Chapter 11

Oxidations and Reductions

THE MAIN IDEA

Oxidation is the loss of electrons, and reduction is the gain of electrons.

11.7 Producing Metals

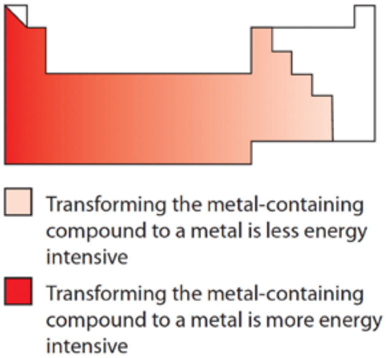
To convert a metal-containing compound to a metal requires an oxidation-reduction reaction. In the metal-containing compound, the metal exists as a positively charged ion, because it has lost one or more of its electrons to its bonding partner. To convert metal ions to neutral metal atoms requires that they gain electrons; that is, they must be reduced:

M^+	+	e^-	→	M^0
Metal ion		Electron		Metal atom

The tendency of a metal ion to be reduced depends on its location in the periodic table, as summarized in **Figure 11.24**. As discussed in Chapter 6, metals on the left in the periodic table readily lose electrons. This means it is relatively difficult to give electrons back to these metal ions—in other words, they are difficult to reduce. A sodium atom, for example, being on the left in the periodic table, loses electrons easily. Any ionic compound it forms, such as sodium chloride, tends to be very stable. Reducing the sodium ion, $Na+$, to sodium metal, Na^0, is difficult because doing so requires giving electrons to the sodium ion.

Metals on the left and especially the lower left of the periodic table therefore require the most energy-intensive methods of recovery, which include electrolysis. As was shown in the previous section, during electrolysis, an electric current supplies electrons to positively charged metal ions, thus reducing them.

Metals commonly recovered by electrolysis include the metals of groups 1–3, which occur most frequently as halides, carbonates, and phosphates. In addition, aluminum is commonly recovered by electrolysis, and other metals are obtained using electrolysis when very high purity is needed. The reactions involved when copper is produced this way are shown in **Figure 11.25**.



☐ Transforming the metal-containing compound to a metal is less energy intensive

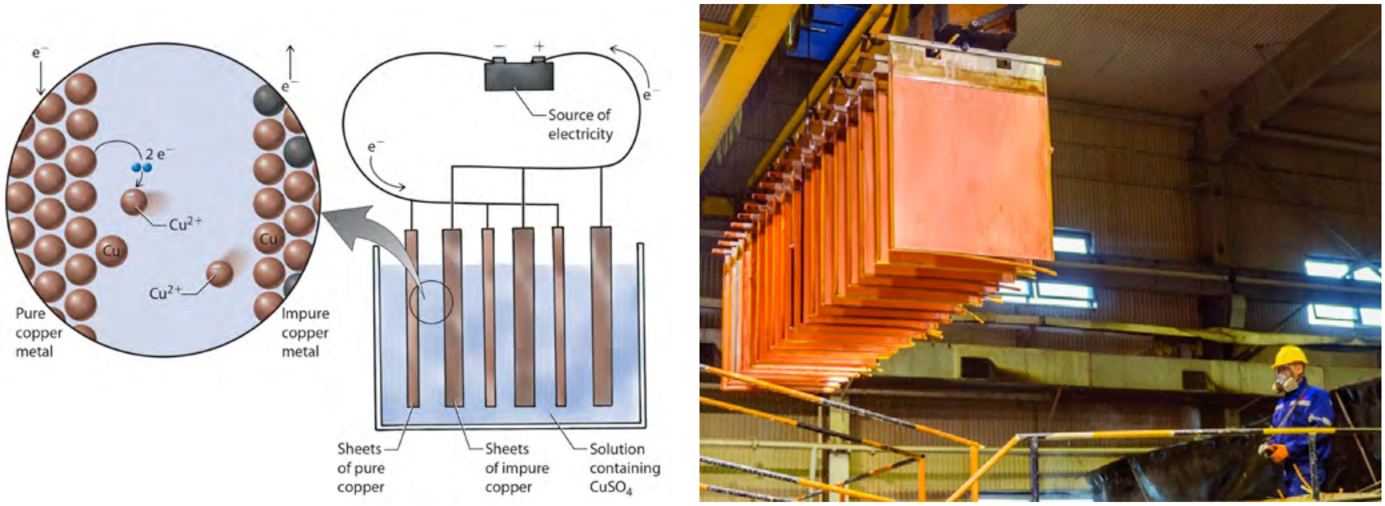
🟥 Transforming the metal-containing compound to a metal is more energy intensive

Λ Figure 11.24

The ions of metallic elements at the lower left of the periodic table are most difficult to reduce. For this reason, obtaining these elements from the metal-containing compounds they form is energy intensive. Metallic elements at the upper right of the periodic table tend to form compounds that require less energy to convert to metals.

READING CHECK

Which metals are most difficult to reduce?



Λ Figure 11.25

High-purity copper is recovered by electrolysis. Pure copper metal deposits on the negative electrode as copper ions in solution gain electrons. The source of these copper ions is a positively charged electrode made of impure copper.

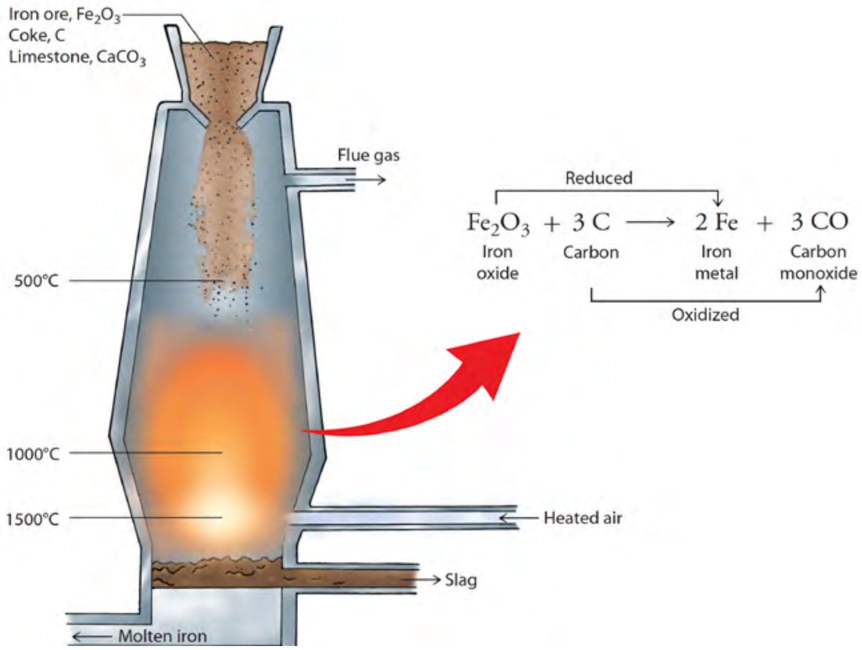
CONCEPT CHECK

Why is it so difficult to obtain a group 1 metal from a compound containing ions of that metal?

CHECK YOUR ANSWER The metal ions do not readily accept electrons to form metal atoms.

Some Metals are Commonly Obtained from Metal Oxides

Ores containing metal oxides can be converted to metals fairly efficiently in a *blast furnace*. First, the ore is mixed with limestone and coke, which is a concentrated form of carbon obtained from coal. Then the mixture is dropped into the furnace, where the coke is ignited and used as a fuel. At high temperatures, the coke also behaves as a reducing agent, yielding electrons to the positively charged metal ions in the oxide and reducing them to metal atoms. **Figure 11.26** shows this method being used to produce iron, which is found in nature primarily as iron oxide.



$$Fe_2O_3 + 3\,C \longrightarrow 2\,Fe + 3\,CO$$

< Figure 11.26

A mixture of iron oxide ore, coke, and limestone is dropped into a blast furnace, where the iron ions in the oxide are reduced to metal atoms. Note how the carbon is oxidized as it gains an oxygen atom to form carbon monoxide.

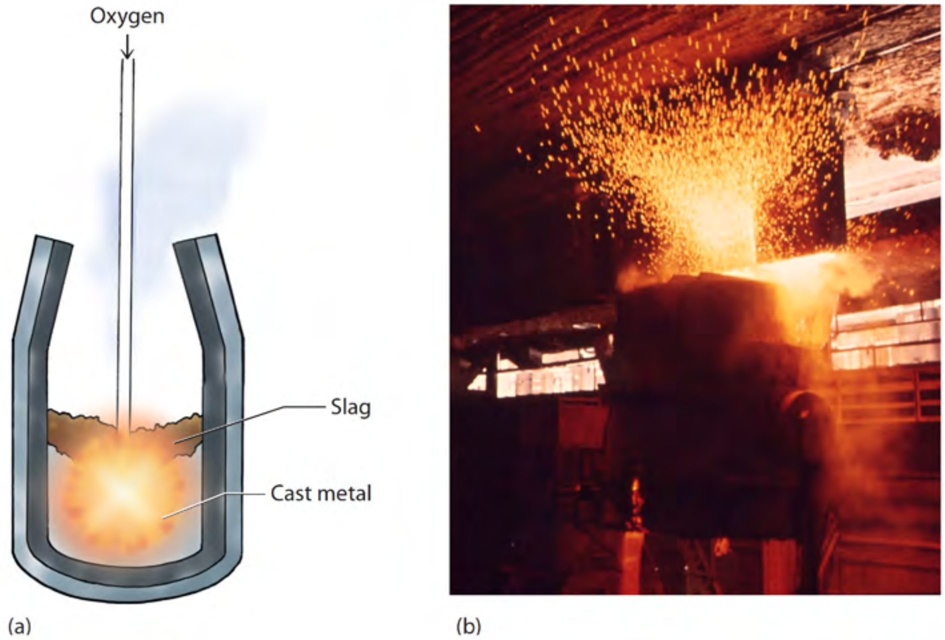
In the furnace, the limestone reacts with ore impurities—predominantly silicon compounds—to form *slag*, which is primarily calcium silicate:

$$\underset{\substack{\text{Silica sand}\\\text{(ore impurity)}}}{SiO_2(s)} + \underset{\text{Limestone}}{CaCO_3(s)} \rightarrow \underset{\substack{\text{Molten slag}\\\text{(calcium silicate)}}}{CaSiO_3(l)} + \underset{\substack{\text{Carbon}\\\text{dioxide}}}{CO_2(g)}$$

Because of the high temperatures, both the metal and the slag are molten. They drain to the bottom of the blast furnace, where they collect in two layers, the less dense slag on top. The metal layer is then tapped through an opening at the bottom of the blast furnace.

Once cooled, the metal from a blast furnace is known as a *cast metal.* (Side note: With iron ore, the cast metal is known as *pig iron*.) A cast metal is brittle and relatively soft for a metal because it still contains impurities, such as phosphorus, sulfur, and carbon. To remove these impurities, oxygen is blown through the molten cast metal in a *basic oxygen furnace*, shown in **Figure 11.27**. The oxygen oxidizes the impurities to form additional slag, which floats to the surface and is skimmed off.

Most phosphorus and sulfur impurities are removed in a basic oxygen furnace, but the purified metal still contains about 3 percent carbon. For the production of iron, this carbon is desirable. Iron atoms are relatively large, and when they pack together, small voids are created between atoms, as shown in **Figure 11.28**. These voids tend to weaken the iron. Carbon atoms are small enough to fill the voids, and having the voids filled strengthens the iron substantially. Iron strengthened by small percentages of carbon is called **steel**. The tendency of steel to rust can be inhibited by alloying the steel with noncorroding metals, such as chromium or nickel. This yields the stainless steel used to manufacture eating utensils and countless other items.



< Figure 11.27

(a) A flow of oxygen through a basic oxygen furnace oxidizes most of the impurities in a cast metal to form additional slag that may be skimmed away as it floats to the surface. (b) The basic oxygen furnace is hoisted and its purified contents can be poured into a reservoir used for molding iron pieces.

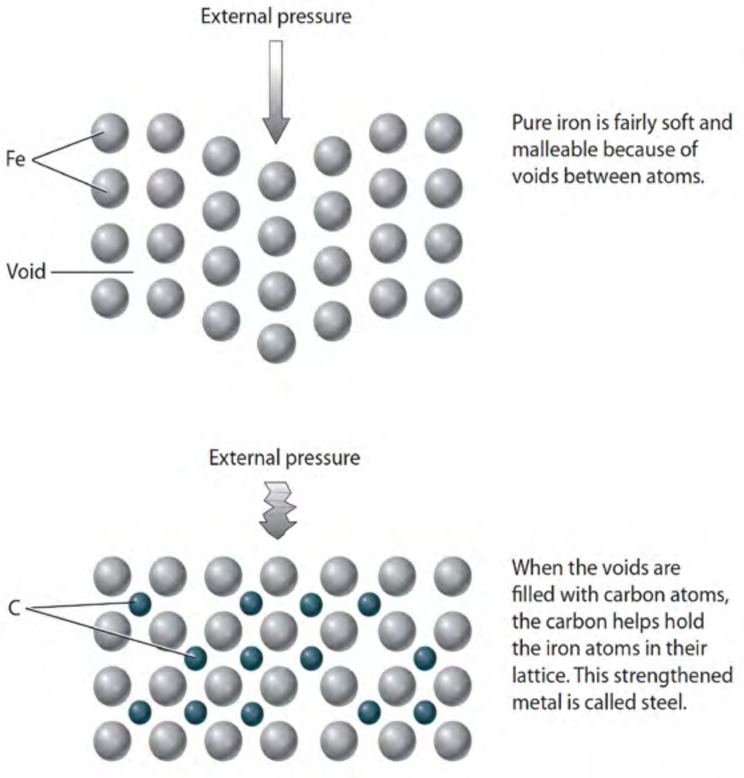
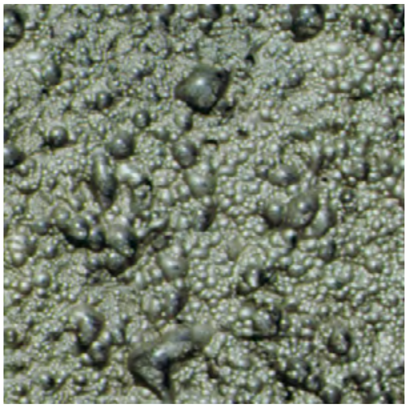


Figure 11.28 >

Steel is stronger than iron because of the small amounts of carbon it contains



∧ Figure 11.29

Air bubbles rising through a flotation container transport metal sulfide particles to the surface.

Other Metals are Commonly Obtained from Metal Sulfides

Metal sulfides can be purified by *flotation*, a technique that takes advantage of the fact that metal sulfides are relatively nonpolar and therefore attracted to oil. An ore containing a metal sulfide is first ground to a fine powder and then mixed vigorously with a lightweight oil and water. Compressed air is then forced up through the mixture. As air bubbles rise, they become coated with oil and metal sulfide particles. At the surface of the liquid, the coated bubbles form a floating froth, as shown in **Figure 11.29**. This froth, which is very rich in the metal sulfide, is then skimmed off.

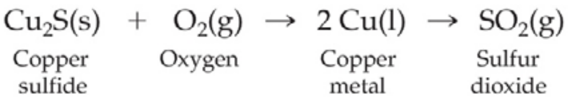
The metal sulfides recovered from the froth are then roasted in the presence of oxygen. The net reaction is the oxidation of S^{2-} in the sulfide to S^{4+} in sulfur dioxide and the reduction of the metal ion to its elemental state:

$$\underset{\text{Metal sulfide}}{MS(s)} + \underset{\text{Oxygen}}{O_2(g)} \rightarrow \underset{\text{Metal}}{M(l)} + \underset{\text{Sulfur dioxide}}{SO_2(g)}$$

The isolation of copper from its most common ore, chalcopyrite, $CuFeS_2$, requires several additional steps because of the presence of iron. First, the chalcopyrite is roasted in the presence of oxygen:

$$\underset{\text{Chalcopyrite}}{2\,CuFeS_2} + \underset{\text{Oxygen}}{O_2(g)} \rightarrow \underset{\substack{\text{Copper}\\\text{sulfide}}}{CuS(s)} + \underset{\substack{\text{Iron}\\\text{oxide}}}{2\,FeO(s)} + \underset{\substack{\text{Sulfur}\\\text{dioxide}}}{2\,SO_2(g)}$$

The copper sulfide and iron oxide from this reaction are then mixed with limestone, $CaCO_3$, and sand, SiO_2, in a blast furnace, where CuS is converted to Cu_2S. The limestone and sand form molten slag, $CaSiO_3$, in which the iron oxide dissolves. The copper sulfide melts and sinks to the bottom of the furnace. The less dense iron-containing slag floats above the molten copper sulfide and is drained off. The isolated copper sulfide is then roasted to copper metal:



$$\underset{\substack{\text{Copper}\\\text{sulfide}}}{Cu_2S(s)} + \underset{\text{Oxygen}}{O_2(g)} \rightarrow \underset{\substack{\text{Copper}\\\text{metal}}}{2\,Cu(l)} \rightarrow \underset{\substack{\text{Sulfur}\\\text{dioxide}}}{SO_2(g)}$$

Roasting metal sulfides requires a fair amount of energy. Furthermore, sulfur dioxide is a toxic gas that contributes to acid rain, so its emission must be minimized. Most companies comply with EPA emissions standards by converting the sulfur dioxide to marketable sulfuric acid, H_2SO_4.

CONCEPT CHECK

Of metal chlorides, metal oxides, and metal sulfides, which are most polar? Which are least polar?

CHECK YOUR ANSWER Metal chlorides, such as sodium chloride, tend to be most polar, while the metal sulfides, such as copper sulfide, tend to be least polar. The oxides, such as iron oxide, tend to be in between. This is an application of periodic trends as discussed in Chapter 6.