Metals II: Properties and Reactions

23

Metals and alloys have a wide variety of uses. Strength, lightness, and corrosion resistance are some properties that are required of metals used in aircraft construction.

OUTLINE

OBJECTIVES

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

- *Describe the properties and occurrence of the Group IA metals*

- *Describe some important reactions of the Group IA metals*

- *Describe some important uses of the Group IA metals and their compounds*

- *Describe the properties and occurrence of the Group IIA metals*

- *Describe some important reactions of the Group IIA metals*

- *Describe some important uses of the Group IIA metals and their compounds*

- *Identify the post-transition metals*

- *Describe some important periodic trends in the properties of Group IIIA metals and some of their compounds*

- *Describe the important properties of aluminum and some of its compounds*

- *Identify the d-transition metals and describe some of their important properties and their typical compounds*

- *Describe typical oxidation states of the transition metals*

- *Describe some oxides, oxyanions, and hydroxides of chromium*

I n this chapter we will discuss some **representative metals** and some ***d*-transition metals.** The representative elements are those in the A groups of the periodic table. They have valence electrons in their outermost *s* and *p* atomic orbitals. Metallic character increases from top to bottom within groups and from right to left within periods. All the elements in Groups IA (except H) and IIA are metals. The heavier members of Groups IIIA, IVA, and VA are called **post-transition metals.**

Hydrogen is included in Group IA in the periodic table, but it is *not* a metal.
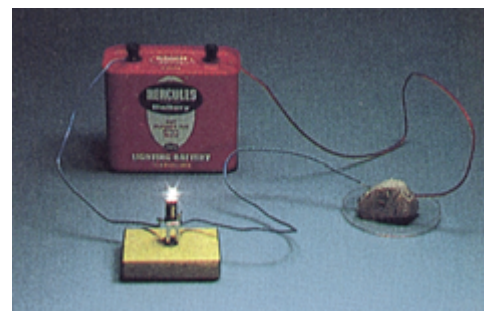

THE ALKALI METALS (GROUP IA)

23-1 GROUP IA METALS: PROPERTIES AND OCCURRENCE

The alkali metals are not found free in nature, because they are so easily oxidized. They are most economically produced by electrolysis of their molten salts. Sodium (2.6% abundance by mass) and potassium (2.4% abundance) are very common in the earth's crust. The other IA metals are quite rare. Francium consists only of short-lived radioactive isotopes formed by alpha-particle emission from actinium (Section 26-4). Both potassium and cesium also have natural radioisotopes. Potassium-40 is important in the potassium–argon radioactive decay method of dating ancient objects (Section 26-12). The properties of the alkali metals vary regularly as the group is descended (Table 23-1).

See the discussion of electrolysis of sodium chloride in Section 21-3.

The free metals, except lithium, are soft, silvery, corrosive metals that can be cut with a knife; lithium is harder. Cesium is slightly golden and melts in the hand (wrapped in plastic because it is so corrosive). The relatively low melting and boiling points of the alkali metals result from their fairly weak bonding forces. Each atom can furnish only one electron for metallic bonding (Section 13-17). Because their outer electrons are so loosely held, the metals are excellent electrical and thermal conductors. They ionize when irradiated with low-energy light (the photoelectric effect). These effects become more pronounced with increasing atomic size. Cesium is used in photoelectric cells.

The low ionization energies of the IA metals show that the single electron in the outer shell is very easily removed. In all alkali metal compounds the metals exhibit the +1 oxidation state. Virtually all are ionic. The extremely high second ionization energies show that removal of an electron from a filled shell is impossible by chemical means.

Alkali metals are excellent conductors of electricity.

TABLE 23-1 *Properties of the Group IA Metals*

Property	Li	Na	K	Rb	Cs	Fr
Outer electrons	$2s^1$	$3s^1$	$4s^1$	$5s^1$	$6s^1$	$7s^1$
Melting point (°C)	186	97.8	63.6	38.9	28.5	27
Boiling point (°C)	1347	904	774	688	678	677
Density (g/cm³)	0.534	0.971	0.862	1.53	1.87	—
Atomic radius (Å)	1.52	1.86	2.27	2.48	2.65	—
Ionic radius, M^+ (Å)	0.90	1.16	1.52	1.66	1.81	—
Electronegativity	1.0	1.0	0.9	0.9	0.8	0.8
E^0 (volts): $M^+(aq) + e^- \longrightarrow M(s)$	−3.05	−2.71	−2.93	−2.93	−2.92	—
Ionization energies (kJ/mol)						
$\quad M(g) \longrightarrow M^+(g) + e^-$	520	496	419	403	377	—
$\quad M^+(g) \longrightarrow M^{2+}(g) + e^-$	7298	4562	3051	2632	2420	—
$\Delta H^0_{\text{hydration}}$ (kJ/mol): $M^+(g) + xH_2O \longrightarrow M^+(aq)$	−544	−435	−351	−293	−264	—

We might expect the standard reduction potentials of the metal ions to become less favorable (more negative) as the ionization energies for the metal atoms become more favorable (less endothermic). The magnitude of the standard reduction potential of Li, −3.05 volts, is unexpectedly large, however. The first ionization energy is the amount of energy absorbed when a mole of *gaseous* atoms ionize. The standard reduction potential, E^0, indicates the ease with which *aqueous* ions are reduced to the metal (Section 21-14). Thus, hydration energies must also be considered (Section 14-2). Because the Li^+ ion is so small, its charge density (ratio of charge to size) is very high. It therefore exerts a stronger attraction for polar H_2O molecules than do the other IA ions. These H_2O molecules must be stripped off during the reduction process in a very endothermic manner, making the E^0 for the Li^+/Li couple very negative (see Table 23-1).

Polarization of an anion refers to distortion of its electron cloud. The ability of a cation to polarize an anion increases with increasing charge density (ratio of charge to size) of the cation.

The high charge density of Li^+ ion accounts for its ability to polarize large anions. This gives a higher degree of covalent character in Li compounds than in other corresponding alkali metal compounds. For example, LiCl is soluble in ethyl alcohol, a less polar solvent than water; NaCl is not. Salts of the alkali metals with small anions are very soluble in water, but salts with large and complex anions, such as silicates and aluminosilicates, are not very soluble.

23-2 REACTIONS OF THE GROUP IA METALS

Many of the reactions of the alkali metals are summarized in Table 23-2. All are characterized by the loss of one electron per metal atom. These metals are very strong reducing agents. Reactions of the alkali metals with H_2 and O_2 were discussed in Sections 6-7 and 6-8, reactions with the halogens in Section 7-2; and reactions with water in Section 4-8, part 2.

The high reactivities of the alkali metals are illustrated by their vigorous reactions with water. Lithium reacts readily; sodium reacts so vigorously that the hydrogen gas it forms may ignite; and potassium, rubidium, and cesium cause the H_2 to burst into flames when

TABLE 23-2	*Some Reactions of the Group IA Metals*
Reaction	**Remarks**
$4M + O_2 \longrightarrow 2M_2O$	Limited O_2
$4Li + O_2 \longrightarrow 2Li_2O$	Excess O_2 (lithium oxide)
$2Na + O_2 \longrightarrow Na_2O_2$	(sodium peroxide)
$M + O_2 \longrightarrow MO_2$	M = K, Rb, Cs; excess O_2 (superoxides)
$2M + H_2 \longrightarrow 2MH$	Molten metals
$6Li + N_2 \longrightarrow 2Li_3N$	At high temperature
$2M + X_2 \longrightarrow 2MX$	X = halogen (Group VIIA)
$2M + S \longrightarrow M_2S$	Also with Se, Te of Group VIA
$12M + P_4 \longrightarrow 4M_3P$	
$2M + 2H_2O \longrightarrow 2MOH + H_2$	K, Rb, and Cs react explosively
$2M + 2NH_3 \longrightarrow 2MNH_2 + H_2$	With $NH_3(\ell)$ in presence of catalyst; with $NH_3(g)$ at high temperature (solutions also contain M^+ + solvated e^-)

the metals are dropped into water. The large amounts of heat evolved provide the activation energy to ignite the hydrogen. The elements also react with water vapor in the air or with moisture from the skin.

$$2K(s) + 2H_2O(\ell) \longrightarrow 2[K^+(aq) + OH^-(aq)] + H_2(g) \qquad \Delta H^0 = -390.8 \text{ kJ/mol rxn}$$
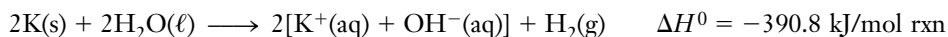
Alkali metals are stored under anhydrous nonpolar liquids such as mineral oil.

As is often true for elements of the second period, Li differs in many ways from the other members of its family. Its ionic charge density and electronegativity are close to those of Mg, so Li compounds resemble those of Mg in some ways. This illustrates the **diagonal similarities** that exist between elements in successive groups near the top of the periodic table.

IA	IIA	IIIA	IVA
Li	Be	B	C
Na	Mg	Al	Si

Lithium is the only IA metal that combines with N_2 to form a nitride, Li_3N. Magnesium readily forms magnesium nitride, Mg_3N_2. Both metals readily combine with carbon to form carbides, whereas the other alkali metals do not react readily with carbon. The solubilities of Li compounds are closer to those of Mg compounds than to those of other IA compounds. The fluorides, phosphates, and carbonates of both Li and Mg are only slightly soluble, but their chlorides, bromides, and iodides are very soluble. Both Li and Mg form normal oxides, Li_2O and MgO, when burned in air at 1 atmosphere pressure. The other alkali metals form peroxides or superoxides.

The IA metal oxides are basic. They react with water to form strong bases.

$$Na_2O(s) + H_2O(\ell) \longrightarrow 2[Na^+(aq) + OH^-(aq)]$$

$$K_2O(s) + H_2O(\ell) \longrightarrow 2[K^+(aq) + OH^-(aq)]$$
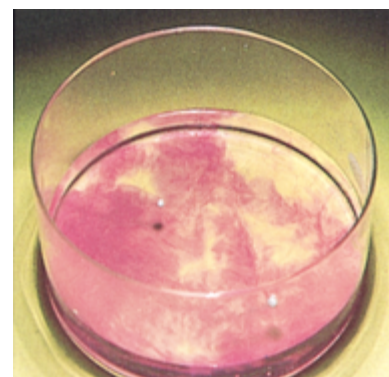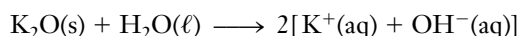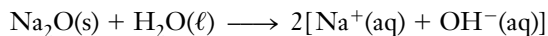
Sodium reacts vigorously with water.

$$2Na(s) + 2H_2O(\ell) \longrightarrow$$
$$2[Na^+(aq) + OH(aq)] + H_2(g)$$
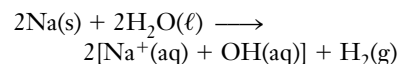
The indicator, phenolphthalein, was added to the water. As NaOH forms, the solution turns pink.

23-3 USES OF GROUP IA METALS AND THEIR COMPOUNDS

Lithium, Li

Metallic lithium has the highest heat capacity of any element. It is used as a heat transfer medium in experimental nuclear reactors. Extremely lightweight lithium–aluminum alloys are used in aircraft construction. Lithium compounds are used in some lightweight dry cells and storage batteries because they have very long lives, even in extreme temperatures. LiCl and LiBr are very hygroscopic and are used in industrial drying processes and air conditioning. Lithium compounds are used for the treatment of some types of mental disorders (mainly manic depression).

Sodium, Na

Sodium is by far the most widely used alkali metal because it is so abundant. Its salts are essential for life. The metal itself is used as a reducing agent in the manufacture of drugs and dyes and in the metallurgy of such metals as titanium and zirconium.

$$TiCl_4(g) + 4Na(\ell) \xrightarrow{\text{heat}} 4NaCl(s) + Ti(s)$$
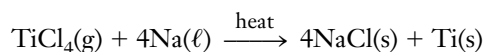
Highway lamps often incorporate Na arcs, which produce a bright yellow glow. A few examples of the uses of sodium compounds are NaOH, called caustic soda, lye, or soda lye (used for production of rayon, cleansers, textiles, soap, paper, and many polymers); Na_2CO_3, called soda or soda ash, and $Na_2CO_3 \cdot 10H_2O$, called washing soda (also used as a substitute for NaOH when a weaker base is acceptable); $NaHCO_3$, called baking soda

The yellowish glow of some highway lamps is due to a sodium arc. Mercury lamps give a bluish glow.
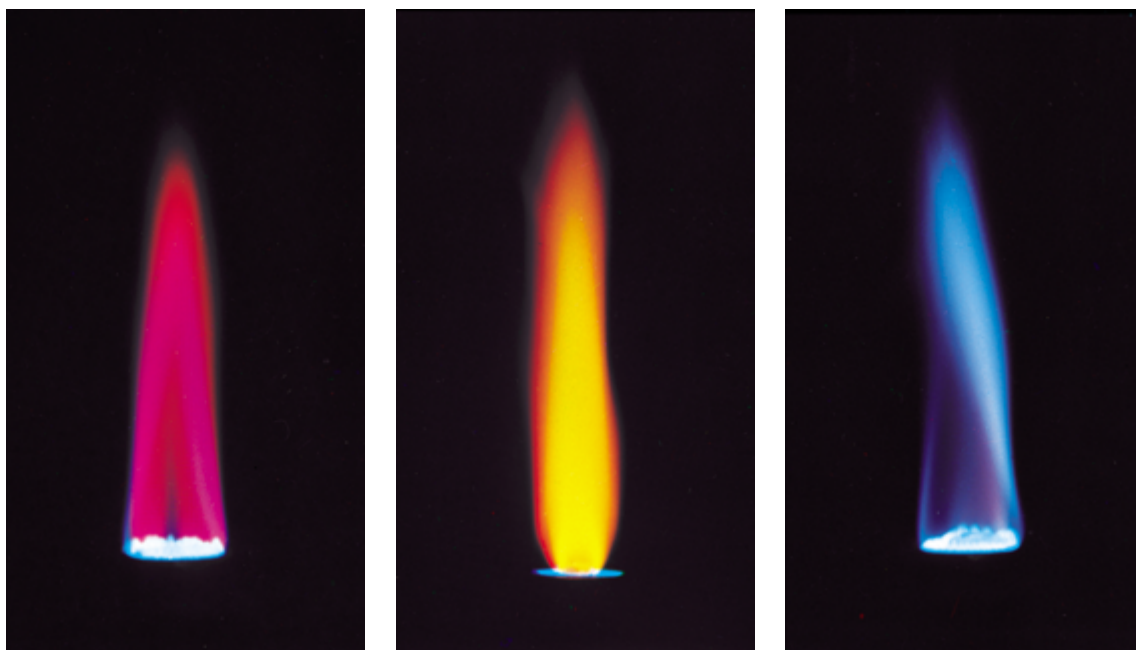
Spacings of energy levels are different for different alkali metals. The salts of the alkali metals impart characteristic colors to flames: lithium (*red*), sodium (*yellow*), and potassium (*violet*).

CHEMISTRY IN USE

The Development of Science

Trace Elements and Life

More than 300 years ago iron was the first trace element shown to be essential in the human diet. An English physician, Thomas Sedenham, soaked "iron and steel filings" in cold Rhenish wine. He used the resulting solution to treat patients suffering from chlorosis, now known to be an iron-deficiency anemia. Nearly 20 trace elements are now believed to be required by humans. The discovery of the biological functions of trace elements is an exciting and controversial area of human nutrition research.

The trace elements can be classified into several categories (see table). In 1989, the National Research Council recognized that iron, iodine, zinc, selenium, copper, chromium, manganese, and molybdenum were dietary essentials for humans. Fluorine is also considered to be valuable for human health, because of its benefits to the teeth and skeleton. These nine trace elements are required by humans and other animals because they are essential components in metalloenzymes and hormones or because they promote health in a specific tissue (such as fluorine in the teeth and skeleton). The trace elements required by the human body in milligram quantities include iron, zinc, copper, manganese, and fluorine. Trace elements required in microgram (μg) quantities include iodine, selenium, chromium, and molybdenum. Although probably required in μg quantities, no dietary recommendations have been made for arsenic, nickel, silicon, and boron even though there is evidence, primarily from animals, that they are essential. There is only weak evidence that cadmium, lead, lithium, tin, vanadium, and bromine are essential for humans.

Iron deficiency is one of the most common nutrient deficiencies in the world, occurring in up to 60% of the women, infants, and children of some countries. Anemia, characterized by a low concentration of hemoglobin in the blood or by a low volume of packed red blood cells, is the usual symptom of iron deficiency. Other symptoms include fatigue and cognitive disorders. Up to 1% of the population may have the genetic disease known as hereditary hemochromatosis, which results in excess absorption of dietary iron, and can lead to liver and heart damage. Concern about this disease may eventually lead to routine screening so that persons with this disorder can be treated before severe symptoms develop and can avoid foods and supplements with large amounts of iron. The recommended dietary allowance for iron for women aged 23 to 50 years is 50% higher than that for men in the same age group because of the iron lost in menstrual bleeding.

Many dietary supplements include essential trace elements.

Dietary Trace Elements

Known to Be Essential	Known or Suspected Functions
iron	Hemoglobin, energy metabolism
iodine	Thyroid hormones
zinc	Enzymes, protein synthesis, cell division
copper	Hemoglobin, bone, nerves, vascular system
selenium	Enzymes, protect against oxidant stress
chromium	Insulin action
manganese	Enzymes, bone
molybdenum	Enzymes, sulfur metabolism
fluorine	Bones, teeth

Substantial Evidence for Essentiality	Known or Suspected Functions
arsenic	Amino acid metabolism
boron	Metabolism of calcium, magnesium, hormones
nickel	Not known, suspected in some enzymes
silicon	Bone and connective tissue

Weak Evidence for Essentiality	Known or Suspected Functions
bromine	Not yet known
cadmium	Not yet known
lead	Not yet known
lithium	Not yet known
tin	Not yet known
vanadium	Not yet known

Iodine deficiency remains a major cause of mental retardation and infant mortality and morbidity throughout the world—even though iodine was shown to be essential for human health nearly 100 years ago. More than 1 billion people are believed to be at risk for iodine deficiency. In 1986, the International Council for the Control of Iodine Deficiency Disorders was established in an effort to improve iodine nutrition and alleviate human suffering. This council works closely with the World Health Organization, the United Nations International Children's Fund, and the United Nations to alleviate iodine deficiency. Iodine is required for the thyroid hormones, thyroxine and tri-iodothyronine, that regulate the metabolic rate and O_2 consumption of cells. Iodine is also intimately involved in the control of growth and development, particularly during fetal and infant life.

In the 1930s, zinc was discovered to be a dietary essential in animals. Zinc deficiency was recognized as a potential public health problem in the 1960s in Iran, where endemic hypogonadism (delayed sexual development) and dwarfism

were discovered in adolescents consuming insufficient dietary zinc. More than 200 zinc enzymes have been discovered. Zinc is also important for the structure and function of biomembranes. Loss of zinc from these membranes results in increased susceptibility to oxidative damage, structural strains, and alterations in specific receptor sites and transport systems. Zinc also helps to stabilize the structures of RNA, DNA, and ribosomes. Several transcription factors contain "Zn fingers," which are needed for the binding of these transcription factors to the DNA. Thus, zinc is absolutely necessary for adequate growth, protein synthesis, and cell division. The best sources of zinc in the human diet are animal foods such as meat, fish, poultry, and dairy products.

Copper was also shown to be essential in the early 1900s. Copper is needed for the absorption and mobilization of iron, so a deficiency of copper causes a type of anemia that is difficult to distinguish from iron deficiency anemia. Copper is also needed for the cardiovascular system, bone, brain, and nervous system. Premature and malnourished infants are particularly susceptible to developing copper deficiency, in part because milk is a poor source of copper. Whole grains, legumes, and nuts are the major dietary sources of copper.

Selenium was first suspected of being a dietary essential in the 1950s. Selenium is considered to be an antioxidant nutrient because it is present in enzymes that help protect against toxic species of oxygen and free radicals. Selenium deficiency is a major public health problem in certain parts of China, where it increases the risk of heart disease, bone and joint disorders, and liver cancer. Selenium is currently under intensive investigation as a possible protector against cancer. The content of selenium in foods is highly variable and dependent on the selenium content of the soil. Generally the best sources of selenium are muscle meats, cereals, and grains.

The 1950s also saw the first evidence that chromium might be a dietary essential. Chromium is believed to promote the action of insulin and thus influences the metabolism of carbohydrates, fats, and proteins. Reports of severe human deficiency of chromium are rare and have been found primarily in people receiving only intravenous feedings for several months or years. Only a few laboratories in the world can accurately measure the amount of chromium in foods and body tissues because chromium is present in stainless steel, which is ubiquitous in analytical laboratories and easily contaminates biological samples.

Manganese and molybdenum are essential for enzymes in humans and other animals, but a dietary deficiency of these minerals is exceedingly rare in humans. Cobalt is essential for vitamin B_{12}, but the human body cannot make vitamin B_{12} from cobalt and thus requires the preformed vitamin from dietary sources. (It is possible to derive some vitamin B_{12} from bacterial synthesis in the digestive tract.)

Efforts to discover whether other elements might be essential intensified during the 1970s. Although it is believed that arsenic, nickel, silicon, and boron are probably essential to humans, it has been difficult to determine whether other minerals have specific biological functions in humans or other animals.

There are several reasons why it is difficult to establish the essentiality of trace elements. Some elements, such as arsenic and selenium, were first recognized for their extreme toxicity, so it has been difficult to convince many health specialists that a toxic element might also be a dietary essential at low levels. Also, most trace elements are present in extremely small amounts in diets and in tissues, and few laboratories are equipped to prevent contamination of samples and to measure these elements with the necessary precision.

Two factors have aided in the discovery of the roles of many trace elements. One is the availability of two highly sensitive analytical techniques, activation analysis and electrothermal atomic absorption spectroscopy, that allow detection of these elements in concentrations of only a few parts per billion. The other is the use of special isolation chambers that allow study of animals under carefully controlled conditions, free of unwanted contaminants. The diets fed to animals and their air supply must be carefully purified to keep out even traces of unwanted elements, and their cages must be made of plastics that contain no metals.

Our understanding of the biological functions of trace elements is changing the way scientists think about diet and health. For example, supplements of manganese, copper, and zinc in combination with calcium have recently been shown to improve human bone health to a greater extent than just calcium alone. Silicon and boron are also believed to be important for bone health. Deficiencies of selenium or copper are suspected by some scientists of increasing the risk of cancer or heart disease. Because chromium, copper, and zinc influence glucose metabolism, future prevention and treatment strategies for diabetes may involve these nutrients.

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or bicarbonate of soda (used for baking and other household uses); NaCl (used as table salt and as the source of all other compounds of Na and Cl); $NaNO_3$, called Chile salt-peter (a nitrogen fertilizer); Na_2SO_4, called salt cake, a by-product of HCl manufacture (used for production of brown wrapping paper and cardboard boxes); and NaH (used for synthesis of $NaBH_4$, which is used to recover silver and mercury from waste water).

Other Group IA Metals

Like salts of Na (and probably Li), those of potassium are essential for life. KNO_3, commonly known as niter or saltpeter, is used as a potassium and nitrogen fertilizer. Most other major industrial uses for K can be satisfied with the more abundant and less expensive Na.

There are very few practical uses for the rare metals rubidium, cesium, and francium. Cesium is used in some photoelectric cells (Section 5-11).
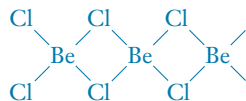
THE ALKALINE EARTH METALS (GROUP IIA)

23-4 GROUP IIA METALS: PROPERTIES AND OCCURRENCE

The alkaline earth metals are all silvery white, malleable, ductile, and somewhat harder than their neighbors in Group IA. Activity increases from top to bottom within the group, with Ca, Sr, and Ba being considered quite active. Each has two electrons in its highest occupied energy level. Both electrons are lost in ionic compound formation, though not as easily as the outer electron of an alkali metal. Compare the ionization energies in Tables 23-1 and 23-3. Most IIA compounds are ionic, but those of Be exhibit a great deal of covalent character. This is due to the extremely high charge density of Be^{2+}. Compounds of beryllium therefore resemble those of aluminum in Group IIIA (diagonal similarities). The IIA elements exhibit the $+2$ oxidation state in all their compounds. The tendency to form $2+$ ions increases from Be to Ra.

The alkaline earth metals show a wider range of chemical properties than the alkali metals. The IIA metals are not as reactive as the IA metals, but they are much too reactive to occur free in nature. They are obtained by electrolysis of their molten chlorides. Calcium and magnesium are abundant in the earth's crust, especially as carbonates and sulfates. Beryllium, strontium, and barium are less abundant. All known radium isotopes are radioactive and are extremely rare.

In Section 8-5 we found that gaseous $BeCl_2$ is linear. The Be atoms in $BeCl_2$ molecules, however, act as Lewis acids. In the solid state, the Cl atoms form coordinate covalent bonds to Be, resulting in a polymeric structure. In such compounds, Be follows the octet rule.

23-5 REACTIONS OF THE GROUP IIA METALS

Table 23-4 summarizes some reactions of the alkaline earth metals, which, except for stoichiometry, are similar to the corresponding reactions of the alkali metals. Reactions with hydrogen and oxygen were discussed in Sections 6-7 and 6-8.

Except for Be, all the alkaline earth metals are oxidized to oxides in air. The IIA oxides (except BeO) are basic and react with water to give hydroxides. Beryllium hydroxide, $Be(OH)_2$, is quite insoluble in water and is amphoteric. Magnesium hydroxide, $Mg(OH)_2$, is only slightly soluble in water. The hydroxides of Ca, Sr, and Ba are strong bases.

Beryllium is at the top of Group IIA. Its oxide is amphoteric, whereas oxides of the heavier members are basic. Metallic character increases from top to bottom within a group

Amphoterism is the ability of a substance to react with both acids and bases (see Section 10-6).

TABLE 23-3 **Properties of the Group IIA Metals**

Property	Be	Mg	Ca	Sr	Ba	Ra
Outer electrons	$2s^2$	$3s^2$	$4s^2$	$5s^2$	$6s^2$	$7s^2$
Melting point (°C)	1283	649	839	770	725	700
Boiling point (°C)	2484	1105	1484	1384	1640	1140
Density (g/cm^3)	1.85	1.74	1.55	2.60	3.51	5
Atomic radius (Å)	1.12	1.60	1.97	2.15	2.22	2.20
Ionic radius, M^{2+} (Å)	0.59	0.85	1.14	1.32	1.49	—
Electronegativity	1.5	1.2	1.0	1.0	1.0	1.0
E^0 (volts): $M^{2+}(aq) + 2e^- \longrightarrow 2M(s)$	−1.85	−2.37	−2.87	−2.89	−2.90	−2.92
Ionization energies (kJ/mol)						
$\quad M(g) \longrightarrow M^+(g) + e^-$	899	738	599	550	503	509
$\quad M^+(g) \longrightarrow M^{2+}(g) + e^-$	1757	1451	1145	1064	965	(979)
$\Delta H^0_{hydration}$ (kJ/mol): $M^{2+}(g) \longrightarrow M^{2+}(aq)$	—	−1925	−1650	−1485	−1276	—

and from right to left across a period. This results in increasing basicity and decreasing acidity of the oxides in the same directions, as shown in the following table.

Group IA	Group IIA	Group IIIA
Li_2O (basic)	BeO (amphoteric)	B_2O_3 (amphoteric)
Na_2O (basic)	MgO (basic)	Al_2O_3 (amphoteric)
K_2O (basic)	CaO (basic)	Ga_2O_3 (amphoteric)
		In_2O_3 (basic)

Increasing metallic character of elements

Decreasing acidity of oxides

Increasing basicity of oxides

Increasing metallic character of elements

Decreasing acidity of oxides

Increasing basicity of oxides

TABLE 23-4 **Some Reactions of the Group IIA Metals**

Reaction	Remarks
$2M + O_2 \longrightarrow 2MO$	Very exothermic (except Be)
$Ba + O_2 \longrightarrow BaO_2$	Almost exclusively
$M + H_2 \longrightarrow MH_2$	M = Ca, Sr, Ba at high temperatures
$3M + N_2 \longrightarrow M_3N_2$	At high temperatures
$6M + P_4 \longrightarrow 2M_3P_2$	At high temperatures
$M + X_2 \longrightarrow MX_2$	X = halogen (Group VIIA)
$M + S \longrightarrow MS$	Also with Se, Te of Group VIA
$M + 2H_2O \longrightarrow M(OH)_2 + H_2$	M = Ca, Sr, Ba at 25°C; Mg gives MgO at high temperatures
$M + 2NH_3 \longrightarrow M(NH_2)_2 + H_2$	M = Ca, Sr, Ba in $NH_3(\ell)$ in presence of catalyst; $NH_3(g)$ with heat

Magnesium burns in air.

Beryllium does not react with pure water even at red heat. It reacts with solutions of strong bases to form the complex ion, $[Be(OH)_4]^{2-}$, and H_2. Magnesium reacts with steam to produce MgO and H_2. Ca, Sr, and Ba react with water at 25°C to form hydroxides and H_2 (see Table 23-4). Group IIA compounds are generally less soluble in water than corresponding IA compounds, but many are quite soluble.

23-6 USES OF GROUP IIA METALS AND THEIR COMPOUNDS

Beryllium, Be

Because of its rarity, beryllium has only a few practical uses. It occurs mainly as beryl, $Be_3Al_2Si_6O_{18}$, a gemstone which, with appropriate impurities, may be aquamarine (blue) or emerald (green). Because it is transparent to X-rays, "windows" for X-ray tubes are constructed of beryllium. Beryllium compounds are quite toxic.

Magnesium, Mg

The tires on the Hummer vehicles used in the Gulf War were made blowout-proof by strong, lightweight magnesium inserts. This is a photograph of a civilian model.

Metallic magnesium burns in air with such a brilliant white light that it is used in photographic flash accessories and fireworks. It is very lightweight and is currently used in many alloys for building materials. Like aluminum, it forms an impervious coating of oxide that protects it from further oxidation. Given its inexhaustible supply in the oceans, it is likely that many more structural uses will be found for it as the reserves of iron ores dwindle.

Calcium, Ca

Calcium and its compounds are widely used commercially. The element is used as a reducing agent in the metallurgy of uranium, thorium, and other metals. It is also used as a scavenger to remove dissolved impurities such as oxygen, sulfur, and carbon in molten metals and to remove residual gases in vacuum tubes. It is a component of many alloys.

Limestone is mainly calcium carbonate.

A laboratory X-ray tube (*left*) and a close-up view of one of its windows (*right*). The windows are made of beryllium metal.

Heating limestone, $CaCO_3$, produces *quicklime*, CaO, which can then be treated with water to form *slaked lime*, $Ca(OH)_2$, an inexpensive base for which industry finds many uses. When slaked lime is mixed with sand and exposed to the CO_2 of the air, it hardens to form mortar. Heating gypsum, $CaSO_4 \cdot 2H_2O$, produces plaster of Paris, $2CaSO_4 \cdot H_2O$.

$$2[CaSO_4 \cdot 2H_2O(s)] \xrightarrow{heat} 2CaSO_4 \cdot H_2O(s) + 3H_2O(g)$$
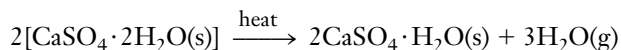
Strontium, Sr

Strontium salts are used in fireworks and flares, which show the characteristic red glow of strontium in a flame. Strontium chloride is used in some toothpastes for persons with sensitive teeth. The metal itself has no practical uses.

Barium, Ba

Barium is a constituent of alloys that are used for spark plugs because of the ease with which it emits electrons when heated. It is used as a degassing agent for vacuum tubes. A slurry of finely divided barium sulfate, $BaSO_4$, is used to coat the gastrointestinal tract in preparation for X-ray photographs because it absorbs X-rays so well. It is so insoluble that it is not poisonous; all soluble barium salts are very toxic.

Calcium carbonate and calcium phosphate occur in seashells and animal bones.

THE POST-TRANSITION METALS

The metals below the stepwise division of the periodic table in Groups IIIA through VA are the **post-transition metals.** These include aluminum, gallium, indium, and thallium from Group IIIA; tin and lead from Group IVA; and bismuth from Group VA. Aluminum is the only post-transition metal that is considered very reactive. We will focus our discussion on the metals of Group IIIA.

There are no true metals in Groups VIA, VIIA, and VIIIA.

23-7 GROUP IIIA: PERIODIC TRENDS

The properties of the elements in Group IIIA (Table 23-5) vary less regularly down the groups than those of the IA and IIA metals. The Group IIIA elements are all solids. Boron, at the top of the group, is a nonmetal. Its melting point, 2300°C, is very high because it crystallizes as a covalent solid. The other elements, aluminum through thallium, form metallic crystals and have considerably lower melting points.

Aluminum, Al

Aluminum is the most reactive of the post-transition metals. It is the most abundant metal in the earth's crust (7.5%) and the third most abundant element. Aluminum is inexpensive compared with most other metals. It is soft and can be readily extruded into wires or rolled, pressed, or cast into shapes.

Because of its relatively low density, aluminum is often used as a lightweight structural metal. It is often alloyed with Mg and some Cu and Si to increase its strength. Many buildings are sheathed in aluminum, which resists corrosion by forming an oxide coating.

Pure aluminum conducts about two thirds as much electric current per unit volume as copper, but it is only one third as dense (Al, 2.70 g/cm³; Cu, 8.92 g/cm³). As a result, a mass of aluminum can conduct twice as much current as the same mass of copper.

This aluminum honeycomb material is made by bonding aluminum foil sheets to form hexagonal cells. It is used to make sandwich construction panels that have a very high strength-to-weight ratio.

| TABLE 23-5	Properties of the Group IIIA Elements				
Property	B	Al	Ga	In	Tl
Outer electrons	$2s^2 2p^1$	$3s^2 3p^1$	$4s^2 4p^1$	$5s^2 5p^1$	$6s^2 6p^1$
Physical state (25°C, 1 atm)	solid	solid	solid	solid	solid
Melting point (°C)	2300	660	29.8	156.6	303.5
Boiling point (°C)	2550	2367	2403	2080	1457
Density (g/cm³)	2.34	2.70	5.91	7.31	11.85
Atomic radius (Å)	0.85	1.43	1.35	1.67	1.70
Ionic radius, M^{3+} (Å)	(0.20)*	0.68	0.76	0.94	1.03
Electronegativity	2.0	1.5	1.7	1.6	1.6
E^0 (volts): $M^{3+}(aq) + 3e^- \longrightarrow M(s)$	(−0.90)*	−1.66	−0.53	−0.34	0.916
Oxidation states	−3 to +3	+3	+1, +3	+1, +3	+1, +3
Ionization energies (kJ/mol)					
$M(g) \longrightarrow M^+(g) + e^-$	801	578	579	558	589
$M^+(g) \longrightarrow M^{2+}(g) + e^-$	2427	1817	1971	1813	1961
$M^{2+}(g) \longrightarrow M^{3+}(g) + e^-$	3660	2745	2952	2692	2867
$\Delta H^0_{hydration}$ (kJ/mol): $M^{3+}(g) + xH_2O \longrightarrow M^{3+}(aq)$	—	−4750	−4703	−4159	−4117

*For the covalent +3 oxidation state.

Aluminum is now used in electrical transmission lines and has been used in wiring in homes. The latter use has been implicated as a fire hazard, however, due to the heat that can be generated during high current flow at the junction of the aluminum wire and fixtures of other metals.

Aluminum is a strong reducing agent.

$$Al^{3+}(aq) + 3e^- \longrightarrow Al(s) \qquad E^0 = -1.66 \text{ V}$$

Aluminum is quite reactive, but a thin, very hard transparent film of Al_2O_3 forms when Al comes into contact with air. This protects it from further oxidation. For this reason it is even passive toward nitric acid, HNO_3, a strong oxidizing agent. When the oxide coating is sanded off, Al reacts vigorously with HNO_3.
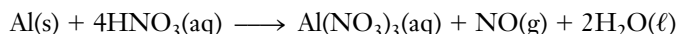
Passive toward means "does not react with."

$$Al(s) + 4HNO_3(aq) \longrightarrow Al(NO_3)_3(aq) + NO(g) + 2H_2O(\ell)$$
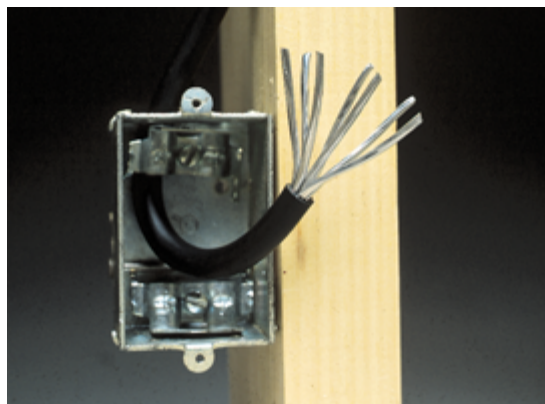
Aluminum wiring in a house.

(a)   **(b)**   **(c)**
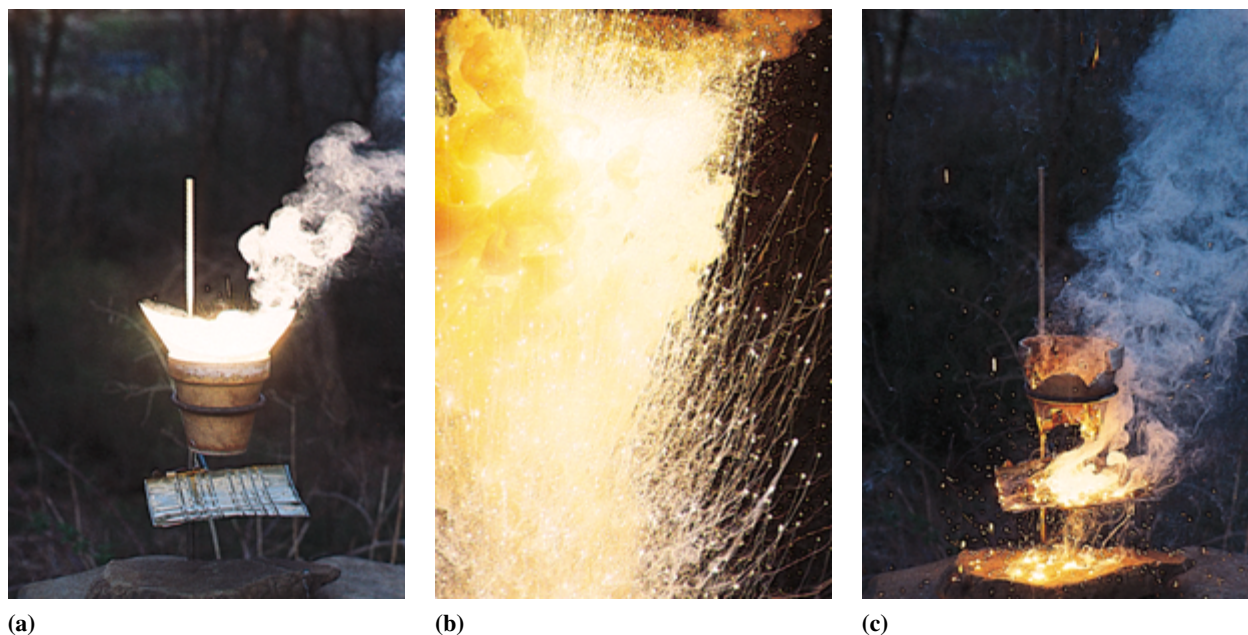
Figure 23-1 The thermite reaction. A mixture of Fe_2O_3 and aluminum powder was placed in a clay pot with a piece of magnesium ribbon as a fuse. (a) The reaction was initiated by lighting the magnesium fuse. (b) So much heat was produced by the reaction that the iron melted as it was produced. (c) The molten iron dropped out of the clay pot and burned through a sheet of iron that was placed under the pot.

The very negative enthalpy of formation of aluminum oxide makes Al a very strong reducing agent for other metal oxides. The **thermite reaction** is a spectacular example (Figure 23-1). It generates enough heat to produce molten iron for welding steel.

$$2Al(s) + Fe_2O_3(s) \longrightarrow 2Fe(s) + Al_2O_3(s) \qquad \Delta H^0 = -852 \text{ kJ/mol}$$

Anhydrous Al_2O_3 occurs naturally as the extremely hard, high-melting mineral *corundum*, which has a network structure. It is colorless when pure, but becomes colored when transition metal ions replace a few Al^{3+} ions in the crystal. *Sapphire* is usually blue and contains some iron and titanium. *Ruby* is red due to the presence of small amounts of chromium.

Small amounts of different transition metal ions give different colors to sapphire, which is mostly aluminum oxide, Al_2O_3.

Other Group IIIA Metals

Gallium is unusual in that it melts when held in the hand. It has the largest liquid state temperature range of any element (29.8° to 2403°C). It is used in transistors and high-temperature thermometers. Gallium-67 was one of the first artificially produced isotopes to be used in medicine. It concentrates in inflamed areas and in certain melanomas.

Indium is a soft, bluish metal that is used in some alloys with silver and lead to make good heat conductors. Most indium is used in electronics. Thallium is a soft, heavy metal that resembles lead. It is quite toxic and has no important practical uses as a free metal.

Gallium metal melts below body temperature. ▶

CHEMISTRY IN USE   *The Development of Science*

The Most Valuable Metal in the World

Imagine paying $8 million for one pound of aluminum! Although aluminum currently costs less than $1.00 a pound, it was considered the most valuable metal in 1827. Aluminum was so cherished by royalty in the early to mid-1800s that they alone ate with aluminum spoons and forks while their lower-class guests dined with cheaper gold and silver service. Aluminum is the most abundant metal in the earth's crust (7.5%); why was it originally so expensive?

Aluminum was first prepared by the following displacement reaction.

$$AlCl_3 + 3K \longrightarrow Al + 3KCl$$

Potassium was also expensive because it was made by passing an electric current (from a voltaic cell) through molten KCl. In addition to the great cost of energy required to melt large quantities of KCl, copper and zinc (used in voltaic cells) were also expensive metals in the early 1800s. Thus, the very small amount of aluminum produced by this displacement reaction was extremely expensive.

It was not practical to produce aluminum by passing an electric current through molten Al_2O_3 because it has a high melting point, 2000°C. This high temperature is difficult to achieve and maintain; the components of most voltaic cells melt below this temperature. Zinc melts at 420°C and copper at 1083°C.

The cost of aluminum began to drop as the result of two major advances in the late 1800s. The first came with the invention of the electric generator, which could produce electricity using steam or water. Electricity generated by steam or water was quite inexpensive compared with electricity generated by voltaic cells. Despite this cost reduction, aluminum still cost more than $100,000 a pound. The second advance

took place in 1886, when chemists discovered that they could lower the melting point of aluminum oxide by mixing it with complex salts, such as $Na_3[AlF_6]$. Since 1886, the price of aluminum has decreased markedly because of lower electricity costs, improved production techniques, and recycling of discarded aluminum products.

Although aluminum is no longer used in table services by royalty, it is of inestimable value in energy conservation. Around our homes we find energy-saving items such as aluminum storm doors and windows, insulation backed with aluminum foil, and aluminum siding. Because vehicle weight significantly affects gas mileage, substituting aluminum for heavier metals in cars, trucks, trains, and aircraft helps preserve our petroleum supplies. Although the cost of aluminum has decreased drastically, it is still a valuable metal because of its ability to help us conserve energy and to improve our standard of living at the same time.

Ronald DeLorenzo
Middle Georgia College

Periodic Trends

The atomic radii do not increase regularly as Group IIIA is descended (Table 6-1). The atomic radius of Ga, 1.35 Å, is *less* than that of Al, 1.43 Å, which is directly above Ga. The transition elements are located between calcium (IIA) and gallium (IIIA), strontium (IIA) and indium (IIIA), and barium (IIA) and thallium (IIIA). The increase in nuclear charge that accompanies filling of the $(n - 1)d$ subshell results in the contraction of the size of the atoms. This contraction is caused by the stronger attraction of the more highly charged nuclei for the outer electrons. This causes the radii of Ga, In, and Tl to be smaller

than would be predicted from the radii of B and Al. Atomic radii strongly influence other properties. For example, Ga, In, and Tl are each much denser than the elements above them due to their unusually small atomic radii.

The Group IIIA elements have the ns^2np^1 outer electron configuration. Aluminum shows only the +3 oxidation state in its compounds. The heavier metals (Ga, In, Tl) can lose or share either the single p valence electron or the p and both s electrons to exhibit the +1 or +3 oxidation state, respectively. In general the post-transition metals can exhibit oxidation states of $(g - 2)+$ and $g+$, where g = periodic group number. As examples, TlCl and TlCl$_3$ both exist, as do SnCl$_2$ and SnCl$_4$. The stability of the lower state increases as the groups are descended. This is called the **inert *s*-pair effect** because the two s electrons remain nonionized, or unshared, for the $(g - 2)+$ oxidation state. To illustrate, AlCl$_3$ exists but not AlCl; TlCl$_3$ is less stable than TlCl.

Compare the radii and densities of these elements with those of Group IA and IIA metals in the same rows.

As is generally true, for each pair of compounds, covalent character is greater for the higher (more polarizing) oxidation state of the metal.

THE *d*-TRANSITION METALS

The term "transition elements" denotes elements in the middle of the periodic table. They provide a transition between the "base formers" on the left and the "acid formers" on the right. The term applies to both the *d*- and *f*-transition elements (*d* and *f* atomic orbitals are being filled across this part of the periodic table). All are metals. We commonly use the term "transition metals" to refer to the *d*-transition metals.

Oxides of most nonmetals are acidic, and oxides of most metals are basic (except those having high oxidation states).

IIIB	IVB	VB	VIB	VIIB	VIIIB			IB	IIB
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
Ac	Rf	Db	Sg	Bh	Hs	Mt			

The *d*-transition metals are located between Groups IIA and IIIA in the periodic table. Strictly speaking, a *d*-transition metal must have a partially filled set of *d* orbitals. Zinc, cadmium, and mercury (Group IIB) and their cations have completely filled sets of *d* orbitals, but they are often discussed with *d*-transition metals because their properties are similar. All of the other elements in this region have partially filled sets of *d* orbitals, except the IB elements and palladium, which have completely filled sets. Some of the cations of these latter elements have partially filled sets of *d* orbitals.

Many transition metal ions are highly colored. These flasks contain (*left to right*), aqueous solutions of $Fe(NO_3)_3$, $Co(NO_3)_2$, $Ni(NO_3)_2$, $Cu(NO_3)_2$, and $Zn(NO_3)_2$. Colorless Zn^{2+} ions differ from the others by having completely filled $3d$ orbitals.

In the "building" of electron configurations by the Aufbau Principle, the outer *s* orbitals are occupied before the inner *d* orbitals (Section 5-17).

23-8 GENERAL PROPERTIES

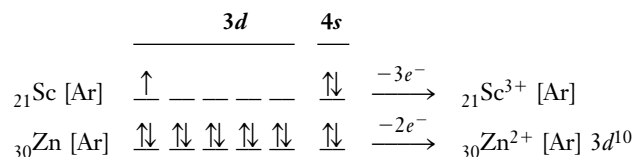The following are general properties of transition elements.

1. All are metals.
2. Most are harder and more brittle and have higher melting points, boiling points, and heats of vaporization than nontransition metals.
3. Their ions and their compounds are usually colored.
4. They form many complex ions (Chapter 25).
5. With few exceptions, they exhibit multiple oxidation states.
6. Many of them are paramagnetic, as are many of their compounds.
7. Many of the metals and their compounds are effective catalysts.

Some properties of $3d$-transition metals are listed in Table 23-6.

23-9 OXIDATION STATES

Most transition metals exhibit more than one nonzero oxidation state. The *maximum* oxidation state is given by a metal's group number, but this is often not its most stable oxidation state (Table 23-7).

The outer *s* electrons lie outside the *d* electrons and are *always* the first ones lost in ionization. In the first transition series, scandium and zinc exhibit just one nonzero oxidation state. Scandium loses its two $4s$ electrons and its only $3d$ electron to form Sc^{3+}. Zinc loses its two $4s$ electrons to form Zn^{2+}.

	$3d$	$4s$		
$_{21}Sc$ [Ar]	↑ _ _ _ _	↑↓	$\xrightarrow{-3e^-}$	$_{21}Sc^{3+}$ [Ar]
$_{30}Zn$ [Ar]	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑↓	$\xrightarrow{-2e^-}$	$_{30}Zn^{2+}$ [Ar] $3d^{10}$

TABLE 23-6 *Properties of Metals in the First Transition Series*

Properties	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Melting point (°C)	1541	1660	1890	1850	1244	1535	1495	1453	1083	420
Boiling point (°C)	2831	3287	3380	2672	1962	2750	2870	2732	2567	907
Density (g/cm³)	2.99	4.54	6.11	7.18	7.21	7.87	8.9	8.91	8.96	7.13
Atomic radius (Å)	1.62	1.47	1.34	1.25	1.29	1.26	1.25	1.24	1.28	1.34
Ionic radius, M^{2+} (Å)	—	0.94	0.88	0.89	0.80	0.74	0.72	0.69	0.70	0.74
Electronegativity	1.3	1.4	1.5	1.6	1.6	1.7	1.8	1.8	1.8	1.6
E^0 (V) for $M^{2+}(aq) + 2e^- \longrightarrow M(s)$	−2.08*	−1.63	−1.2	−0.91	−1.18	−0.44	−0.28	−0.25	+0.34	−0.76
IE (kJ/mol) first	631	658	650	652	717	759	758	757	745	906
second	1235	1310	1414	1592	1509	1561	1646	1753	1958	1733

*For $Sc^{3+}(aq) + 3e^- \rightarrow Sc(s)$.

TABLE 23-7	*Nonzero Oxidation States of the 3d-Transition Metals**								
IIIB	IVB	VB	VIB	VIIB	VIIIB			IB	IIB
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
								+1 r	
				+2	+2 r	+2	+2	+2	+2
+3		+3 r	+3		+3	+3 o			
	+4	+4		+4 o					
		+5 o							
			+6 o						
				+7 o					

Abbreviations: o = oxidizing agent; r = reducing agent.

Titanium and nickel also have only a single nonzero oxidation state. All of the other 3*d*-transition metals exhibit at least two oxidation states in their compounds. For example, cobalt can form Co^{2+} and Co^{3+} ions.

$$_{27}Co\;[Ar]\quad \underline{\uparrow\downarrow}\;\underline{\uparrow\downarrow}\;\underline{\uparrow}\;\underline{\uparrow}\;\underline{\uparrow}\quad \underline{\uparrow\downarrow}\quad \xrightarrow{-2e^-}\quad _{27}Co^{2+}\;[Ar]\quad \underline{\uparrow\downarrow}\;\underline{\uparrow\downarrow}\;\underline{\uparrow}\;\underline{\uparrow}\;\underline{\uparrow}\quad \underline{}$$

$$_{27}Co\;[Ar]\quad \underline{\uparrow\downarrow}\;\underline{\uparrow\downarrow}\;\underline{\uparrow}\;\underline{\uparrow}\;\underline{\uparrow}\quad \underline{\uparrow\downarrow}\quad \xrightarrow{-3e^-}\quad _{27}Co^{3+}\;[Ar]\quad \underline{\uparrow\downarrow}\;\underline{\uparrow}\;\underline{\uparrow}\;\underline{\uparrow}\;\underline{\uparrow}\quad \underline{}$$
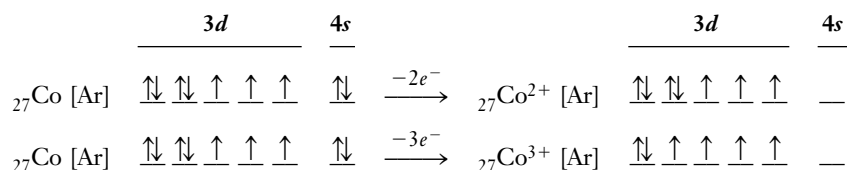
The most common oxidation states of the 3*d*-transition elements are +2 and +3. The elements in the middle of each series exhibit more oxidation states than those to the left or right. As one moves down a group, higher oxidation states become more stable and more common (opposite to the trend for representative elements). This is because the *d* electrons are more effectively shielded from the nucleus as the group is descended and are therefore more easily lost or more readily available for sharing. For example, cobalt commonly exhibits the +2 and +3 oxidation states. Rh and Ir are just below Co. Their common oxidation states are +3 and +4. The +4 state is slightly more stable for Ir than for the lighter Rh.
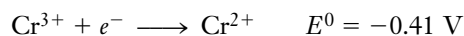
The oxides and hydroxides of lower oxidation states of a given transition metal are basic. Those containing intermediate oxidation states tend to be amphoteric, and those containing high oxidation states tend to be acidic. This is illustrated for the oxides and hydroxides of Cr in the next section.

Pentaamminechlorocobalt(III) chloride, [Co(NH₃)₅(Cl)]Cl₂, is a compound that contains cobalt in the +3 oxidation state (*left*). Hexaaquacobalt(II) chloride, [Co(OH₂)₆]Cl₂, contains cobalt in the +2 oxidation state (*right*).

23-10 CHROMIUM OXIDES, OXYANIONS, AND HYDROXIDES

Typical of the metals near the middle of a transition series, chromium shows several oxidation states. The most common are +2, +3, and +6 (Table 23-8).

Oxidation–Reduction

The most stable oxidation state of Cr is +3. Solutions of blue chromium(II) salts are easily air-oxidized to chromium(III).
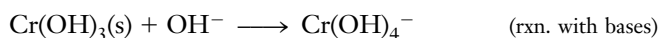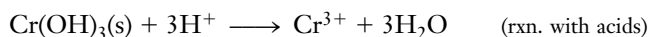
$$Cr^{3+} + e^- \longrightarrow Cr^{2+} \qquad E^0 = -0.41\ V$$

Aqueous solutions of some compounds that contain chromium. (*Left to right*) Chromium(II) chloride (CrCl₂) is blue; chromium(III) chloride (CrCl₃) is green; potassium chromate (K₂CrO₄) is yellow; potassium dichromate (K₂Cr₂O₇) is orange.

TABLE 23-8 *Some Compounds of Chromium*

Ox. State	Oxide	Hydroxide	Name	Acidic/Basic	Related Salt	Name
+2	CrO black	$Cr(OH)_2$	chromium(II) hydroxide	basic	$CrCl_2$ anhydr. colorless aq. lt. blue	chromium(II) chloride
+3	Cr_2O_3 green	$Cr(OH)_3$	chromium(III) hydroxide	amphoteric	$CrCl_3$ anhydr. violet aq. green $KCrO_2$ green	chromium(II) chloride potassium chromite
+6	CrO_3 dk. red	H_2CrO_4 or $[CrO_2(OH)_2]$ $H_2Cr_2O_7$ or $[Cr_2O_5(OH)_2]$	chromic acid dichromic acid	weakly acidic acidic	K_2CrO_4 yellow $K_2Cr_2O_7$ orange	potassium chromate potassium dichromate

Chromium(VI) species are oxidizing agents. Basic solutions containing chromate ions, CrO_4^{2-}, are weakly oxidizing. Acidification produces the dichromate ion, $Cr_2O_7^{2-}$, and chromium(VI) oxide, both powerful oxidizing agents.

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O \qquad E^0 = +1.33 \text{ V}$$

Chromate–Dichromate Equilibrium

Red chromium(VI) oxide, CrO_3, is the acid anhydride of two acids: chromic acid, H_2CrO_4, and dichromic acid, $H_2Cr_2O_7$. Neither acid has been isolated in pure form, although chromate and dichromate salts are common. CrO_3 reacts with H_2O to produce strongly acidic solutions containing hydrogen ions and (predominantly) dichromate ions.

$$2CrO_3 + H_2O \longrightarrow [2H^+ + Cr_2O_7^{2-}] \qquad \text{dichromic acid (red-orange)}$$

From such solutions orange dichromate salts can be crystallized after adding a stoichiometric amount of base. Addition of excess base produces yellow solutions from which only yellow chromate salts can be obtained. The two anions exist in solution in a pH-dependent equilibrium.

$$\underset{\text{yellow}}{2\overset{+6}{Cr}O_4^{2-} + 2H^+} \rightleftharpoons \underset{\text{orange}}{\overset{+6}{Cr_2}O_7^{2-} + H_2O} \qquad K_c = \frac{[Cr_2O_7^{2-}]}{[CrO_4^{2-}]^2[H^+]^2} = 4.2 \times 10^{14}$$

Adding a strong acid to a solution that contains $CrO_4^{2-}/Cr_2O_7^{2-}$ ions favors the reaction to the right and increases $[Cr_2O_7^{2-}]$. Adding a base favors the reaction to the left and increases $[CrO_4^{2-}]$.

chromate ion, $CrO_4{}^{2-}$

dichromate ion, $Cr_2O_7{}^{2-}$

Chromate ion, $CrO_4{}^{2-}$

Dichromate ion, $Cr_2O_7{}^{2-}$

Dehydration of chromate or dichromate salts with concentrated H_2SO_4 produces CrO_3. Chromium(VI) oxide is a strong oxidizing agent. A powerful "cleaning solution" once used for removing greasy stains and coatings from laboratory glassware was made by adding concentrated H_2SO_4 to a concentrated solution of $K_2Cr_2O_7$. The active ingredients are CrO_3, an oxidizing agent, and H_2SO_4, an excellent solvent.

This cleaning solution must be used with great caution because it is a strong oxidizing agent and is carcinogenic.

Chromium(III) hydroxide is amphoteric (Section 10-6).

$$Cr(OH)_3(s) + 3H^+ \longrightarrow Cr^{3+} + 3H_2O \qquad \text{(rxn. with acids)}$$

$$Cr(OH)_3(s) + OH^- \longrightarrow Cr(OH)_4^- \qquad \text{(rxn. with bases)}$$

Key Terms

Alkali metals   Group IA metals.
Alkaline earth metals   Group IIA metals.
d-Transition metals   Metals that have partially filled sets of d orbitals; the B groups of the periodic table.
Diagonal similarities   Chemical similarities of elements of Period 2 to elements of Period 3 one group to the right; especially evident toward the left of the periodic table.

Inert s-pair effect   The tendency of the two outermost s electrons to remain nonionized or unshared in compounds; characteristic of the post-transition metals.
Post-transition metals   Representative metals in the "p block."
Representative metals   Metals in the A groups in the periodic table; their outermost electrons are in s and p orbitals.

Exercises

1. How do the acidities or basicities of metal oxides vary with oxidation numbers of the same metal?
2. Discuss the general differences in electron configurations of representative elements and d-transition metals.
3. Compare the extents to which the properties of successive elements across the periodic table differ for representative elements and d-transition metals. Explain.
4. Compare the metals and nonmetals with respect to (a) number of outer-shell electrons, (b) electronegativities, (c) standard reduction potentials, and (d) ionization energies.
5. How do the physical properties of metals differ from those of nonmetals?
6. Define "malleable" and "ductile."
7. (a) What is the meaning of the statement, "alkali metals are corrosive?" (b) Are alkali metal ions corrosive? (c) Are alkali metal ions an important part of your diet?
8. Compare the alkali metals with the alkaline earth metals with respect to (a) atomic radii, (b) densities, (c) first ionization energies, and (d) second ionization energies. Explain the comparisons.
9. Summarize the chemical and physical properties of: (a) the alkali metals and (b) the alkaline earth metals.
10. (a) Compare and contrast the physical and chemical properties of the Group IA metals with those of the Group IIA metals. (b) Compare the periodic trends of the two groups.
11. Write the general outer-electron configurations for atoms of the IA and IIA metals. What oxidation state(s) would you predict for these elements? What types of bonding would you expect in most of the compounds of these elements? Why?
12. Write electron configurations ($\uparrow\downarrow$ notation) for (a) Mg, (b) Mg^{2+}, (c) Na, (d) Na^+, (e) Sn, (f) Sn^{2+}, and (g) Sn^{4+}.
13. Write electron configurations ($\uparrow\downarrow$ notation) for (a) K, (b) K^+, (c) Sr, (d) Sr^{2+}, (e) Al, (f) Al^{3+}, and (g) Ga^{3+}.
14. Are the elements in Groups IA and IIA found in the free state in nature? What are the primary sources for these elements?
15. Describe some uses for (a) lithium and its compounds and (b) sodium and its compounds.
16. Where do the metals of Groups IA and IIA fall with respect to H_2 in the activity series? What does this tell us about their reactivities with water and acids?
17. Write chemical equations describing the reactions of O_2 with each of the alkali and alkaline earth metals. Account for differences within each family.
18. Describe some uses for (a) calcium and its compounds and (b) magnesium and its compounds.
19. Write general equations for reactions of alkali metals with (a) hydrogen, (b) sulfur, and (c) ammonia. Represent the metal as M.
20. Write general equations for reactions of alkali metals with (a) water, (b) phosphorus, and (c) halogens. Represent the metal as M and the halogen as X.

21. Write general equations for reactions of alkaline earth metals with (a) hydrogen, (b) sulfur, and (c) ammonia. Represent the metal as M.
22. Write general equations for reactions of alkaline earth metals with (a) water, (b) phosphorus, and (c) chlorine. Represent the metal as M.
23. What is meant by the term "diagonal relationships"?
24. Give some illustrations of diagonal relationships in the periodic table, and explain each.
25. What is hydration energy? How does it vary for cations of the alkali metals?
26. How do hydration energies vary for cations of the alkaline earth metals?
27. How do the standard reduction potentials of the alkali metal cations vary? Why?
28. How do the standard reduction potentials of the alkaline earth metal cations vary? Why?
29. Why are the standard reduction potentials of lithium and beryllium out of line with respect to group trends?
*30. Calculate ΔH^0 values at 25°C for the reactions of 1 mol of each of the following metals with stoichiometric quantities of water to form metal hydroxides and hydrogen. (a) Li, (b) K, and (c) Ca. Rationalize the differences in these values.
31. How are the d-transition metals distinguished from other elements?
32. What are the general properties of the d-transition metals?
33. Why are trends in variations of properties of successive d-transition metals less regular than trends among successive representative elements?
34. Write out the electron configurations for the following species: (a) V; (b) Fe; (c) Cu; (d) Zn^{2+}; (e) Cr^{3+}; (f) Ni^{2+}; (g) Ag; (h) Ag^+.
35. Why do copper and chromium atoms have "unexpected" electron configurations?
36. Discuss the similarities and differences among elements of corresponding A and B groups of the periodic table, IIIA and IIIB for example.
37. Copper exists in the +1, +2, and +3 oxidation states. Which is the most stable? Which would be expected to be a strong oxidizing agent and which would be expected to be a strong reducing agent?
38. For a given transition metal in different oxidation states, how does the acidic character of its oxides increase? How do ionic and covalent character vary? Characterize a series of metal oxides as examples.
39. For different transition metals in the same oxidation state in the same group (vertical column) of the periodic table, how do covalent character and acidic character of their oxides vary? Why? Cite evidence for the trends.
40. Chromium(VI) oxide is the acid anhydride of which two acids? Write their formulas. What is the oxidation state of the chromium in these acids?

CONCEPTUAL EXERCISES

41. Some of the oxides of the transition metals are amphoteric. (a) What is meant by the term "amphoteric?" (b) Identify five oxides that are amphoteric, five oxides that are basic, and five oxides that are acidic.
42. Calcium carbonate is a very common compound on this planet. Name five common items that are composed primarily of calcium carbonate.
43. Magnesium and some of the magnesium alloys will burn if heated to a high enough temperature. Some magnesium alloys are used in construction and may have to be welded at a high temperature. Suggest techniques or requirements for welding these alloys so that they do not ignite.
44. Some mental disorders are treated with medications that contain lithium salts. Why is pure lithium unsuitable for such purposes?

Pure lithium.

45. Gallium thermometers are high-temperature thermometers. (a) Why can't they be used near room temperature? (b) Propose a reason why mercury thermometers cannot be used to measure temperatures in the upper range of gallium thermometers.

BUILDING YOUR KNOWLEDGE

*46. How many grams of Co_3O_4 (a mixed oxide, $CoO \cdot Co_2O_3$) must react with excess aluminum to produce 190. g of metallic cobalt, assuming 72.5% yield?

$$3Co_3O_4 + 8Al \xrightarrow{\text{heat}} 9Co + 4Al_2O_3$$

*47. Calculate ΔH^0, ΔS^0, and ΔG^0 for the reaction of 1 mol of Na with water to form aqueous NaOH and hydrogen.
*48. Calculate ΔH^0, ΔS^0, and ΔG^0 for the reaction of 1 mol of Rb with water to form aqueous RbOH and hydrogen. Compare the spontaneity of this reaction with that in Exercise 47.
*49. What is the ratio of $[Cr_2O_7^{2-}]$ to $[CrO_4^{2-}]$ at 25°C in a solution prepared by dissolving 1.5×10^{-3} mol of sodium chromate, Na_2CrO_4, in enough of an aqueous solution buffered at pH = 2.00 to produce 250. mL of solution?