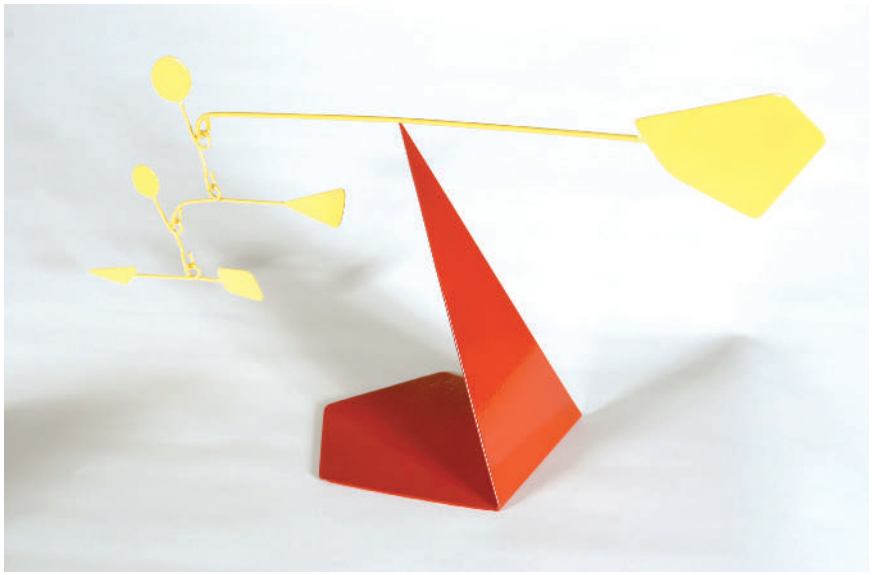
20 Chemistry of the Metals

The stabile *Equilibrium* is made up of metals. These were refined from ores using some of the processes discussed in this chapter.



Bruce Gray

The fields of Nature long
prepared and fallow—
the silent cyclic chemistry;
The slow and steady ages
plodding—the
unoccupied surface
ripening—the rich ores
forming beneath;

—WALT WHITMAN
Song of the Redwood Tree

Chapter Outline

As you can see from the periodic table on the inside cover or opening pages of this text, the overwhelming majority of elements, about 88%, are metals (shown in blue). In discussing the descriptive chemistry of the metals, we concentrate on

- the *main-group metals in Groups 1 and 2* at the far left of the periodic table. These are commonly referred to as the *alkali metals* (Group 1) and *alkaline earth metals* (Group 2). The group names reflect the strongly basic nature of the oxides (K_2O, CaO, . . .) and hydroxides (KOH, $Ca(OH)_2$, . . .) of these elements.
- *the transition metals,* located in the center of the periodic table. There are three series of transition metals, each consisting of ten elements, located in the fourth, fifth, and sixth periods. We focus on a few of the more important transition metals (Figure 20.1), particularly those toward the right of the first series.

Section 20-1 deals with the processes by which these metals are obtained from their principal ores. Section 20-2 describes the reactions of the alkali and alkaline earth metals, particularly those with hydrogen, oxygen, and water. Section 20-3 considers the redox chemistry of the transition metals, their cations (e.g., Fe^{2+}, Fe^{3+}), and their oxoanions (e.g., CrO_4^{2-}).

20-1 Metallurgy

The processes by which metals are extracted from their **ores** fall within the science of **metallurgy.** As you might expect, the chemical reactions involved depend on the type of ore (Figure 20.2). We consider some typical processes used to obtain metals from chloride, oxide, sulfide, or "native" ores.

An ore is a natural source from which a metal can be extracted profitably.

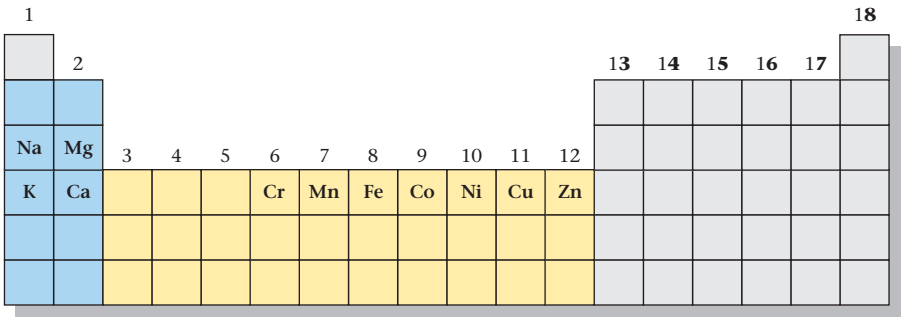


Figure 20.1 Metals and the periodic table. The periodic table groups discussed in this chapter are Groups 1 and 2, the alkali and alkaline earth metals (shaded in blue), and the transition metals (shaded in yellow). Symbols are shown for the more common metals.

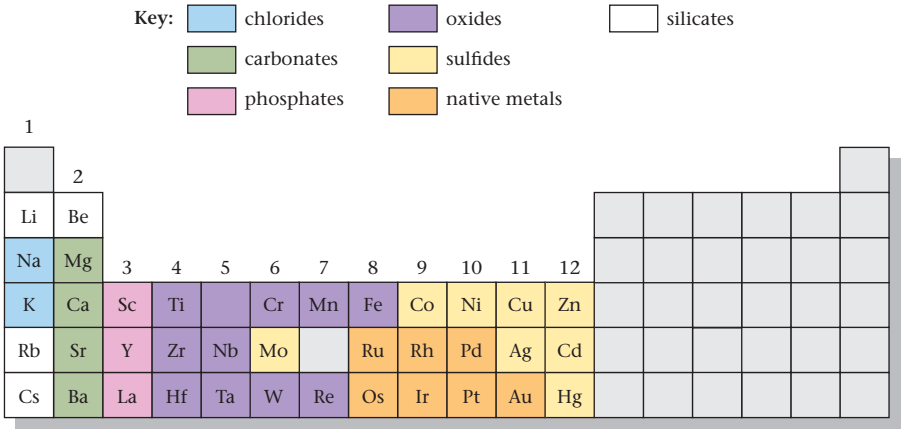


Figure 20.2 Principal ores of the Group 1, Group 2, and transition metals.

Chloride Ores: Na from NaCl

Sodium metal is obtained by the electrolysis of molten sodium chloride (Figure 20.3). The electrode reactions are quite simple:

$$\text{cathode:} \quad 2Na^+(l) + 2e^- \longrightarrow 2Na(l)$$

$$\text{anode:} \quad 2Cl^-(l) \longrightarrow Cl_2(g) + 2e^-$$

$$2NaCl(l) \longrightarrow 2Na(l) + Cl_2(g)$$

$Na^+(l)$ and $Cl^-(l)$ are the ions present in molten NaCl.

The cell is operated at about 600°C to keep the electrolyte molten; calcium chloride is added to lower the melting point. About 14 kJ of electrical energy is required to produce one gram of sodium, which is drawn off as a liquid (mp of Na = 98°C). The chlorine gas produced at the anode is a valuable byproduct.

It's cheaper to electrolyze NaCl(*aq*), but you don't get sodium metal that way.

EXAMPLE 20.1

Consider the electrolysis of NaCl(*l*) at 600°C:

$$2NaCl(l) \longrightarrow 2Na(l) + Cl_2(g)$$

where $\Delta H° = 820$ kJ and $\Delta S° = 0.180$ kJ/K.

a What is $\Delta G°$ at the electrolysis temperature?

ANALYSIS

Information given:	equation for the reaction ($2NaCl(l) \longrightarrow 2Na(l) + Cl_2(g)$) $\Delta H°$(820 kJ); $\Delta S°$(0.180 kJ/K) T(600°C = 873 K)
Asked for:	$\Delta G°$ at 600°C

continued

STRATEGY

Substitute into the Gibbs-Helmholtz equation (Chapter 16):

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

SOLUTION

ΔG°	$\Delta G^\circ = 820\ \text{kJ} - [873\ \text{K}(0.180\ \text{kJ/K})] = 663\ \text{kJ}$

b What is the voltage required to carry out the electrolysis?

ANALYSIS

Information given:	from part (a) $\Delta G^\circ = 663$ kJ
Information implied:	Faraday constant, $F(9.648 \times 10^4\ \text{J/mol} \cdot \text{V})$
Asked for:	voltage required (E°)

STRATEGY AND SOLUTION

Substitute into the equation relating E° and ΔG° (Chapter 17):

E°

$$E^\circ = \frac{-\Delta G^\circ}{\text{nF}} = \frac{-663 \times 10^3\ \text{J}}{(2\ \text{mol})(9.648 \times 10^4\ \text{J/mol} \cdot \text{V})} = -3.44\ \text{V}$$

At least 3.44 V must be applied to carry out the electrolysis.

END POINT

Notice that the value of ΔG° calculated in part (a), 663 kJ, is for two moles of Na (2 mol × 22.99 g/mol = 45.98 g). The value of the free energy change per gram is

663 kJ/45.98 g Na = 14.4 kJ/g Na

This is consistent with the statement in the text that "about 14 kJ of electrical energy is required to produce one gram of sodium. . . ."

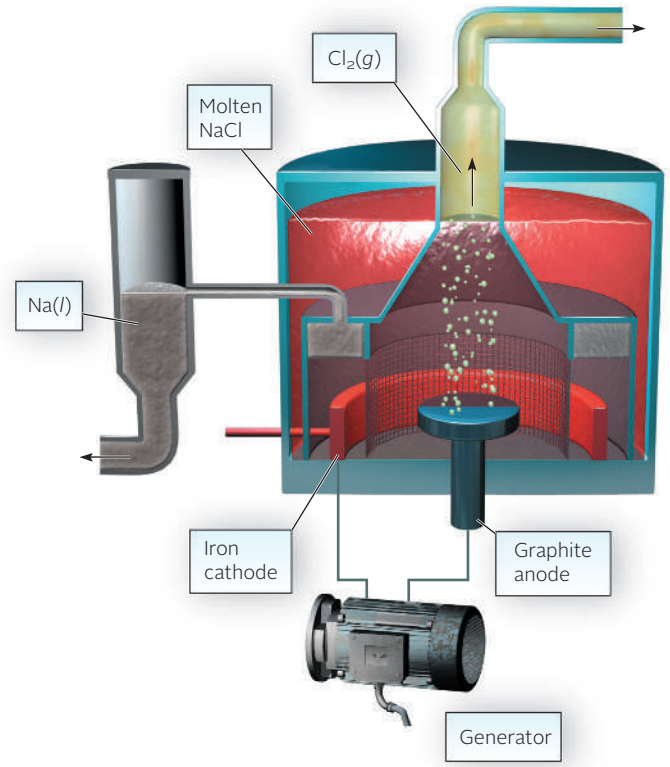


Figure 20.3 Electrolysis of molten sodium chloride. Calcium chloride ($CaCl_2$) is added to lower the melting point. The iron screen prevents sodium and chlorine from coming into contact with each other.

Oxide Ores: Al from Al_2O_3, Fe from Fe_2O_3

Oxides of very reactive metals such as calcium or aluminum are reduced by electrolysis. In the case of aluminum, bauxite ore, Al_2O_3, is used.

$$2Al_2O_3(l) \longrightarrow 4Al(l) + 3O_2(g)$$

Cryolite, Na_3AlF_6, is added to Al_2O_3 to produce a mixture melting at about 1000°C. (A mixture of AlF_3, NaF, and CaF_2 may be substituted for cryolite.) The cell is heated electrically to keep the mixture molten so that ions can move through it, carrying the electric current. About 30 kJ of electrical energy is consumed per gram of aluminum formed. The high energy requirement explains in large part the value of recycling aluminum cans.

The process for obtaining aluminum from bauxite was worked out in 1886 by Charles Hall (1863–1914), just after he graduated from Oberlin College. The problem that Hall faced was to find a way to electrolyze Al_2O_3 at a temperature below its melting point of 2000°C. His general approach was to look for ionic compounds in which Al_2O_3 would dissolve at a reasonable temperature. After several unsuccessful attempts, Hall found that cryolite was the ideal "solvent." Curiously enough, the same electrolytic process was worked out by Paul Héroult (1863–1914) in France, also in 1886.

Chemistry majors can be very productive.

With less active metals, a chemical reducing agent can be used to reduce a metal cation to the element. The most common reducing agent in metallurgical processes is carbon, in the form of coke or, more exactly, carbon monoxide formed from the coke.

The most important metallurgical process involving carbon is the reduction of hematite ore, which consists largely of iron(III) oxide, Fe_2O_3, mixed with silicon dioxide, SiO_2. Reduction occurs in a blast furnace (Figure 20.4a) typically 30 m high and 10 m in diameter. The furnace is lined with refractory brick, capable of withstanding temperatures that may go as high as 1800°C. The solid charge, admitted at the top of the furnace, consists of iron ore, coke, and limestone ($CaCO_3$). To get the process started, a blast of compressed air or pure O_2 at 500°C is blown into the furnace through nozzles near the bottom. Several different reactions occur, of which three are most important:

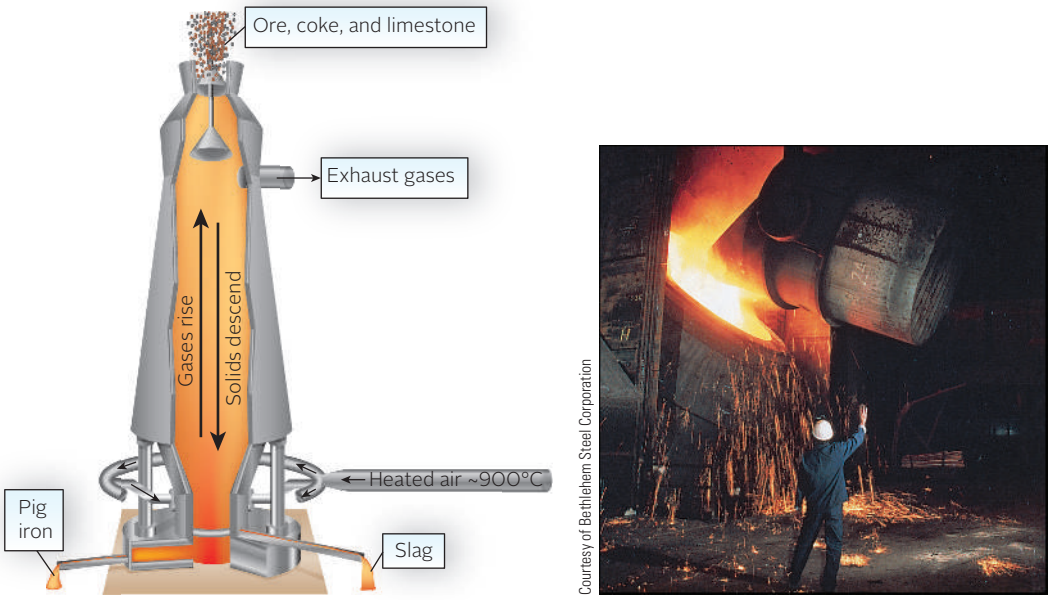


Figure 20.4 Iron and steel production. (a) A blast furnace for the production of pig iron. (b) A basic oxygen furnace, where the carbon content of pig iron is lowered by heating it with oxygen to form steel.

1. *Conversion of carbon to carbon monoxide.* In the lower part of the furnace, coke burns to form carbon dioxide, CO_2. As the CO_2 rises through the solid mixture, it reacts further with the coke to form carbon monoxide, CO. The overall reaction is

$$2C(s) + O_2(g) \longrightarrow 2CO(g) \qquad \Delta H = -221 \text{ kJ}$$

The heat given off by this reaction maintains a high temperature within the furnace.

This is the key reaction; it produces molten iron.

2. *Reduction of Fe^{3+} ions to Fe.* The carbon monoxide reacts with the iron(III) oxide in the ore:

$$Fe_2O_3(s) + 3CO(g) \longrightarrow 2Fe(l) + 3CO_2(g)$$

Molten iron, formed at a temperature of 1600°C, collects at the bottom of the furnace. Four or five times a day, it is drawn off. The daily production of iron from a single blast furnace is about 1500 metric tons.

3. *Formation of slag.* The limestone added to the furnace decomposes at about 800°C:

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$$

The calcium oxide formed reacts with impurities in the iron ore to form a glassy material called *slag*. The main reaction is with SiO_2 to form calcium silicate, $CaSiO_3$:

$$CaO(s) + SiO_2(s) \longrightarrow CaSiO_3(l)$$

The slag, which is less dense than molten iron, forms a layer on the surface of the metal. This makes it possible to draw off the slag through an opening in the furnace above that is used to remove the iron. The slag is used to make cement and as a base in road construction.

The product that comes out of the blast furnace, called "pig iron," is highly impure. On the average, it contains about 4% carbon along with lesser amounts of silicon, manganese, and phosphorus. To make steel from pig iron, the carbon content must be lowered below 2%. Most of the steel produced in the world today is made by the basic oxygen process (Figure 20.4b). The "converter" is filled with a mixture of about 70% molten iron from the blast furnace, 25% scrap iron or steel, and 5% limestone. Pure oxygen under a pressure of about 10 atm is blown through the molten metal. The reaction

$$C(s) + O_2(g) \longrightarrow CO_2(g)$$

occurs rapidly; at the same time, impurities such as silicon are converted to oxides, which react with limestone to form a slag. When the carbon content drops to the desired level, the supply of oxygen is cut off. At this stage, the steel is ready to be poured. The whole process takes from 30 min to 1 h and yields about 200 metric tons of steel in a single "blow."

EXAMPLE 20.2

Write balanced equations for the reduction of each of the following oxide ores by carbon monoxide:

ZnO, MnO_2, and Fe_3O_4 ($FeO \cdot Fe_2O_3$)

STRATEGY

The metal oxides are reduced to metal and CO is oxidized to CO_2.

SOLUTION

ZnO	$ZnO(s) + CO(g) \longrightarrow Zn(s) + CO_2(g)$
MnO_2	$MnO_2(s) + 2CO(g) \longrightarrow Mn(s) + 2CO_2(g)$
Fe_3O_4	$Fe_3O_4(s) + 4CO(g) \longrightarrow 3Fe(s) + 4CO_2(g)$

Sulfide Ores: Cu from Cu_2S

Sulfide ores, after preliminary treatment, most often undergo **roasting**, that is, heating with air or pure oxygen. With a relatively reactive transition metal such as zinc, the product is the oxide

Because Cu can be produced by simple "roasting," it was one of the first metals known.

$$2ZnS(s) + 3O_2(g) \longrightarrow 2ZnO(s) + 2SO_2(g)$$

which can then be reduced to the metal with carbon. With sulfides of less reactive metals such as copper or mercury, the free metal is formed directly on roasting. The reaction with cinnabar, the sulfide ore of mercury, is

$$HgS(s) + O_2(g) \longrightarrow Hg(g) + SO_2(g)$$

Among the several ores of copper, one of the most important is chalcocite, which contains copper(I) sulfide, Cu_2S, in highly impure form. Rocky material typically lowers the fraction of copper in the ore to 1% or less. The Cu_2S is concentrated by a process called *flotation* (Figure 20.5), which raises the fraction of copper to 20%–40%. The concentrated ore is then converted to the metal by blowing air through it at a high temperature, typically above 1000°C. (Pure O_2 is often used instead of air.) The overall reaction that occurs is a simple one:

$$Cu_2S(s) + O_2(g) \longrightarrow 2Cu(s) + SO_2(g)$$

The solid produced is called "blister copper." It has an irregular appearance due to air bubbles that enter the copper while it is still molten. Blister copper is impure, containing small amounts of several other metals.

Copper is purified by electrolysis. The anode, which may weigh as much as 300 kg, is made of blister copper. The electrolyte is 0.5 to 1.0 *M* $CuSO_4$, adjusted to a pH of about 0 with sulfuric acid. The cathode is a piece of pure copper, weighing perhaps 150 kg. The half-reactions are

$$\text{oxidation:} \quad Cu(s, \text{impure}) \longrightarrow Cu^{2+}(aq) + 2e^-$$
$$\text{reduction:} \quad Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s, \text{pure})$$

The overall reaction, obtained by adding these two half-reactions, is

$$Cu(s, \text{impure}) \longrightarrow Cu(s, \text{pure})$$

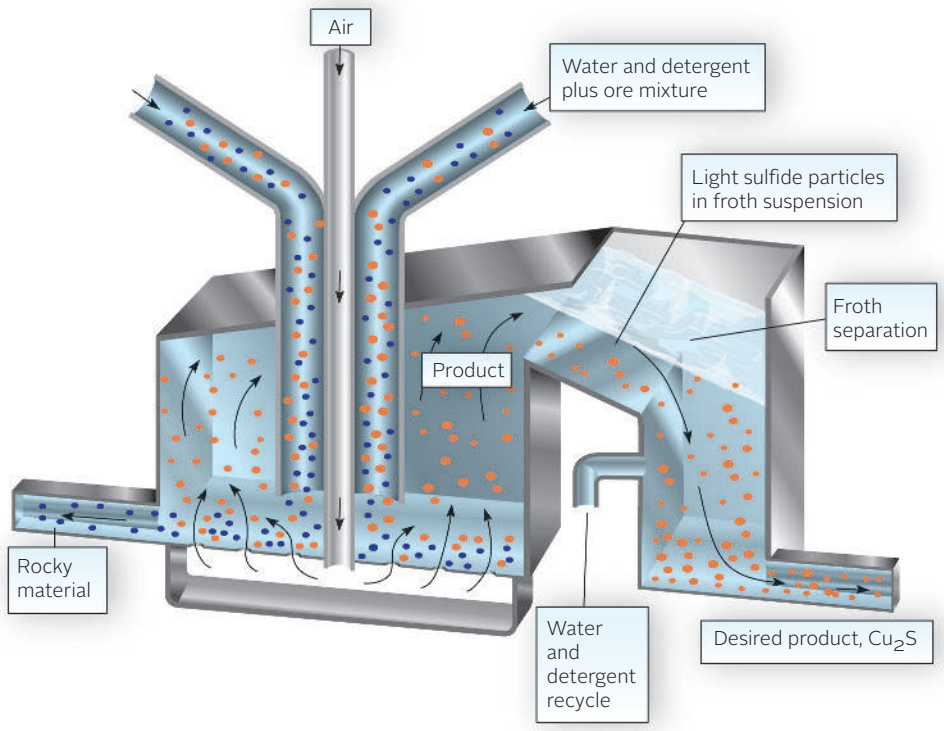


Figure 20.5 Flotation process for concentrating a sulfide ore. Low-grade sulfide ores, including Cu_2S, are often concentrated by flotation. The finely divided sulfide particles are trapped in soap bubbles; the rocky waste sinks to the bottom and is discarded.

Thus the net effect of electrolysis is to transfer copper metal from the impure blister copper used as one electrode to the pure copper sheet used as the other electrode. Electrolytic copper is 99.95% pure.

EXAMPLE 20.3

A major ore of bismuth is bismuth(III) sulfide, Bi_2S_3. By roasting in air, it is converted to the corresponding oxide; sulfur dioxide is a byproduct. What volume of SO_2, at 25°C and 1.00 atm, is formed from one metric ton (10^6 g) of ore containing 1.25% Bi_2S_3?

ANALYSIS

Information given:	T(25°C); P(1.00 atm) mass of the ore (1 metric ton = 1×10^6 g) % Bi_2S_3 in ore (1.25%)
Information implied:	R value in L · atm/mol · K molar mass of Bi_2S_3
Asked for:	Volume of SO_2 formed

STRATEGY

1. Write a balanced equation for the reaction. Recall that roasting in air means reacting with oxygen gas.
2. Find the mass of Bi_2S_3 in the ore.
3. Calculate the moles of SO_2 formed.

   mass $Bi_2S_3 \longrightarrow$ mol $Bi_2S_3 \longrightarrow$ mol SO_2
4. Use the ideal gas law to find the volume of SO_2.

SOLUTION

1. Equation: $2Bi_2S_3(s) + 9O_2(g) \longrightarrow 2Bi_2O_3(s) + 6SO_2(g)$
2. Mass of Bi_2S_3: $(1 \times 10^6 \text{ g ore})(1.25 \text{ g } Bi_2S_3/100 \text{ g of ore}) = 1.25 \times 10^4 \text{ g } Bi_2S_3$
3. mol SO_2:
$$1.25 \times 10^4 \text{ g } Bi_2S_3 \times \frac{1 \text{ mol } Bi_2S_3}{514.2 \text{ g}} \times \frac{6 \text{ mol } SO_2}{2 \text{ mol } Bi_2S_3} = 72.9 \text{ mol } SO_2$$
4. Volume SO_2:
$$V = \frac{nRT}{P} = \frac{(72.9 \text{ mol})(298 \text{ K})(0.0821 \text{ L} \cdot \text{atm/mol} \cdot \text{K})}{1.00 \text{ atm}} = 1.78 \times 10^3 \text{ L}$$

END POINT

That volume (1.78×10^3 L) is equal to 1.78 cubic meters. The roasting of sulfide ores is a major source of the gaseous pollutant SO_2, which contributes to acid rain (Chapter 14).

Tiffany & Co.

Figure 20.6 Modern gold jewelry. The gold was probably obtained by the cyanide process.

Native Metals: Au

A few very unreactive metals, notably silver and gold, are found in nature in elemental form, mixed with large amounts of rocky material. For countless centuries, people have extracted gold by taking advantage of its high density (19.3 g/mL). In ancient times, gold-bearing sands were washed over sheepskins, which retained the gold; this is believed to be the source of the "Golden Fleece" of Greek mythology. The forty-niners in California obtained gold by swirling gold-bearing sands with water in a pan. Less dense impurities were washed away, leaving gold nuggets or flakes at the bottom of the pan.

Nowadays, the gold content of ores is much too low for these simple mechanical separation methods to be effective. Instead, the ore is treated with very dilute (0.01 M) sodium cyanide solution (Figure 20.6), through which air is blown. The following redox reaction takes place:

$$4Au(s) + 8CN^-(aq) + O_2(g) + 2H_2O \longrightarrow 4Au(CN)_2^-(aq) + 4OH^-(aq)$$

The oxidizing agent is O_2, which takes gold to the +1 state. The cyanide ion acts as a complexing ligand, forming the stable $Au(CN)_2^-$ ion. Metallic gold is

recovered from solution by adding zinc; the gold in the complex ion is reduced to the metal.

$$Zn(s) + 2Au(CN)_2^-(aq) \longrightarrow Zn(CN)_4^{2-}(aq) + 2Au(s)$$

20-2 Reactions of the Alkali and Alkaline Earth Metals

The metals in Groups 1 and 2 are among the most reactive of all elements (Table 20.1). Their low ionization energies and high E°_{ox} values explain why they are so readily oxidized to cations, +1 cations for Group 1, +2 for Group 2. The alkali metals and the heavier alkaline earth metals (Ca, Sr, Ba) are commonly stored under dry mineral oil or kerosene to prevent them from reacting with oxygen or water vapor in the air. Magnesium is less reactive; it is commonly available in the form of ribbon or powder. Beryllium, as one would expect from its position in the periodic table, is the least metallic element in these two groups. It is also the least reactive toward water, oxygen, or other nonmetals.

Not under water!

EXAMPLE 20.4

Write balanced equations for the reaction of sodium with hydrogen and barium with oxygen.

STRATEGY

Use Table 20.1 to deduce the formulas of the products. Note that barium forms two products with oxygen.

SOLUTION

Na with H_2	$2Na(s) + H_2(g) \longrightarrow 2NaH(s)$
Ba with O_2	$2Ba(s) + O_2(g) \longrightarrow 2BaO(s)$
	$Ba(s) + O_2(g) \longrightarrow BaO_2(s)$

BaO_2 is barium peroxide.

Table 20.1 Reactions of the Alkali and Alkaline Earth Metals

Reactant	Product	Comments
	Alkali Metals (M)	
$H_2(g)$	$MH(s)$	On heating in hydrogen gas
$X_2(g)$	$MX(s)$	X = F, Cl, Br, I
$N_2(g)$	$M_3N(s)$	Only Li reacts; product contains N^{3-} ion
$S(s)$	$M_2S(s)$	On heating
$O_2(g)$	$M_2O(s)$ $M_2O_2(s)$ $MO_2(s)$	Li; product is an oxide (O^{2-} ion) Na; product is a peroxide (O_2^{2-} ion) K, Rb, Cs; product is a superoxide (O_2^- ion)
$H_2O(l)$	$H_2(g)$, M^+, OH^-	Violent reaction with Na, K
	Alkaline Earth Metals (M)	
$H_2(g)$	$MH_2(s)$	All except Be; heating required
$X_2(g)$	$MX_2(s)$	Any halogen
$N_2(g)$	$M_3N_2(s)$	All except Be; heating required
$S(s)$	$MS(s)$	On heating
$O_2(g)$	$MO(s)$ $MO_2(s)$	All; product contains O^{2-} ion Ba; product contains O_2^{2-} ion
$H_2O(l)$	$H_2(g)$, M^{2+}, OH^-	Ca, Sr, Ba

Reaction with Hydrogen

The compounds formed by the reaction of hydrogen with the alkali and alkaline earth metals contain H^- ions; for example, sodium hydride consists of Na^+ and H^- ions. These white crystalline solids are often referred to as saline hydrides because of their physical resemblance to NaCl. Chemically, they behave quite differently from sodium chloride; for example, they react with water to produce hydrogen gas. Typical reactions are

$$NaH(s) + H_2O(l) \longrightarrow H_2(g) + Na^+(aq) + OH^-(aq)$$
$$CaH_2(s) + 2H_2O(l) \longrightarrow 2H_2(g) + Ca^{2+}(aq) + 2OH^-(aq)$$

In this way, saline hydrides can serve as compact, portable sources of hydrogen gas for inflating life rafts and balloons.

Reaction with Water

The alkali metals react vigorously with water (Figure 20.7) to evolve hydrogen and form a water solution of the alkali hydroxide. The reaction of sodium is typical:

$$2Na(s) + 2H_2O(l) \longrightarrow 2Na^+(aq) + 2OH^-(aq) + H_2(g) \qquad \Delta H° = -368.6 \text{ kJ}$$

The heat evolved in the reaction frequently causes the hydrogen to ignite.

Among the Group 2 metals, Ca, Sr, and Ba react with water in much the same way as the alkali metals. The reaction with calcium is

$$Ca(s) + 2H_2O(l) \longrightarrow Ca^{2+}(aq) + 2OH^-(aq) + H_2(g)$$

Figure 20.8 shows the reaction of a calcium compound, CaH_2, with water. Beryllium does not react with water at all. Magnesium reacts very slowly with boiling water but reacts more readily with steam at high temperatures:

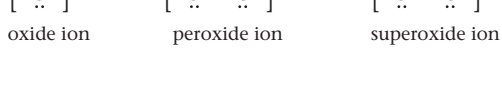
$$Mg(s) + H_2O(g) \longrightarrow MgO(s) + H_2(g)$$

This reaction, like that of sodium with water, produces enough heat to ignite the hydrogen. Firefighters who try to put out a magnesium fire by spraying water on it have discovered this reaction, often with tragic results. The best way to extinguish burning magnesium is to dump dry sand on it.

Reaction with Oxygen

Note from Table 20.1 that several different products are possible when an alkali or alkaline earth metal reacts with oxygen. The product may be a normal oxide (O^{2-} ion), a **peroxide** (O_2^{2-} ion), or **superoxide** (O_2^- ion).

The superoxide ion has an unpaired electron; KO_2 is paramagnetic.



Mama G. Clarke

Figure 20.7 Reaction of sodium with water. When a *very small* piece of sodium is added to water, it reacts violently with the water. The OH^- ions formed in the reaction turn the acid-base indicator phenolphthalein from colorless to pink.

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Figure 20.8 Reaction of calcium hydride (CaH_2) with water.

Lithium is the only Group 1 metal that forms the normal oxide in good yield by direct reaction with oxygen. The other Group 1 oxides (Na_2O, K_2O, Rb_2O, Cs_2O) must be prepared by other means. In contrast, the Group 2 metals usually react with oxygen to give the normal oxide. Beryllium and magnesium must be heated strongly to give BeO and MgO (Figure 20.9). Calcium and strontium react more readily to give CaO and SrO. Barium, the most reactive of the Group 2 metals, catches fire when exposed to moist air. The product is a mixture of the normal oxide BaO (Ba^{2+}, O^{2-} ions) and the peroxide BaO_2 (Ba^{2+}, O_2^{2-} ions). The higher the temperature, the greater the fraction of BaO in the mixture.

The oxides of these metals react with water to form hydroxides:

$$Li_2O(s) + H_2O(l) \longrightarrow 2LiOH(s)$$
$$CaO(s) + H_2O(l) \longrightarrow Ca(OH)_2(s)$$

The oxides of the Group 1 and Group 2 metals are sometimes referred to as "basic anhydrides" (bases without water) because of this reaction. The reaction with CaO is referred to as the "slaking" of lime; it gives off 65 kJ of heat per mole of $Ca(OH)_2$ formed. A similar reaction with MgO takes place slowly to form $Mg(OH)_2$, the antacid commonly referred to as "milk of magnesia."

When sodium burns in air, the principal product is yellowish sodium peroxide, Na_2O_2:

$$2Na(s) + O_2(g) \longrightarrow Na_2O_2(s)$$

Addition of sodium peroxide to water gives hydrogen peroxide, H_2O_2:

$$Na_2O_2(s) + 2H_2O(l) \longrightarrow 2Na^+(aq) + 2OH^-(aq) + H_2O_2(aq)$$

Through this reaction, sodium peroxide finds use as a bleaching agent in the pulp and paper industry.

The heavier alkali metals (K, Rb, Cs) form the superoxide when they burn in air. For example,

$$K(s) + O_2(g) \longrightarrow KO_2(s)$$

Potassium superoxide is used in self-contained breathing devices for firefighters and miners. It reacts with the moisture in exhaled air to generate oxygen:

$$4KO_2(s) + 2H_2O(g) \longrightarrow 3O_2(g) + 4KOH(s)$$

The carbon dioxide in the exhaled air is removed by reaction with the KOH formed:

$$KOH(s) + CO_2(g) \longrightarrow KHCO_3(s)$$

A person using a mask charged with KO_2 can rebreathe the same air for an extended period of time. This allows that person to enter an area where there are poisonous gases or oxygen-deficient air.

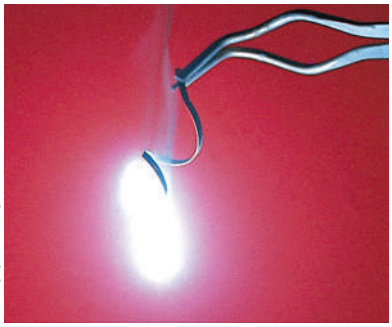

Figure 20.9 Burning magnesium. A piece of magnesium ribbon bursts into flame when heated in the air; the product of the reaction is MgO(*s*).

EXAMPLE 20.5

Consider the compounds strontium hydride, radium peroxide, and cesium superoxide.

a Give the formulas of these compounds.

STRATEGY

The formulas can be deduced from the charges of the ions. Sr and Ra are in Group 2 and thus have a charge of +2. Cs is in Group 1 and has a charge of +1. Hydride is H^-, peroxide is O_2^{2-}, and superoxide is O_2^-.

continued

SOLUTION

strontium hydride	$Sr^{2+} + H^- = SrH_2$
radium peroxide	$Ra^{2+} + O_2^{2-} = RaO_2$
cesium superoxide	$Cs^+ + O_2^- = CsO_2$

b Write equations for the formation of these compounds from the elements.

STRATEGY

Write the formula of the products (from (a)) on the product side, put the elements that make them up on the reactant side, and write the states and balance.

SOLUTION

strontium hydride	$Sr(s) + H_2(g) \longrightarrow SrH_2(s)$
radium peroxide	$Ra(s) + O_2(g) \longrightarrow RaO_2(s)$
cesium superoxide	$Cs(s) + O_2(g) \longrightarrow CsO_2(s)$

c Write equations for the reactions of strontium hydride and radium peroxide with water.

STRATEGY

Recall from the preceding discussion that

$$\text{hydride} + H_2O \longrightarrow H_2 + \text{metal cation} + OH^-$$

$$\text{peroxide} + H_2O \longrightarrow H_2O_2 + \text{metal cation} + OH^-$$

SOLUTION

Reaction with water:

$$SrH_2(s) + 2H_2O(l) \longrightarrow 2H_2(g) + Sr^{2+}(aq) + 2OH^-(aq)$$

$$RaO_2(s) + 2H_2O(l) \longrightarrow H_2O_2(l) + Ra^{2+}(aq) + 2OH^-(aq)$$

20-3 Redox Chemistry of the Transition Metals

The transition metals, unlike those in Groups 1 and 2, typically show several different oxidation numbers in their compounds. This tends to make their redox chemistry more complex (and more colorful). Only in the lower oxidation states (+1, +2, +3) are the transition metals present as cations (e.g., Ag^+, Zn^{2+}, Fe^{3+}). In higher oxidation states (+4 to +7) a transition metal is covalently bonded to a nonmetal atom, most often oxygen.

Reactions of the Transition Metals with Oxygen

Table 20.2 lists the formulas of the oxides formed when the more common transition metals react with oxygen. With one exception (Cu_2O), the transition metal is present as a +2 and/or a +3 ion. In Co_3O_4 and in other oxides of general formula M_3O_4, there are two different types of cations: +2 and +3. To be specific, there are twice as many +3 as +2 cations; we might show the composition of Co_3O_4 as

$$1Co^{2+} : 2Co^{3+} : 4O^{2-}$$

We should point out that many oxides of the transition metals beyond those listed in Table 20.2 can be prepared indirectly. For example, although silver does not react directly with oxygen, silver(I) oxide, Ag_2O, can be made by treating a solution of a silver salt with strong base.

$$2Ag^+(aq) + 2OH^-(aq) \longrightarrow Ag_2O(s) + H_2O$$

In another case, cobalt(II) oxide can be prepared by heating the carbonate in the absence of air.

$$CoCO_3(s) \longrightarrow CoO(s) + CO_2(g)$$

Table 20.2 Products of Reactions of the Transition Metals with Oxygen

Metal	Product
Cr	Cr_2O_3
Mn	Mn_3O_4
Fe	Fe_2O_3, Fe_3O_4
Co	Co_3O_4
Ni	NiO
Cu	Cu_2O, CuO
Zn	ZnO
Ag	—
Cd	CdO
Au	—
Hg	HgO

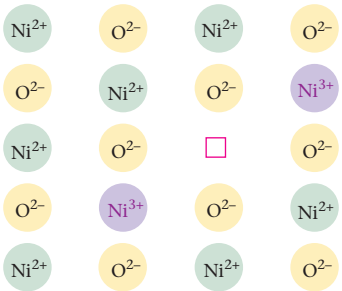

Figure 20.10 Nonstoichiometric nickel(II) oxide. For each missing Ni^{2+} ion, two others are converted to Ni^{3+} ions to maintain charge balance.

Courtesy of Edmund Scientific

Figure 20.11 A superconductor. A pellet of superconducting material, previously cooled to 77 K with liquid nitrogen, floats above a magnet.

Many oxides of the transition metals can be *nonstoichiometric;* the atom ratios of the elements differ slightly from whole-number values. Stoichiometric nickel(II) oxide, in which the atom ratio is exactly 1 : 1 (i.e., $Ni_{1.00}O_{1.00}$), is a green, nonconducting solid. If this compound is heated to 1200°C in pure oxygen, it turns black and undergoes a change in composition to something close to $Ni_{0.97}O_{1.00}$. This nonstoichiometric solid was one of the early semiconductors; it has the structure shown in Figure 20.10. A few Ni^{2+} ions are missing from the crystal lattice; to maintain electrical neutrality, two Ni^{2+} ions are converted to Ni^{3+} ions for each missing Ni^{2+}.

Nonstoichiometry is relatively common among "mixed" metal oxides, in which more than one metal is present. In 1986 it was discovered that certain compounds of this type showed the phenomenon of *superconductivity;* on cooling to about 100 K, their electrical resistance drops to zero (Figure 20.11). A typical formula here is $YBa_2Cu_3O_x$, where x varies from 6.5 to 7.2, depending on the method of preparation of the solid.

Reaction of Transition Metals with Acids

Any metal with a positive standard oxidation voltage, E°_{ox}, can be oxidized by the H^+ ions present in a 1 *M* solution of a strong acid. All the transition metals in the left column of Table 20.3 react spontaneously with dilute solutions of such strong acids as HCl, HBr, and H_2SO_4. The products are hydrogen gas and a cation of the transition metal. A typical reaction is that of nickel:

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

Table 20.3 Ease of Oxidation of Transition Metals

Metal		Cation	E°_{ox} (V)	Metal		Cation	E°_{ox} (V)
Mn	⟶	Mn^{2+}	+1.182	Cu	⟶	Cu^{2+}	−0.339
Cr	⟶	Cr^{2+}	+0.912	Ag	⟶	Ag^+	−0.799
Zn	⟶	Zn^{2+}	+0.762	Hg	⟶	Hg^{2+}	−0.852
Fe	⟶	Fe^{2+}	+0.409	Au	⟶	Au^{3+}	−1.498
Cd	⟶	Cd^{2+}	+0.402				
Co	⟶	Co^{2+}	+0.282				
Ni	⟶	Ni^{2+}	+0.236				

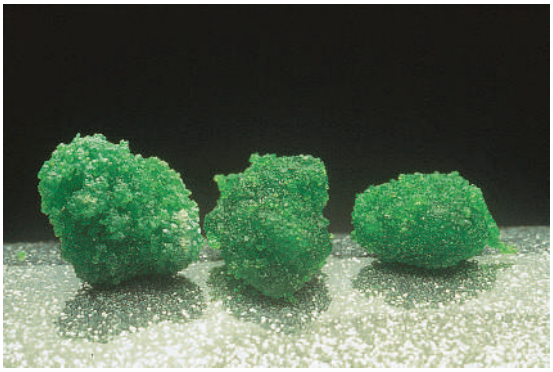

Figure 20.12 Oxidation of nickel. Nickel reacts slowly with hydrochloric acid to form $H_2(g)$ and Ni^{2+} ions in solution. Evaporation of the solution formed gives green crystals of $NiCl_2 \cdot 6H_2O$.

The end result of this reaction is shown in Figure 20.12. With metals that can form more than one cation, such as iron, the reaction product with H^+ in the absence of air is ordinarily the cation of lower charge, for example, Fe^{2+}:

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

Metals with negative values of E°_{ox}, listed at the right of Table 20.3, are too inactive to react with hydrochloric acid. The H^+ ion is not a strong enough oxidizing agent to convert a metal such as copper ($E^\circ_{ox} = -0.339$ V) to a cation. However, copper can be oxidized by nitric acid. The oxidizing agent is the nitrate ion, NO_3^-, which may be reduced to NO_2 or NO:

$$3Cu(s) + 8H^+(aq) + 2NO_3^-(aq) \longrightarrow 3Cu^{2+}(aq) + 2NO(g) + 4H_2O$$
$$E^\circ = E^\circ_{ox}\ Cu + E^\circ_{red}\ NO_3^- = -0.339\ V + 0.964\ V = +0.625\ V$$

EXAMPLE 20.6

Write balanced equations for the reactions, if any, at standard conditions of chromium with hydrochloric acid and silver with nitric acid.

STRATEGY

1. The metals can only be oxidized. Use Table 20.3 to obtain E°_{ox}.
2. An aqueous solution of HCl contains only H^+ and Cl^- ions.
   Only H^+ can be reduced to H_2. Chloride ions cannot be reduced.
   Find E° for the reaction between H^+ and the metal. The reaction will occur if $E^\circ > 0$.
3. An aqueous solution of HNO_3 contains only H^+ and NO_3^- ions.
   Both H^+ and NO_3^- can be reduced, H^+ to H_2 and NO_3^- to NO.
   Find E° for the reaction between H^+ and the metal and for NO_3^- and the metal. The reaction will occur if $E^\circ > 0$.
4. Write balanced half-reactions to get the overall equation for the reaction.

SOLUTION

Cr and HCl

1. Metal: $Cr \longrightarrow Cr^{2+}$: $E^\circ_{ox} = 0.912$ V
2. HCl: $H^+ \longrightarrow H_2$: $E^\circ_{red} = 0.000$ V
3. E°: $E^\circ = 0.912\ V + 0.000\ V = 0.912\ V$ The reaction will occur.
4. Equation:

$$Cr(s) \longrightarrow Cr^{2+}(aq) + 2e^-$$
$$2H^+(aq) + 2e^- \longrightarrow H_2(g)$$
$$Cr(s) + 2H^+(aq) \longrightarrow Cr^{2+}(aq) + H_2(g)$$

Ag and HNO_3

1. Metal: $Ag \longrightarrow Ag^+$: $E^\circ_{ox} = -0.799$ V
2. HNO_3: $H^+ \longrightarrow H_2$: $E^\circ_{red} = 0.000$ V; $NO_3^- \longrightarrow NO$: $E^\circ_{red} = 0.964$ V

continued

3. $E°$	$Ag + NO_3^-$ will occur. ($E° = 0.165$ V) $Ag + H^+$ will not occur. ($E° = -0.799$ V)
4. Equation	$3(Ag(s) \longrightarrow Ag^+(aq) + e^-)$ $NO_3^-(aq) + 4H^+(aq) + 3e^- \longrightarrow NO(g) + 2H_2O$ $3Ag(s) + NO_3^-(aq) + 4H^+(aq) \longrightarrow 3Ag^+(aq) + NO(g) + 2H_2O$

Although gold is not oxidized by nitric acid, it can be brought into solution in *aqua regia*, a 3:1 mixture by volume of 12 *M* HCl and 16 *M* HNO_3:

"Aqua regia" = royal water.

$$Au(s) + 4H^+(aq) + 4Cl^-(aq) + NO_3^-(aq) \longrightarrow AuCl_4^-(aq) + NO(g) + 2H_2O$$

The nitrate ion of the nitric acid acts as the oxidizing agent. The function of the hydrochloric acid is to furnish Cl^- ions to form the very stable complex ion $AuCl_4^-$.

Equilibria Between Different Cations of a Transition Metal

Several transition metals form more than one cation. For example, chromium forms Cr^{2+} and Cr^{3+}; copper forms Cu^+ and Cu^{2+}. Table 20.4 lists values of $E°_{red}$ for several such systems. Using the data in this table and in Table 17.1, it is possible to decide on the relative stabilities of different transition metal cations in water solution.

Cations for which $E°_{red}$ is a large, positive number are readily reduced and hence tend to be unstable in water solution. A case in point is the Mn^{3+} ion, which reacts spontaneously with water:

$$2Mn^{3+}(aq) + H_2O(l) \longrightarrow 2Mn^{2+}(aq) + \tfrac{1}{2}O_2(g) + 2H^+(aq)$$
$$E° = E°_{red}\,Mn^{3+} + E°_{ox}\,H_2O = +1.559\text{ V} - 1.229\text{ V} = +0.330\text{ V}$$

As a result of this reaction, Mn^{3+} cations are never found in water solution. Manganese(III) occurs only in insoluble oxides and hydroxides such as Mn_2O_3 and MnO(OH).

Co^{3+} is also rare, except in complexes.

The cations in the center column of Table 20.4 (Cr^{2+}, Mn^{2+}, . . .) are in an intermediate oxidation state. They can be either oxidized to a cation of higher charge ($Cr^{2+} \longrightarrow Cr^{3+}$) or reduced to the metal ($Cr^{2+} \longrightarrow Cr$). With certain cations of this type, these two half-reactions occur simultaneously. This reaction type is called **disproportionation**. Consider, for example, the Cu^+ ion. In water solution, copper(I) salts *disproportionate*, undergoing reduction (to copper metal) and oxidation (to Cu^{2+}) at the same time:

$$2Cu^+(aq) \longrightarrow Cu(s) + Cu^{2+}(aq); \qquad E° = +0.518\text{ V} - 0.161\text{ V} = +0.357\text{ V}$$

As a result, the only stable copper(I) species are insoluble compounds such as CuCN or complex ions such as $Cu(CN)_2^-$.

The Cu^+ ion is one of the few species in the center column of Table 20.4 that disproportionates in water, undergoing simultaneous reduction to the metal and oxidation to a cation of higher charge. However, cations of this type may be unstable for a quite different reason. Water ordinarily contains dissolved air; the O_2 in air may oxidize the cation. When a blue solution of chromium(II) salt is exposed to air, the color quickly changes to violet or green as the Cr^{3+} ion is formed by the reaction

$$2Cr^{2+}(aq) \longrightarrow 2Cr^{3+}(aq) + 2e^- \qquad E°_{ox} = +0.408\text{ V}$$
$$\tfrac{1}{2}O_2(g) + 2H^+(aq) + 2e^- \longrightarrow H_2O \qquad E°_{red} = +1.229\text{ V}$$
$$2Cr^{2+}(aq) + \tfrac{1}{2}O_2(g) + 2H^+(aq) \longrightarrow 2Cr^{3+}(aq) + H_2O \qquad E° = +1.637\text{ V}$$

Table 20.4 Ease of Reduction E°_{red} (V) of Transition Metal Cations

Chromium	Cr^{3+}	$\xrightarrow{-0.408\ V}$	Cr^{2+}	$\xrightarrow{-0.912\ V}$	Cr
Manganese	Mn^{3+}	$\xrightarrow{+1.559\ V}$	Mn^{2+}	$\xrightarrow{-1.182\ V}$	Mn
Iron	Fe^{3+}	$\xrightarrow{+0.769\ V}$	Fe^{2+}	$\xrightarrow{-0.409\ V}$	Fe
Cobalt	Co^{3+}	$\xrightarrow{+1.953\ V}$	Co^{2+}	$\xrightarrow{-0.282\ V}$	Co
Copper	Cu^{2+}	$\xrightarrow{+0.161\ V}$	Cu^{+}	$\xrightarrow{+0.518\ V}$	Cu
Gold	Au^{3+}	$\xrightarrow{+1.400\ V}$	Au^{+}	$\xrightarrow{+1.695\ V}$	Au
Mercury	Hg^{2+}	$\xrightarrow{+0.908\ V}$	Hg_2^{2+} ◂	$\xrightarrow{+0.796\ V}$	Hg

The Hg_2^{2+} ion has the structure $(Hg—Hg)^{2+}$.

As a result of this reaction, chromium(II) salts are difficult to prepare and even more difficult to store.

The Fe^{2+} ion ($E^\circ_{ox} = -0.769$ V) is much more stable toward oxidation than Cr^{2+}. However, iron(II) salts in water solution are slowly converted to iron(III) by dissolved oxygen. ◂ In acidic solution, the reaction is

Solid Fe^{2+} salts are often contaminated with Fe^{3+}.

$$2Fe^{2+}(aq) + \tfrac{1}{2}O_2(g) + 2H^+(aq) \longrightarrow 2Fe^{3+}(aq) + H_2O$$

$$E^\circ = E^\circ_{ox}\ Fe^{2+} + E^\circ_{red}\ O_2 = -0.769\ V + 1.229\ V = +0.460\ V$$

A similar reaction takes place in basic solution. Iron(II) hydroxide is pure white when first precipitated, but in the presence of air it turns first green and then brown as it is oxidized by O_2:

$$2Fe(OH)_2(s) + \tfrac{1}{2}O_2(g) + H_2O(l) \longrightarrow 2Fe(OH)_3(s)$$

EXAMPLE 20.7

Using Table 20.4, find

(a) three different cations, in addition to Mn^{3+}, that react with H_2O to form $O_2(g)$ ($E^\circ_{ox}\ H_2O = -1.229$ V).

(b) another cation, in addition to Cu^+, that disproportionates in water.

(c) two other cations, in addition to Cr^{2+} and Fe^{2+}, that are oxidized by $O_2(g)$ dissolved in water ($E^\circ_{red}\ O_2 = +1.229$ V).

STRATEGY AND SOLUTION

Use Table 20.4 and look for two half-reactions (one an oxidation, the other a reduction) that give $E^\circ > 0$ when E°_{red} and E°_{ox} are combined.

(a) E°_{red} must be larger than 1.229 V since $E^\circ_{ox} = -1.229$ V.
The ions are: Co^{3+}: $E^\circ_{red} = 1.953$ V
Au^{3+}: $E^\circ_{red} = 1.400$ V
Au^{+}: $E^\circ_{red} = 1.695$ V

(b) Recall that disproportionation means that the same ion or element is reduced and oxidized. Look at the ions in the middle column and add E°_{ox} and E°_{red} on either side of the ion. Don't forget to change the sign for E°_{ox}.

$Cr^{2+} \longrightarrow Cr$: $E^\circ_{red} = -0.912$ V	$Cr^{2+} \longrightarrow Cr^{3+}$: $E^\circ_{ox} = 0.408$ V	$E^\circ < 0$
$Mn^{2+} \longrightarrow Mn$: $E^\circ_{red} = -1.182$ V	$Mn^{2+} \longrightarrow Mn^{3+}$: $E^\circ_{ox} = -1.559$ V	$E^\circ < 0$
$Fe^{2+} \longrightarrow Fe$: $E^\circ_{red} = -0.409$ V	$Fe^{2+} \longrightarrow Fe^{3+}$: $E^\circ_{ox} = -0.769$ V	$E^\circ < 0$
$Au^{+} \longrightarrow Au$: $E^\circ_{red} = 1.695$ V	$Au^{+} \longrightarrow Au^{3+}$: $E^\circ_{ox} = -1.400$ V	$E^\circ > 0$

Au^+ is the other cation.

continued

(c) E°_{ox} must be larger than −1.229 V.
Use the species in the center column as reactants to be oxidized.
You may not use the species on the right-hand column because they are not cations. (The question asks for cations.)
You may not use the cations on the left-hand column because they cannot be oxidized.

$$Mn^{2+} \longrightarrow Mn^{3+}: E^\circ_{ox} = -1.559\ V < -1.229\ V$$
$$Co^{2+} \longrightarrow Co^{3+}: E^\circ_{ox} = -1.953\ V < -1.229\ V$$
$$Cu^{+} \longrightarrow Cu^{2+}: E^\circ_{ox} = -0.161\ V > -1.229\ V$$
$$Au^{+} \longrightarrow Au^{3+}: E^\circ_{ox} = -1.400\ V < -1.229\ V$$
$$Hg_2^{2+} \longrightarrow Hg^{2+}: E^\circ_{ox} = -0.908\ V > -1.229\ V$$

Cu^+ and Hg_2^{2+} are the other cations.

Oxoanions of the Transition Metals (CrO_4^{2-}, $Cr_2O_7^{2-}$, MnO_4^-)

Chromium in the +6 state forms two different oxoanions, the yellow chromate ion, CrO_4^{2-}, and the red dichromate ion, $Cr_2O_7^{2-}$ (Figure 20.13). The chromate ion is stable in basic or neutral solution; in acid, it is converted to the dichromate ion:

$$\underset{\text{yellow}}{2CrO_4^{2-}(aq)} + 2H^+(aq) \rightleftharpoons \underset{\text{red}}{Cr_2O_7^{2-}(aq)} + H_2O(l) \qquad K = 3 \times 10^{14}$$

The dichromate ion in acidic solution is a powerful oxidizing agent,

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l) \qquad E^\circ_{red} = +1.33\ V$$

As you might expect from the half-equation for its reduction, the oxidizing strength of the dichromate ion decreases as the concentration of H^+ decreases (increasing pH).

The $Cr_2O_7^{2-}$ ion can act as an oxidizing agent in the solid state as well as in water solution. In particular, it can oxidize the NH_4^+ ion to molecular nitrogen. When a pile of ammonium dichromate is ignited, a spectacular reaction occurs (Figure 20.14).

$$\underset{\text{red}}{(NH_4)_2Cr_2O_7(s)} \longrightarrow N_2(g) + 4H_2O(g) + \underset{\text{green}}{Cr_2O_3(s)}$$

The ammonium dichromate resembles a tiny volcano as it burns, emitting hot gases, sparks, and a voluminous green dust of chromium(III) oxide.

Chromates and dichromates are gradually disappearing from chemistry teaching laboratories because of concern about their toxicity. Long-term exposure of industrial workers to dust containing chromates has, in a few cases, been implicated in lung cancer. More commonly, repeated contact with chromate salts leads to skin disorders; a few people are extremely allergic to CrO_4^{2-} and $Cr_2O_7^{2-}$ ions, breaking into a rash on first exposure.

This makes a great lecture demonstration.

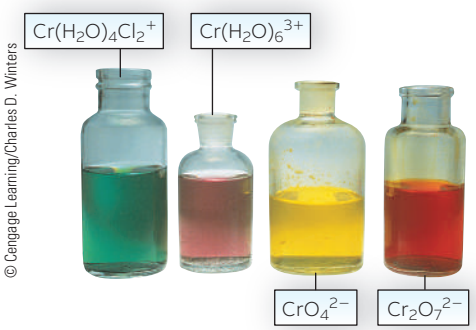

Figure 20.13 Oxidation states of chromium. The first two bottles contain +3 chromium. Each bottle in the right-hand pair contains +6 chromium.

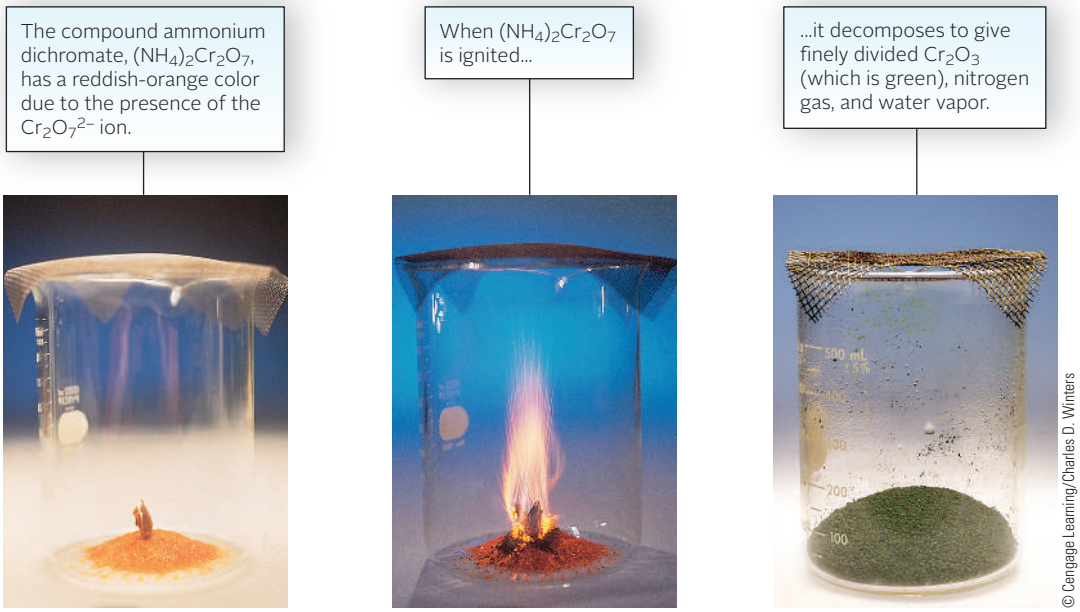

Figure 20.14 **Ammonium dichromate volcano.**

The permanganate ion, MnO_4^-, has an intense purple color easily visible even in very dilute solution.* Crystals of solid potassium permanganate, $KMnO_4$, have a deep purple, almost black color. This compound is used to treat such diverse ailments as "athlete's foot" and rattlesnake bites. These applications depend on the fact that the MnO_4^- ion is a very powerful oxidizing agent. This is especially true in acidic solution, where MnO_4^- is reduced to Mn^{2+}:

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O \qquad E^\circ_{red} = +1.512\ V$$

In basic solution, MnO_4^- is reduced to MnO_2, with a considerably smaller value of E°_{red}:

$$MnO_4^-(aq) + 2H_2O + 3e^- \longrightarrow MnO_2(s) + 4OH^-(aq) \qquad E^\circ_{red} = +0.596\ V$$

However, even in basic solution, MnO_4^- can oxidize water:

$$4MnO_4^-(aq) + 2H_2O \longrightarrow 4MnO_2(s) + 3O_2(g) + 4OH^-(aq)$$
$$E^\circ = E^\circ_{red}\ MnO_4^- + E^\circ_{ox}\ H_2O = +0.596\ V - 0.401\ V = +0.195\ V$$

This reaction accounts for the fact that laboratory solutions of $KMnO_4$ slowly decompose, producing a brownish solid (MnO_2) and gas bubbles (O_2).

*The purple color of old bottles exposed to the sun for a long time is due to MnO_4^- ions. These are formed when ultraviolet light oxidizes manganese compounds in the glass.

CHEMISTRY **BEYOND** THE CLASSROOM

Essential Metals in Nutrition

Four of the main-group cations are essential in human nutrition (Table A). Of these, the most important is Ca^{2+}. About 90% of the calcium in the body is found in bones and teeth, largely in the form of hydroxyapatite, $Ca(OH)_2 \cdot 3Ca_3(PO_4)_2$. Calcium ions in bones and teeth exchange readily with those in the blood; about 0.6 g of Ca^{2+} enters and leaves your bones every day. In a normal adult this exchange is in balance, but in elderly people, particularly women, there is sometimes a net loss of bone calcium, leading to the disease known as osteoporosis.

Although sodium is an essential metal, it has been statistically associated with hypertension. About 50% of people with high blood pressure (10% of the general population)

Foods high in iron.

are sensitive to high concentrations of Na^+ ions. For that reason, it is recommended that the daily consumption of Na^+ be limited to 2.4 g. The simplest way to cut back on Na^+ is to read the label carefully before buying processed foods, which account for about 75% of our sodium intake. For example, a single serving of packaged scalloped potatoes can contain as much as 0.5 g of Na^+ ion as opposed to only 0.006 g for a large baked potato.

Of the ten trace elements known to be essential to human nutrition, seven are transition metals. For the most part, transition metals in biochemical compounds are present as complex ions, chelated by organic ligands. You will recall (Chapter 19) that hemoglobin has such a structure with Fe^{2+} as the central ion of the complex. The Co^{3+} ion occupies a similar position in vitamin B_{12}, octahedrally coordinated to molecules in somewhat similar fashion to those in hemoglobin.

As you can judge from Table A, transition metal cations are frequently found in enzymes. The Zn^{2+} ion alone is known to be a component of at least 70 different enzymes. One of these, referred to as "alcohol dehydrogenase," is concentrated in the liver, where it acts to break down alcohols. Another zinc-containing enzyme is involved in the normal functioning of oil glands in the skin, which accounts for the use of Zn^{2+} compounds in the treatment of acne.

Although Zn^{2+} is essential to human nutrition, compounds of the two elements below zinc in the periodic table, Cd and Hg, are extremely toxic. This reflects the fact that Cd^{2+} and Hg^{2+}, in contrast to Zn^{2+}, form very stable complexes with ligands containing sulfur atoms. As a result, these two cations react with and thereby deactivate enzymes containing —SH groups.

Table A Essential Metal Ions

Major Species (Main-Group Cations)

Ion	Amount in Body	Daily Requirement	Function in Body	Rich Sources*
Na^+	63 g	~2 g	Principal cation *outside* cell fluid	Table salt, many processed and preserved foods
K^+	150 g	~2 g	Principal cation *within* cell fluid	Fruits, nuts, fish, coffee, wheat bran
Mg^{2+}	21 g	0.35 g	Activates enzymes for body processes	Chocolate, nuts, coffee, wheat bran
Ca^{2+}	1160 g	0.8 g	Bone and tooth formation	Milk, cheese, broccoli, canned salmon (with bones)

Trace Species (Transition Metal Cations)

Ion	Amount in Body	Daily Requirement	Function in Body	Rich Sources*
Fe^{2+}, Fe^{3+}	5000 mg	15 mg	Component of hemoglobin, myoglobin	Liver, meat, clams, spinach
Zn^{2+}	3000 mg	15 mg	Component of many enzymes, hormones	Oysters, crab, meat, nuts
Cu^{2+}, Cu^+	100 mg	2 mg	Iron metabolism, component of enzymes	Lobster, cherries, chocolate
Mn^{2+}	15 mg	3 mg	Metabolism of carbohydrates, lipids	Beet greens, nuts, blueberries
Mo(IV,V,VI)	10 mg	0.3 mg	Fe, N metabolism; component of enzymes	Legumes, ice cream
Cr^{3+}	5 mg	0.2 mg	Glucose metabolism; affects action of insulin	Corn, clams, nuts
Co^{2+}, Co^{3+}	1 mg	0.005 mg	Component of vitamin B_{12}	Liver, shellfish

*Other, more mundane, sources can be found in any nutrition textbook.

Key Concepts

1. Calculate $\Delta G°$ from thermodynamic data. **(Example 20.1; Problems 5, 6, 35)**
2. Write balanced equations to represent
   - metallurgical processes. **(Examples 20.2 and 20.3; Problems 1–4, 7, 8)**
   - reactions of Group 1 and Group 2 metals. **(Examples 20.4 and 20.5; Problems 13–16)**
   - redox reactions of transition metals. **(Example 20.6; Problems 19–24)**
3. Determine $E°$ and reaction spontaneity from standard potentials. **(Example 20.7; Problems 25–28)**

Key Terms

disproportionation
metallurgy
ores
peroxide
superoxide

Summary Problem

Consider the alkaline earth metal strontium and the transition metal manganese.

(a) Write a balanced equation for the reaction of strontium with oxygen; with water.

(b) Give the formulas of strontium hydride, strontium nitride, and strontium sulfide.

(c) Electrolysis of strontium chloride gives strontium metal and chlorine gas. What mass of the chloride must be electrolyzed to form one kilogram of strontium? One liter of $Cl_2(g)$ at STP?

(d) Give the formulas of three manganese compounds containing manganese in different oxidation states.

(e) Write a balanced equation for the reaction of manganese metal with hydrochloric acid; Mn^{3+} with water; Mn with O_2.

(f) Write a balanced equation for the reduction of the principal ore of manganese, pyrolusite, MnO_2, with CO.

(g) For the reaction

$$MnO(s) + H_2(g) \longrightarrow Mn(s) + H_2O(g),\ \Delta H^\circ = +143\ \text{kJ},\ \Delta S^\circ = +0.0297\ \text{kJ/K}$$

Would it be feasible to reduce MnO to the metal by heating with hydrogen?

(h) Given that E°_{red} $Mn^{3+} \longrightarrow Mn^{2+} = +1.559$ V, E°_{red} $Mn^{2+} \longrightarrow Mn = -1.182$ V, and E°_{red} $O_2(g) \longrightarrow H_2O = +1.229$ V, show by calculation whether Mn^{2+} in water solution will disproportionate; whether it will be oxidized to Mn^{3+} by dissolved oxygen; whether it will be reduced by hydrogen gas to the metal.

(i) Given

$$MnO_4^-(aq) + 2H_2O + 3e^- \longrightarrow MnO_2(s) + 4OH^-(aq) \qquad E^\circ_{red} = +0.59\ \text{V}$$

write a balanced equation for the reaction of MnO_4^- in basic solution with Fe^{2+} to form $Fe(OH)_3$. Calculate E_{red} for the MnO_4^- ion at pH 9.0, taking $[MnO_4^-] = 1$ M.

Answers

(a) $2Sr(s) + O_2(g) \longrightarrow 2SrO(s)$
$Sr(s) + 2H_2O \longrightarrow Sr^{2+}(aq) + 2OH^-(aq) + H_2(g)$
(b) SrH_2; Sr_3N_2; SrS
(c) 1.809 kg; 7.07 g
(d) $MnCl_2$, Mn_2O_3, $KMnO_4$
(e) $Mn(s) + 2H^+(aq) \longrightarrow Mn^{2+}(aq) + H_2(g)$
$2Mn^{3+}(aq) + H_2O \longrightarrow 2Mn^{2+}(aq) + \frac{1}{2}O_2(g) + 2H^+(aq)$
$3Mn(s) + 2O_2(g) \longrightarrow Mn_3O_4(s)$
(f) $MnO_2(s) + 2CO(g) \longrightarrow Mn(s) + 2CO_2(g)$
(g) no; $T_{calc} \approx 4800$ K
(h) no; in all cases, E° is negative
(i) $MnO_4^-(aq) + 3Fe^{2+}(aq) + 5OH^-(aq) + 2H_2O \longrightarrow MnO_2(s) + 3Fe(OH)_3(s)$ $\quad E_{red} = +0.99$ V

Questions and Problems

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

20-1 Metallurgy

1. Write a balanced equation to represent the electrolysis of molten sodium chloride. What volume of Cl_2 at STP is formed at the anode when 1.00 g of sodium is formed at the cathode?

2. Write a balanced equation to represent the electrolysis of aluminum oxide. If 2.00 L of O_2 at 25°C and 751 mm Hg is formed at the anode, what mass of Al is formed at the cathode?

3. Write a balanced equation to represent
(a) the roasting of nickel(II) sulfide to form nickel(II) oxide.
(b) the reduction of nickel(II) oxide by carbon monoxide.

4. Write a balanced equation to represent the roasting of copper(I) sulfide to form "blister copper."

5. Show by calculation whether the reaction in Problem 3(b) is spontaneous at 25°C and 1 atm.

6. Calculate ΔG° at 200°C for the reaction in Problem 4.

7. Write a balanced equation for the reaction that occurs when
(a) finely divided gold is treated with $CN^-(aq)$ in the presence of $O_2(g)$.
(b) finely divided zinc metal is added to the solution formed in (a).

8. Write a balanced equation for the reaction that occurs when
(a) iron(III) oxide is reduced with carbon monoxide.
(b) the excess carbon in pig iron is removed by the basic oxygen process.

9. How many cubic feet of air (assume 21% by volume of oxygen in air) at 25°C and 1.00 atm are required to react with coke to form the CO needed to convert one metric ton of hematite ore (92% Fe_2O_3) to iron?

10. Zinc is produced by electrolytic refining. The electrolytic process, which is similar to that for copper, can be represented by the two half-reactions

$$Zn(\text{impure}, s) \longrightarrow Zn^{2+} + 2e^-$$
$$Zn^{2+} + 2e^- \longrightarrow Zn(\text{pure}, s)$$

For this process, a voltage of 3.0 V is used. How many kilowatt hours are needed to produce one metric ton of pure zinc?

11. When 2.876 g of a certain metal sulfide is roasted in air, 2.368 g of the metal oxide is formed. If the metal has an oxidation number of +2, what is its molar mass?

12. Chalcopyrite, $CuFeS_2$, is an important source of copper. A typical chalcopyrite ore contains about 0.75% Cu. What volume of sulfur dioxide at 25°C and 1.00 atm pressure is produced when one boxcar load (4.00×10^3 ft^3) of chalcopyrite ore (d = 2.6 g/cm^3) is roasted? Assume all the sulfur in the ore is converted to SO_2 and no other source of sulfur is present.

20-2 Reactions of Alkali Metals and Alkaline Earth Metals

13. Give the formula and name of the compound formed by strontium with

(**a**) nitrogen (**b**) bromine
(**c**) water (**d**) oxygen

14. Give the formula and name of the compound formed by potassium with

(**a**) nitrogen (**b**) iodine (**c**) water
(**d**) hydrogen (**e**) sulfur

15. Write a balanced equation and give the names of the products for the reaction of

(**a**) magnesium with chlorine.
(**b**) barium peroxide with water.
(**c**) lithium with sulfur.
(**d**) sodium with water.

16. Write a balanced equation and give the names of the products for the reaction of

(**a**) sodium peroxide and water.
(**b**) calcium and oxygen.
(**c**) rubidium and oxygen.
(**d**) strontium hydride and water.

17. To inflate a life raft with hydrogen to a volume of 25.0 L at 25°C and 1.10 atm, what mass of calcium hydride must react with water?

18. What mass of KO_2 is required to remove 90.0% of the CO_2 from a sample of 1.00 L of exhaled air (37°C, 1.00 atm) containing 5.00 mole percent CO_2?

20-3 Redox Chemistry of Transition Metals

19. Write a balanced equation to show

(**a**) the reaction of chromate ion with strong acid.
(**b**) the oxidation of water to oxygen gas by permanganate ion in basic solution.
(**c**) the reduction half-reaction of chromate ion to chromium(III) hydroxide in basic solution.

20. Write a balanced equation to show

(**a**) the formation of gas bubbles when cobalt reacts with hydrochloric acid.
(**b**) the reaction of copper with nitric acid.
(**c**) the reduction half-reaction of dichromate ion to Cr^{3+} in acid solution.

21. Write a balanced redox equation for the reaction of mercury with *aqua regia*, assuming the products include $HgCl_4^{2-}$ and $NO_2(g)$.

22. Write a balanced redox equation for the reaction of cadmium with *aqua regia*, assuming the products include $CdCl_4^{2-}$ and $NO(g)$.

23. Balance the following redox equations.

(**a**) $Cu(s) + NO_3^-(aq) \longrightarrow Cu^{2+}(aq) + NO_2(g)$ (acidic)

(**b**) $Cr(OH)_3(s) + ClO^-(aq) \longrightarrow CrO_4^{2-}(aq) + Cl^-(aq)$ (basic)

24. Balance the following redox equations.

(**a**) $Fe(s) + NO_3^-(aq) \longrightarrow Fe^{3+}(aq) + NO_2(g)$ (acidic)

(**b**) $Cr(OH)_3(s) + O_2(g) \longrightarrow CrO_4^{2-}(aq)$ (basic)

25. Show by calculation which of the following metals will react with hydrochloric acid (standard concentrations).

(**a**) Cd (**b**) Cr (**c**) Co
(**d**) Ag (**e**) Au

26. Show by calculation which of the metals in Problem 25 will react with nitric acid to form NO (standard concentrations).

27. Of the cations listed in Table 20.4, show by calculation which one (besides Cu^+) will disproportionate at standard conditions.

28. Using Table 17.1 (Chapter 17) calculate $E°$ for

(**a**) $2Co^{3+}(aq) + H_2O \longrightarrow 2Co^{2+}(aq) + \frac{1}{2}O_2(g) + 2H^+(aq)$

(**b**) $2Cr^{2+}(aq) + I_2(s) \longrightarrow 2Cr^{3+}(aq) + 2I^-(aq)$

29. Using Table 20.4, calculate, for the disproportionation of Fe^{2+},

(**a**) the equilibrium constant, K.
(**b**) the concentration of Fe^{3+} in equilibrium with 0.10 M Fe^{2+}.

30. Using Table 20.4, calculate, for the disproportionation of Au^+,

(**a**) K.
(**b**) the concentration of Au^+ in equilibrium with 0.10 M Au^{3+}.

Unclassified

31. A sample of sodium liberates 2.73 L of hydrogen at 752 mm Hg and 22°C when it is added to a large amount of water. How much sodium is used?

32. A self-contained breathing apparatus contains 248 g of potassium superoxide. A firefighter exhales 116 L of air at 37°C and 748 mm Hg. The volume percent of water in exhaled air is 6.2. What mass of potassium superoxide is left after the water in the exhaled air reacts with it?

33. Taking K_{sp} $PbCl_2 = 1.7 \times 10^{-5}$ and assuming $[Cl^-] = 0.20\ M$, calculate the concentration of Pb^{2+} at equilibrium.

34. The equilibrium constant for the reaction

$$2CrO_4^{2-}(aq) + 2H^+(aq) \rightleftharpoons Cr_2O_7^{2-}(aq) + H_2O$$

is 3×10^{14}. What must the pH be so that the concentrations of chromate and dichromate ion are both 0.10 M?

35. Using data in Appendix 1, estimate the temperature at which Fe_2O_3 can be reduced to iron, using hydrogen gas as a reducing agent (assume $H_2O(g)$ is the other product).

36. A 0.500-g sample of zinc-copper alloy was treated with dilute hydrochloric acid. The hydrogen gas evolved was collected by water displacement at 27°C and a total pressure of 755 mm Hg. The volume of the water displaced by the gas is 105.7 mL. What is the percent composition, by mass, of the alloy? (Vapor pressure of H_2O at 27°C is 26.74 mm Hg.) Assume only the zinc reacts.

37. One type of stainless steel contains 22% nickel by mass. How much nickel sulfide ore, NiS, is required to produce one metric ton of stainless steel?

38. Silver is obtained in much the same manner as gold, using NaCN solution and O_2. Describe with appropriate equations the extraction of silver from argentite ore, Ag_2S. (The products are SO_2 and $Ag(CN)_2^-$, which are reduced with zinc.)

39. Iron(II) can be oxidized to iron(III) by permanganate ion in acidic solution. The permanganate ion is reduced to manganese(II) ion.

(**a**) Write the oxidation half-reaction, the reduction half-reaction, and the overall redox equation.

(**b**) Calculate $E°$ for the reaction.

(**c**) Calculate the percentage of Fe in an ore if a 0.3500-g sample is dissolved and the Fe^{2+} formed requires for titration 55.63 mL of a 0.0200 *M* solution of $KMnO_4$.

40. Of the cations listed in the center column of Table 20.4, which one is the

(**a**) strongest reducing agent?

(**b**) strongest oxidizing agent?

(**c**) weakest reducing agent?

(**d**) weakest oxidizing agent?

Challenge Problems

41. A sample of 20.00 g of barium reacts with oxygen to form 22.38 g of a mixture of barium oxide and barium peroxide. Determine the composition of the mixture.

42. Rust, which you can take to be $Fe(OH)_3$, can be dissolved by treating it with oxalic acid. An acid-base reaction occurs, and a complex ion is formed.

(**a**) Write a balanced equation for the reaction.

(**b**) What volume of 0.10 *M* $H_2C_2O_4$ would be required to remove a rust stain weighing 1.0 g?

43. A 0.500-g sample of steel is analyzed for manganese. The sample is dissolved in acid and the manganese is oxidized to permanganate ion. A measured excess of Fe^{2+} is added to reduce MnO_4^- to Mn^{2+}. The excess Fe^{2+} is determined by titration with $K_2Cr_2O_7$. If 75.00 mL of 0.125 *M* $FeSO_4$ is added and the excess requires 13.50 mL of 0.100 *M* $K_2Cr_2O_7$ to oxidize Fe^{2+}, calculate the percent by mass of Mn in the sample.

44. Calculate the temperature in °C at which the equilibrium constant (K) for the following reaction is 1.00.

$$MnO_2(s) \longrightarrow Mn(s) + O_2(g)$$

45. A solution of potassium dichromate is made basic with sodium hydroxide; the color changes from red to yellow. Addition of silver nitrate to the yellow solution gives a precipitate. This precipitate dissolves in concentrated ammonia but re-forms when nitric acid is added. Write balanced net ionic equations for all the reactions in this sequence.