peroxide, $SrO_2(s)$, is formed at high oxygen pressure; and barium peroxide, $BaO_0(s)$, forms readily in air at 500°C.

Because various automobile parts may contain magnesium, only sand or an extinguisher rated for metal fires (class D) and never water or carbon dioxide should be used to contain a car fire.

Beryllium is somewhat anomalous when compared to the other Group 2 metals in that its binary compounds have less ionic character. Also, beryllium does not react readily with water at room temperature.

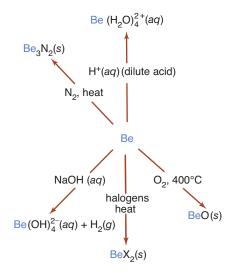
Except for beryllium, the alkaline-earth metals react vigorously with dilute acids, for example

$$Mg(s) + 2HCl(aq) \rightarrow MgCl_{s}(aq) + H_{s}(g)$$

The alkaline-earth metals react with most of the nonmetals to form binary ionic compounds. Representative reactions of beryllium are shown in Figure I.5 and those of the other alkaline-earth metals are summarized in Figure I.6.

Many alkaline-earth-metal compounds are important commercially. Magnesium hydroxide is only slightly soluble in water, and suspensions of it are sold as the antacid Milk of Magnesia. Magnesium sulfate heptahydrate, ${\rm MgSO_4}\cdot 7\,{\rm H_2O}(s)$, known as Epsom salt, is used as a cathartic, or purgative. The name Epsom comes from the place where the compound was first discovered in a natural spring in Epsom, England, in 1695.

Calcium, as the Ca²⁺ ion, is an essential constituent of bones and teeth, limestone, plants, egg shells, insect exoskeletons, and the shells of marine organisms. The Ca²⁺ ion plays a major role in muscle contraction, vision, and nerve excitation.



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Figure 1.5 Representative reactions of beryllium.

Calcium oxide, or quicklime, is made by heating limestone according to

$$CaCO_3(s) \xrightarrow{high T} CaO(s) + CO_2(g)$$

Calcium oxide is one of the most important industrial chemicals and is used extensively in construction. It is mixed with water to form calcium hydroxide, which is also called slaked lime, according to

$$CaO(s) + H_{\circ}O(l) \rightarrow Ca(OH)_{\circ}(aq)$$

Slaked lime is used to make cement, mortar, and plaster.

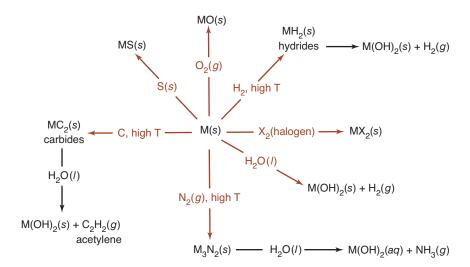


Figure 1.6 Representative reactions of Group 2 metals other than beryllium.



Figure I.7 Red signal flares. The red color arises from light emitted by electronically excited strontium atoms.

$$\begin{aligned} \text{CaSO}_4 \cdot \text{H}_2 \text{O}(s) + \text{H}_2 \text{O}(l) &\rightarrow \text{CaSO}_4 \cdot 2 \, \text{H}_2 \text{O}(s) \\ \text{plaster of Paris} & \text{gypsum} \end{aligned}$$

Plaster of Paris is $CaSO_4 \cdot H_2O(s)$, which combines with water to form gypsum (Frontispiece). Gypsum is used in drywall, plaster, molds, and other such materials.

Asbestos is a calcium magnesium silicate, a naturally occurring mineral, with the approximate composition $CaMg_3(SiO_3)_4(s)$. It can resist very high temperatures, but because small asbestos fibers are carcinogenic, it has been phased out as a construction material.

Strontium salts are used in signal flares and fireworks (Figure I.7). The radioactive isotope strontium-90, which is produced in atomic bomb explosions, is a major health hazard because it behaves like calcium and becomes incorporated in bone marrow, causing various cancers.

Table I.2 summarizes the principal sources and commercial uses of the alkaline-earth metals. Some other industrially important alkaline-earth metal compounds are listed in Table I.3.

I-2. Boron Is a Semimetal; Aluminum, Gallium, Indium, and Thallium Are Group 13 Metals

The Group 13 elements are boron, aluminum, gallium, indium, and thallium. Some of the physical properties of Group 13 elements are presented in Table I.4.

The chemistry of boron, the first member of the group, differs in many respects from that of the rest of the group. Boron is a semimetal, and the other members of the series are metals, with the metallic character of the elements increasing as we descend the group in the periodic table. Boron has a metallic luster but behaves more like the semimetal silicon than like the metal aluminum (Figure I.8).

Boron(III) is always covalently bonded; boron forms no simple ionic cations of the type B^{3+} . For example, the boron trihalides, BX_3 , are trigonal planar molecules with X–B–X bond angles of 120° , as predicted by VSEPR theory.

The boron trihalides react with water to form boric acid, $\mathrm{B(OH)}_3(aq)$, and the corresponding hydrohalic acid. For example,

$$BCl_{3}(g) + 3H_{9}O(l) \rightarrow B(OH)_{3}(aq) + 3HCl(aq)$$

TABLE 1.2 Major sources and uses of the alkaline-earth metals

Metal	Sources	Uses
beryllium	beryllium aluminum silicates, including beryl, $\mathrm{Be_3Al_2Si_6O_{18}}$	lightweight alloys (improves corrosion resistance and resistance to metal fatigue and temperature changes); gyroscopes; nuclear reactors; missiles and satellites.
magnesium	dolomite, CaMg(CO ₃) ₂ ; carbonates and silicates; seawater and well brines	alloys for airplanes; fuses; pyrotechnics; lightweight automobile engine blocks; corrosion protection for metals
calcium	limestone, $CaCO_3$; gypsum, $CaSO_4 \cdot 2H_2O$; apatite, $Ca_{10}(PO_4)_6X$, where X = F, Cl, Br, or OH	alloys; $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$ (major constituent of tooth enamel) production of chromium and other metals
strontium	celestite, ${\rm SrSO_4};$ strontianite, ${\rm SrCO_3}$	alloys
barium	witherite, $BaCO_3$; barite, $BaSO_4$	lubricant on rotors of anodes in vacuum X-ray tubes; spark-plug alloys
radium	pitchblende, UO_2 ; carnotite, $\mathrm{K_2(\mathrm{UO}_2)_2(\mathrm{VO}_4)_2\cdot 3 H_2O}$	skin cancer treatments

TABLE 1.3 Important compounds of the Group 2 elements

Compound	Uses
beryllium oxide, BeO(s)	nuclear reactor fuel moderator; electrical insulator
magnesium oxide, MgO(s)	talcum powder; component of fire bricks; optical instruments
magnesium perchlorate, $\mathrm{Mg(ClO_4)}_2(s)$	desiccant
calcium hydrogen sulfite, $\text{Ca(HSO}_3)_2(s)$	germicide, preservative, disinfectant; beer manufacture
calcium carbonate, $CaCO_3(s)$	antacid in wine making; manufacture of pharmaceuticals, chalk
calcium chloride, $CaCl_2(s)$	de-icer on roads; to keep dust down on dirt roads; fire extinguishers
calcium hypochlorite, $Ca(OCl)_2(s)$	bleaching powder; sugar refining; algaecide
strontium nitrate, $Sr(NO_3)_2(s)$	red signal flares
strontium sulfide, SrS(s)	luminous paints
barium carbonate, $BaCO_3(s)$	rat poison
barium nitrate, $\mathrm{Ba(NO_3)}_2(s)$	pyrotechnics (green flame); green signal flares

TABLE I.4 Properties of the Group I3 elements

Element	Symbol	Atomic number	Atomic mass	Metal radius/pm	Ionic radius of M ³⁺ /pm	Melting point/°C	Boiling point/°C	Density at 25°C/g·cm ⁻³
boron*	В	5	10.811	85	20	2075	4000	2.34
aluminum	Al	13	26.918538	125	50	660.32	2519	2.70
gallium	Ga	31	69.723	130	62	29.7666	2204	5.91
indium	In	49	114.818	155	81	156.60	2072	7.31
thallium	Tl	81	204.3833	190	95 [†]	304	1473	11.8

^{*}Boron is a semimetal; the rest are metals.

Boric acid is usually made by adding hydrochloric acid or sulfuric acid to borax, $\text{Na}_2\text{B}_4\text{O}_7\cdot 10\,\text{H}_2\text{O}(s)$ according to

$$\begin{split} \mathrm{Na_2B_4O_7} \cdot 10\,\mathrm{H_2O}(s) + 2\,\mathrm{HCl}(aq) \rightarrow \\ & 4\,\mathrm{B}(\mathrm{OH})_3(aq) + 5\,\mathrm{H_2O}(l) + 2\,\mathrm{NaCl}(aq) \end{split}$$

Boric acid is a moderately soluble monoprotic weak acid in water; its formula is usually written as $\mathrm{B(OH)}_3(aq)$ rather than $\mathrm{H_3BO}_3(aq)$ or $\mathrm{HBO(OH)}_2(aq)$, because it acts as an acid by accepting a hydroxide ion from water rather than by donating a proton, as described by

$$B(OH)_{3}(aq) + H_{9}O(l) \rightleftharpoons B(OH)_{4}^{-}(aq) + H^{+}(aq)$$



Figure I.8 Boron is a semimetal with a metallic luster.

 $^{^{\}dagger} \! \text{Ionic radius of Tl}^{\scriptscriptstyle +} \! : 115 \; \text{pm}.$

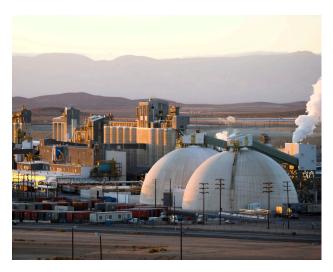


Figure 1.9 A mine in Boron, California, where massive deposits of borax are located.

Boric acid is a good example of a Lewis acid (Section 20-1). Aqueous solutions of boric acid are used in mouth and eye washes. Borax, which is found in large deposits in certain desert regions of California (Figure I.9), was known and used thousands of years ago to glaze pottery.

The principal oxide of boron, $B_2O_3(s)$, is obtained by heating boric acid according to

$$2B(OH)_{s}(s) \rightarrow B_{s}O_{s}(s) + 3H_{s}O(g)$$

Boron trioxide, commonly known as boric oxide, is a colorless, vitreous substance that is extremely difficult to crystallize. It is fused with $SiO_2(s)$ (sand) and $Na_2CO_3(s)$ to make heat-resistant borosilicate glassware such as Pyrex and as a fire-resistant additive for paints.

Boron forms a large number of hydrides. The smaller boron hydrides are volatile, spontaneously flammable in air, and react readily with water. In Chapter 8 we used VSEPR theory to predict that the borane molecule, $\rm BH_3$, is a symmetrical trigonal planar molecule with 120° bond angles. This molecule is not stable, however, and dimerizes to diborane, $\rm B_2H_6$ according to the chemical equation

$$2BH_{3}(g) \rightarrow B_{9}H_{6}(g)$$

Diborane, which is the simplest boron hydride that can be synthesized in appreciable quantities, can be prepared by reacting sodium borohydride, NaBH₄(s), with sulfuric acid, H₉SO₄(aq), as described by

$$\begin{split} 2\operatorname{NaBH}_4(aq) + \operatorname{H}_2\operatorname{SO}_4(aq) &\leftrightarrows \\ \operatorname{B}_2\operatorname{H}_6(g) + 2\operatorname{H}_2(g) + \operatorname{Na}_2\operatorname{SO}_4(aq) \end{split}$$

The reaction of $B_2H_6(g)$ with water is slow enough to enable $B_2H_6(g)$ to escape from the solution as the gas. Pyrolysis of diborane (rapid heating in the absence of oxygen), in some cases in the presence of $H_2(g)$, is used to prepare more complex boron hydrides such as $B_4H_{10}(g)$, $B_5H_9(l)$, $B_6H_{12}(l)$, and $B_{10}H_{14}(s)$, all of which involve somewhat peculiar B–H–B bridge bonds (Figure I.10).

Aluminum is the most abundant metallic element and the third most abundant element in the earth's crust. In addition to its widespread occurrence in silicate minerals, it is also found in enormous deposits of bauxite, AlO(OH)(s) (Figure I.11), which is the chief source of aluminum. The bauxite is first converted to aluminum oxide, $Al_2O_3(s)$, which is electrolyzed to produce pure aluminum.

Originally, the $Al_2O_3(s)$ was dissolved in molten cryolite, $Na_3AlF_6(s)$, because the $Al_2O_3 \cdot Na_3AlF_6(s)$ mixture melts at a relatively low temperature, but insufficient naturally occurring quantities of cryolite exist for world production of aluminum, so it is now manufactured by reacting $Al_2O_3(s)$ with HF(g) and NaOH(s) in a lead vessel according to

$$12 \operatorname{HF}(g) + \operatorname{Al}_{2} \operatorname{O}_{3}(s) + 6 \operatorname{NaOH}(s) \rightarrow \\ 2 \operatorname{Na}_{3} \operatorname{AlF}_{6}(s) + 9 \operatorname{H}_{2} \operatorname{O}(g)$$
cryolite

The cryolite is used to obtain aluminum metal by the Hall-Héroult process (Chapter 25), in which a molten mixture of cryolite, together with $CaF_2(s)$ and NaF(s), is electrolyzed at $800-1000^{\circ}C$. The other Group 13 metals are also obtained by electrolysis of the appropriate molten halide salt or by electrolysis of aqueous solutions of their salts.

Aluminum reacts with oxygen to form aluminum oxide. The aluminum oxide forms a protective, adherent layer that helps the metal resist corrosion. Freshly polished aluminum has a bright, silvery appearance, but weathered aluminum has a dull tarnish because of the aluminum oxide coating. Structural alloys of aluminum for aircraft, automobiles, and some bicycles contain silicon, copper, magnesium, and other metals, which increase the strength and stiffness of the aluminum.

Gallium, indium, and thallium are soft, silverywhite metals. Gallium has the greatest liquid range

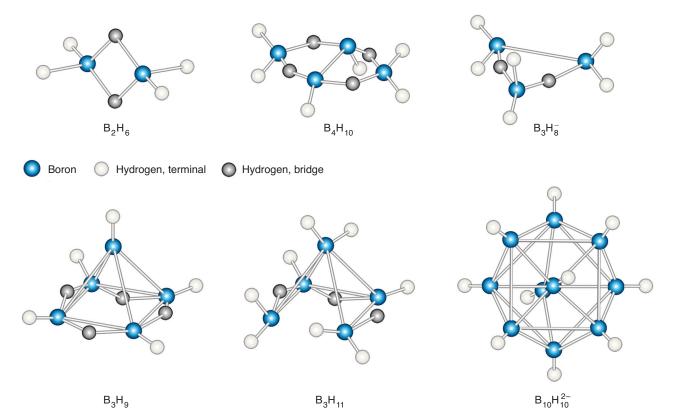


Figure 1.10 Structures of various boron hydrides.

(over 2000°C) of any known substance. Its melting point is 30°C and its boiling point is 2400°C (Figure 3.13). Indium is soft enough to find use as a metallic o-ring material in metal high-vacuum fittings.

Aluminum and gallium dissolve in both acids and bases. The reaction of aluminum with an acid is given by the equation

$$2\text{Al}(s) + 6\text{H}^+(aq) \rightarrow 2\text{Al}^{3+}(aq) + 3\text{H}_{_{0}}(g)$$

and the reaction of aluminum with a base is given by

$$\begin{split} 2\text{Al}(s) + 6\,\text{H}_2\text{O}(l) + 2\,\text{OH}^-(aq) \to \\ 2\text{Al}(\text{OH})_4^-(aq) + 3\,\text{H}_2(g) \\ \text{aluminate ion} \end{split}$$

Substances that dissolve in both acids and bases are called **amphoteric**.

The reaction of aluminum with concentrated aqueous sodium hydroxide is used in the commercial drain cleaner Drāno. The sodium hydroxide breaks down hair, the heat melts the grease, and the gas evolved in the reaction agitates the solid materials blocking the drain.



Figure I.II Aluminum sources: bauxite (*bottom left*), the principal ore of aluminum, and pellets of aluminum oxide (*bottom right*), the principal constituent of bauxite.

Indium and thallium (Figure I.12) react with aqueous solutions of strong acids, but they are unaffected by strong bases. The oxides and hydroxides of indium and thallium are not amphoteric but basic.

In contrast to the other Group 13 metals, thallium exhibits both +3 and +1 ionic charges in aqueous media. Thallium(I) compounds are very poisonous, and even trace amounts can cause complete loss of body hair. The aqueous-solution chemistry of $Tl^+(aq)$ is similar to that of $Ag^+(aq)$; for example, as with Ag^+ , the Cl^- , Br^- , I^- , and S^{2-} salts of Tl^+ are all insoluble and the halide salts darken on exposure to sunlight.

Table I.5 lists the principal sources and uses of the Group 13 metals. Table I.6 lists some commercially important Group 13 compounds.



Figure 1.12 The elements indium (small shiny piece at the left) and thallium (sliced rod showing lustrous metal; the tarnish is due to reaction with air).

TABLE 1.5 Major sources and uses of the Group 13 metals

Metal	Sources	Uses
boron	kernite, $Na_2B_4O_7 \cdot 4H_2O(s)$ borax, $Na_2B_4O_7 \cdot 10H_2O(s)$	in instruments used for absorbing and detecting neutrons; hardening agent in alloys; soaps; borosilicate glasses; flame retardants; insecticides
aluminum	bauxite, $AlO(OH)(s)$; clays	in aircraft and rockets, utensils, electrical conductors, photography, explosives, fireworks, paint, building decoration, and telescope mirrors
gallium	trace impurity in bauxite, zinc, and copper minerals	high-temperature heat-transfer fluid
indium	by-product in lead and zinc production	low-melting alloys in safety devices, sprinklers, high-vacuum o-rings
thallium	by-product from production of other metals	no significant commercial uses

TABLE 1.6 Important compounds of the Group 13 metals

Compound	Uses
boron carbide, $B_4C(s)$	abrasive; wear-resistant tools
boron nitride, BN(s)	lubricant; refractory; rocket nose cone windows; cutting tools
aluminum ammonium sulfate, $\text{Al(NH}_4)(\text{SO}_4)_2(s)$	purification of drinking water; soil acidification
aluminum oxide (alumina), $\text{Al}_2\text{O}_3(s)$	manufacture of abrasives, refractories, ceramics, spark plugs; artificial gems
aluminum borohydride, $\mathrm{Al}\left(\mathrm{BH}_{4}\right)_{3}(s)$	reducing agent; rocket fuel component
aluminum hydroxychloride, $\mathrm{AlOHCl}_2(s)$	antiperspirant; disinfectant
gallium arsenide, GaAs(s)	semiconductors for use in transistors and solar cells
thallium(I) sulfate, $\text{Tl}_2\text{SO}_4(s)$	rat and ant poison

I-3. Germanium Is a Semimetal; Tin and Lead Are Group I4 Metals

Germanium is a semimetal that is found in coal deposits. It is commonly used in transistors, diodes, and other solid-state electronic devices. The common oxidation state of germanium is +4.

Tin and lead are both metals. The principal compounds of both tin and lead involve M(II) and M(IV), although Pb(IV) is known only in the solid state, for example, in $PbO_{\mathfrak{g}}(s)$. Tin is found primarily in the mineral cassiterite, $SnO_{9}(s)$, which occurs in rare but large deposits in Malaysia, China, Russia, and the United States (Figure I.13). Major deposits of tin sulfide ores are found in Bolivia. Total U.S. natural reserves of tin are very small. It is used in plating (tinplated food cans) and in various alloys, including solders, type metal, pewter, and bronze. Tin is also used to line distilled water tanks. Tin objects are subject to a condition called tin disease, which is the conversion of one crystalline form of tin, called white tin, to another crystalline form, called gray tin. This conversion occurs slowly below 13°C; the gray tin that results is a brittle, crumbly metal. A famous compound of tin is tin(II) fluoride (stannous fluoride), $SnF_{o}(s)$, a white crystalline powder that was the first fluoride additive in toothpaste. The physical properties of the Group 14 metals are given in Table I.7.

Lead is obtained primarily from the ore galena, PbS(s) (Figure I.13); commercial deposits occur in over 50 countries. The ore is first roasted in air according to the chemical equation

$$2 \operatorname{PbS}(s) + 3 \operatorname{O}_{\mathfrak{g}}(g) \rightarrow 2 \operatorname{PbO}(s) + 2 \operatorname{SO}_{\mathfrak{g}}(g)$$

and then reduced by carbon in a blast furnace:

$$PbO(s) + CO(g) \rightarrow Pb(l) + CO_{9}(g)$$

Lead is resistant to corrosion and is used in a variety of alloys, in lead storage batteries, cable coverings,



Figure I.13 The minerals galena (left), PbS(s), and cassiterite (right), SnO_s(s).

and ammunition. Lead salts are cumulative poisons that constitute a serious health hazard. The Romans used lead vessels to store wine and other consumables and conducted water in lead-lined aqueducts; thus, lead poisoning may have had more to do with the collapse of the Roman Empire than any other factor. Lead-containing glazes on food containers are now prohibited in the United States and many other countries. Lead paints, which took their yellow color from PbCrO₄(s) and their red color from Pb₉O₄(s), have been discontinued (Figure I.14). The compound tetraethyl lead, $(CH_{\circ}CH_{\circ})_{l}Pb(l)$, was once commonly used as an antiknocking compound in gasoline (it helps the gasoline to burn more smoothly). Leaded gasolines have since been phased out or banned in many countries for environmental and health reasons. Lead ranks fifth (behind iron, copper, aluminum, and zinc) among the metals in the amount used in manufactured goods.

Table I.8 lists the principal sources and commercial uses of the Group 14 metals. Table I.9 lists some important compounds of the Group 14 metals.

The chemistry of Pb(II) is similar to that of the Group 2 metals.

TABLE 1.7 Properties of the Group 14 metals

Element	Symbol	Atomic number	Atomic mass	Atomic radius/pm	Melting point/°C	Boiling point/°C	Density at 25°C/g·cm ⁻³
germanium	Ge	32	72.64	125	938.25	2833	5.3234
tin	Sn	50	118.710	145	231.93	2602	7.287 (white)
lead	Pb	82	207.2	180	327.462	1749	11.3





Figure I.14 (a) Lead(II) chromate, $PbCrO_4(s)$, and (b) the lead oxides (*clockwise from bottom left*) PbO(s), $Pb_3O_4(s)$, and $PbO_9(s)$.

TABLE 1.8 Sources and uses of the Group 14 metals

Element	Principal sources	Uses
germanium	coal ash; by-product of zinc refining	solid-state electronic devices; alloying agent
tin	cassiterite, $SnO_2(s)$	food packaging; tin plate; pewter; bronze; soft solder
lead	galena, $PbS(s)$	lead-acid storage batteries; solder and low-melting alloys; ballast; lead shot; cable covering; shielding; ammunition

TABLE 1.9 Important compounds of germanium, tin, and lead

Compound	Uses
germanium dioxide, $GeO_2(s)$	infrared-transmitting glass; transistors and diodes
$tin(II)$ chloride, $SnCl_2(s)$	reducing agent in dye manufacture; tin galvanizing; soldering flux
$tin(II)$ fluoride, $SnF_2(s)$	toothpaste additive
lead(II) oxide, $PbO(s)$	glazing pottery and ceramics; lead glass
lead dioxide, $PbO_2(s)$	oxidizing agent; matches; lead-acid storage batteries; pyrotechnics
lead tetroxide, $Pb_3O_4(s)$ (or $2PbO \cdot PbO_2$)	lead-acid storage batteries; lead glass; primer paints
lead azide, $Pb(N_3)_2(s)$	detonating agent (primer)

I-4. Bismuth Is the Only Group 15 Metal

Bismuth is a pink-white metal that occurs rarely as the free metal. The most common source of bismuth is the sulfide ore bismuthinite, $\mathrm{Bi}_2\mathrm{S}_3(s)$. The principal compounds of bismuth contain either $\mathrm{Bi}(\mathrm{III})$ or $\mathrm{Bi}(\mathrm{V})$ ions.

Bismuth metal (Figure I.15) is obtained from the ore by roasting with carbon in air. Bismuth is also obtained as a by-product in lead and copper smelting. It burns in air with a bright blue flame, forming the yellow oxide $\operatorname{Bi}_2\operatorname{O}_3(s)$ (Figure I.15), and is used in a variety of alloys, including pewter and other



Figure 1.15 Bismuth metal and bismuth (III) oxide, $Bi_9O_9(s)$.

low-melting alloys that are used in fire-extinguisher sprinkler-head plugs, electrical fuses, and relief valves for compressed-gas cylinders. Bismuth alloys contract on heating and thus find use where other metals might crack because of thermal expansion when subjected to high temperatures.

The oxide $\operatorname{Bi}_2\operatorname{O}_3(s)$ is soluble in strongly acidic aqueous solutions. The bismuthyl ion, $\operatorname{BiO}^+(aq)$, and the bismuthate ion, $\operatorname{BiO}_3^-(aq)$, are important in the aqueous-solution chemistry of bismuth. The bismuthyl ion forms insoluble compounds such as $\operatorname{BiOCl}(s)$ and $\operatorname{BiO}(\operatorname{OH})(s)$; $\operatorname{BiO}_3^-(aq)$ is a powerful oxidizing agent. Bismuth pentafluoride, BiF_5 , is a potent fluorinating agent that transfers fluorine to various compounds and is converted to the trifluoride, $\operatorname{BiF}_3(s)$. Bismuth oxychloride, $\operatorname{BiOCl}(s)$, is used in face powder and in artificial pearls; and bismuth subnitrate, $\operatorname{BiONO}_3(s)$, is used in some cosmetics and as an enamel flux.

TERMS YOU SHOULD KNOW

amphoteric *I7* tin disease *I9*

QUESTIONS

- I-I. How are the Group 2 metals obtained?
- **I-2.** Why should you never throw water on a magnesium fire?
- **I-3**. Give the chemical formula for each of the following substances:
- (a) Milk of Magnesia
- (b) Epsom salt
- (c) quicklime
- (d) limestone
- (e) slaked lime
- **I-4.** Give the chemical formula for each of the following substances:
- (a) plaster of Paris
- (b) gypsum
- (c) asbestos
- (d) bauxite
- (e) tetraethyl lead
- I-5. What substance has the greatest liquid range?
- **l-6.** Write balanced chemical equations describing the dissolution of gallium metal in HCl(aq) and NaOH(aq).
- I-7. List the metals of Groups 13, 14, and 15.
- **I-8**. What is tin disease?
- I-9. How is lead produced from galena?
- I-10. Calculate the number of kilograms of lead that can be obtained from 1.00 kg of each of the following lead ores:
- (a) PbS (galena)
- (b) PbSO₄ (anglesite)
- (c) PbCO₃ (cerussite)
- I-II. Outline, using balanced chemical equations, a method for obtaining tin metal from the tin sulfide ore, SnS(s)