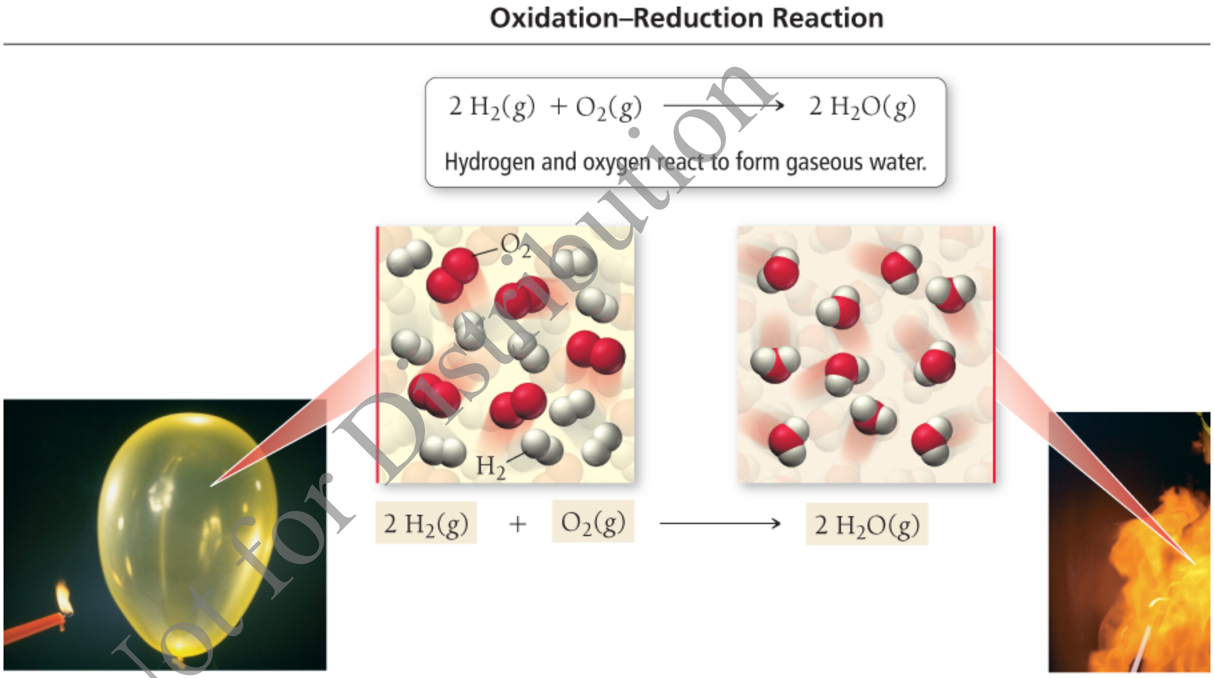
8.9: Oxidation–Reduction Reactions

Oxidation–reduction reactions or **redox reactions** are reactions in which electrons transfer from one reactant to the other. These types of reactions occur both in and out of solution. The rusting of iron, the bleaching of hair, and the production of electricity in batteries involve redox reactions. Many redox reactions involve the reaction of a substance with oxygen (Figure 8.21):

$$\begin{array}{rcll} 4\,\mathrm{Fe}(s) + 3\,\mathrm{O_2}(g) & \rightarrow & 2\,\mathrm{Fe_2O_3}(s) & \text{(rusting of iron)} \\ 2\,\mathrm{C_8H_{18}}(l) + 25\,\mathrm{O_2}(g) & \rightarrow & 16\,\mathrm{CO_2}(g) + 18\,\mathrm{H_2O}(g) & \text{(combustion of octane)} \\ 2\,\mathrm{H_2}(g) + \mathrm{O_2}(g) & \rightarrow & 2\,\mathrm{H_2O}(g) & \text{(combustion of hydrogen)} \end{array}$$

Figure 8.21 **Oxidation–Reduction Reaction**

The hydrogen in the balloon reacts with oxygen upon ignition to form gaseous water (which is dispersed in the flame).


Oxidation–Reduction Reaction
$2\,H_2(g) + O_2(g) \longrightarrow 2\,H_2O(g)$
Hydrogen and oxygen react to form gaseous water.
O_2
H_2
$2\,H_2(g)$ + $O_2(g)$ $\longrightarrow$ $2\,H_2O(g)$

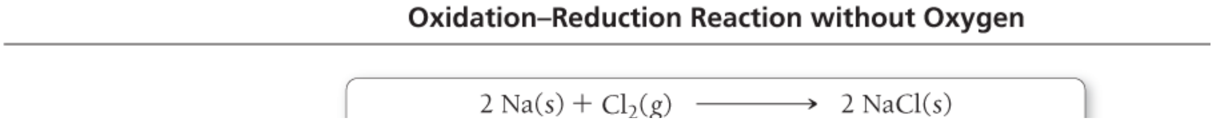
> Oxidation–reduction reactions are covered in more detail in Chapter 19.

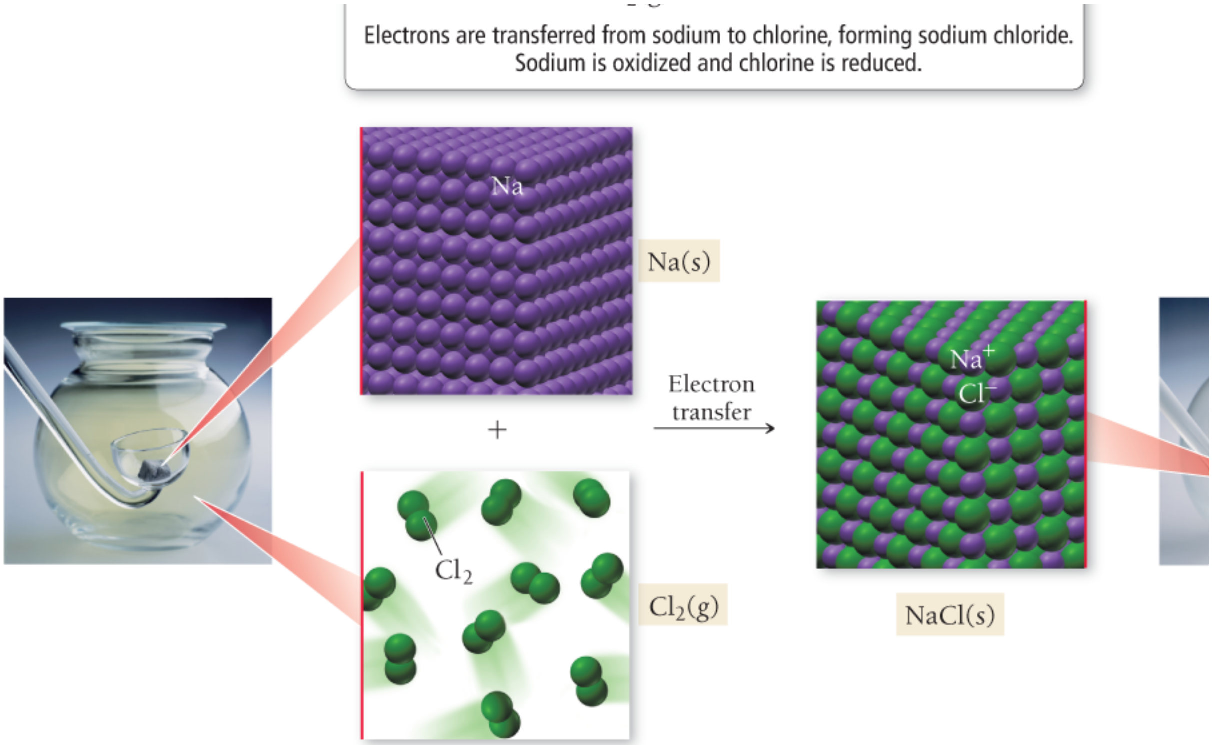
Combustion reactions, first covered in Section 7.6, are a type of redox reaction. However, redox reactions need not involve oxygen. Consider, for example, the reaction between sodium and chlorine to form sodium chloride (NaCl), depicted in Figure 8.22:

$$2\,\mathrm{Na}(s) + \mathrm{Cl_2}(g) \rightarrow 2\,\mathrm{NaCl}(s)$$

Figure 8.22 **Oxidation–Reduction without Oxygen**

When sodium reacts with chlorine, electrons transfer from the sodium to the chlorine, resulting in the formation of sodium chloride. In this redox reaction, sodium is oxidized and chlorine is reduced.


Oxidation–Reduction Reaction without Oxygen
$2\,Na(s) + Cl_2(g) \longrightarrow 2\,NaCl(s)$


Electrons are transferred from sodium to chlorine, forming sodium chloride. Sodium is oxidized and chlorine is reduced.

This reaction is similar to the reaction between sodium and oxygen, which forms sodium oxide (as one possible product):

$$4\ \mathrm{Na}(s) + \mathrm{O_2}(g) \rightarrow 2\ \mathrm{Na_2O}(s)$$

In both cases, a metal (which has a tendency to lose electrons) reacts with a nonmetal (which has a tendency to gain electrons). In both cases, metal atoms lose electrons to nonmetal atoms. A fundamental definition of **oxidation** is the loss of electrons, and a fundamental definition of **reduction** is the gain of electrons.

> Helpful Mnemonic: O I L R I G—**O**xidation **I**s **L**oss; **R**eduction **I**s **G**ain.

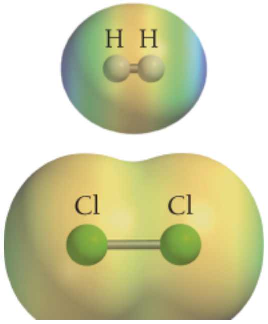
The transfer of electrons does not need to be a *complete* transfer (as occurs in the formation of an ionic compound) for the reaction to qualify as oxidation–reduction. For example, consider the reaction between hydrogen gas and chlorine gas:

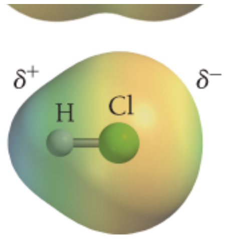
$$\mathrm{H_2}(g) + \mathrm{Cl_2}(g) \rightarrow 2\ \mathrm{HCl}(g)$$

Because chlorine is more electronegative than hydrogen (see Section 5.2), the bond between hydrogen and chlorine is polar (Figure 8.23). Notice that in the reaction, hydrogen has lost some of its electron density to chlorine. Therefore, in the reaction, hydrogen is oxidized and chlorine is reduced—this is a redox reaction.

Figure 8.23 Electrostatic Potential Maps Showing Electron Transfer

When hydrogen bonds to chlorine, the electrons are unevenly shared, resulting in an increase of electron density (reduction) for chlorine and a decrease in electron density (oxidation) for hydrogen.





Oxidation States

Determining whether or not a reaction between a metal and a nonmetal is a redox reaction is fairly straightforward because of ion formation. But how do we identify redox reactions that occur between nonmetals? Chemists have devised a scheme to track electrons before and after a chemical reaction. In this scheme—which is like bookkeeping for electrons—we assign each shared electron to the most electronegative atom. Then we give a number, called the **oxidation state** or **oxidation number**, to each atom based on the electron assignments. In other words, *the oxidation number of an atom in a compound is the "charge" it would have if all shared electrons were assigned to the more electronegative atom*.

For example, consider HCl. Since chlorine is more electronegative than hydrogen, we assign the two shared electrons in the bond to chlorine; then H (which lost an electron in our assignment) has an oxidation state of +1, and Cl (which gained one electron in our assignment) has an oxidation state of −1. Notice that, in contrast to ionic charges, which are usually written with the sign of the charge *after* the magnitude (1+ and 1−, for example), we write oxidation states with the sign of the charge *before* the magnitude (+1 and −1, for example). We use the following rules to assign oxidation states to atoms in elements and compounds:

Rules for Assigning Oxidation States	Examples
(These rules are hierarchical. If any two rules conflict, follow the rule that is higher on the list.)	
1. The oxidation state of an atom in a free element is 0.	Cu 0 ox state $\mathrm{Cl_2}$ 0 ox state
2. The oxidation state of a monoatomic ion is equal to its charge.	$\mathrm{Ca^{2+}}$ +2 ox state $\mathrm{Cl^-}$ -1 ox state
3. The sum of the oxidation states of all atoms in: ▪ a neutral molecule or formula unit is 0. ▪ an ion is equal to the charge of the ion.	$\mathrm{H_2O}$ $2(\text{H ox state}) + 1(\text{O ox state}) = 0$ $\mathrm{NO_3^-}$ $1(\text{N ox state}) + 3(\text{O ox state}) = -1$
4. In their compounds, metals have positive oxidation states. ▪ Group 1A metals *always* have an oxidation state of +1. ▪ Group 2A metals *always* have an oxidation state of +2.	NaCl +1 ox state $\mathrm{CaF_2}$ +2 ox state
5. In their compounds, we assign nonmetals oxidation states according to the table on the right. Entries at the top of the table take precedence over entries at the bottom of the table.	

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Do not confuse oxidation state with ionic charge. Unlike ionic charge—which is a real property of an

Do not confuse oxidation state with ionic charge. Unlike ionic charge—which is a real property of an ion—the oxidation state of an atom is merely a theoretical (but useful) construct.

Nonmetal	Oxidation State	Example
Fluorine	−1	MgF_2 −1 ox state
Hydrogen	+1	H_2O +1 ox state
Oxygen	−2	CO_2 −2 ox state
Group 7A	−1	CCl_4 −1 ox state
Group 6A	−2	H_2S −2 ox state
Group 5A	−3	NH_3 −3 ox state

When assigning oxidation states, these points also apply:

- The oxidation state of any given element generally depends on what other elements are present in the compound. (The exceptions are the group 1A and 2A metals, which are *always* +1 and +2, respectively.)
- Rule 3 must always be followed. Therefore, when following the hierarchy shown in rule 5, we give priority to the element(s) highest on the list and then assign the oxidation state of the element lowest on the list using rule 3.
- When assigning oxidation states to elements that are not covered by rules 4 and 5 (such as carbon), we use rule 3 to deduce their oxidation state once all other oxidation states have been assigned.

Example 8.15 Assigning Oxidation States

Assign an oxidation state to each atom in each element, ion, or compound.

a. Cl_2
b. Na^+
c. KF
d. CO_2
e. SO_4^{2-}
f. K_2O_2

SOLUTION Because Cl_2 is a free element, the oxidation state of both Cl atoms is 0 (rule 1).

a. Cl_2
Cl0Cl0

Because Na^+ is a monoatomic ion, the oxidation state of the Na^+ ion is +1 (rule 2).

b. Na^+
Na^++1

The oxidation state of K is +1 (rule 4). The oxidation state of F is −1 (rule 5). Because this is a neutral compound, the sum of the oxidation states is 0.

c. KF
KF
+1 − 1
sum:+1−1 = 0

The oxidation state of oxygen is −2 (rule 5). You deduce the oxidation state of carbon using rule 3, which says that the sum of the oxidation states of all the atoms must be 0.

d.

$$\begin{gathered}\mathrm{CO_2}\\ (\text{C ox state}) + 2(\text{O ox state}) = 0\\ (\text{C ox state}) + 2(-2) = 0\\ \text{C ox state} = +4\\ \mathrm{CO_2}\\ +4\ -2\\ \text{sum:}+4+2(-2) = 0\end{gathered}$$

The oxidation state of oxygen is −2 (rule 5). You would ordinarily expect the oxidation state of S to be −2 (rule 5). However, if that were the case, the sum of the oxidation states would not equal the charge of the ion. Because O is higher on the list than S, it takes priority and you calculate the oxidation state of sulfur by setting the *sum* of all of the oxidation states equal to −2 (the charge of the ion).

e.

$$\begin{gathered}\mathrm{SO_4{}^{2-}}\\ (\text{S ox state}) + 4(\text{O ox state}) = -2\\ (\text{S ox state}) + 4(-2) = -2\\ \text{S ox state} = +6\\ \mathrm{SO_4{}^{2-}}\\ +6\ -2\\ \text{sum:}+6+4(-2) = -2\end{gathered}$$

The oxidation state of potassium is +1 (rule 4). You would ordinarily expect the oxidation state of O to be −2 (rule 5), but rule 4 takes priority, and you need to deduce the oxidation state of O by setting the sum of all of the oxidation states equal to 0.

f.

$$\begin{gathered}\mathrm{K_2O_2}\\ 2(\text{K ox state}) + 2(\text{O ox state}) = 0\\ 2(+1) + 2(\text{O ox state}) = 0\\ \text{O ox state} = -1\\ \mathrm{K_2O_2}\\ +1\ -1\\ \text{sum: } 2(+1) + 2(-1) = 0\end{gathered}$$

FOR PRACTICE 8.15 Assign an oxidation state to each atom in each element, ion, or compound.

a. Cr

b. $\mathrm{Cr^{3+}}$

c. $\mathrm{CCl_4}$

d. $\mathrm{SrBr_2}$

e. $\mathrm{SO_3}$

f. $\mathrm{NO_3{}^-}$

In most cases, oxidation states are positive or negative integers; however, on occasion an atom within a compound can have a fractional oxidation state. Consider $\mathrm{KO_2}$. We assign the oxidation states as follows:

$$\begin{gathered}\mathrm{KO_2}\\ +1\ -\tfrac{1}{2}\\ \text{sum:}+1+2\left(-\frac{1}{2}\right) = 0\end{gathered}$$

In $\mathrm{KO_2}$, oxygen has a $-\frac{1}{2}$ oxidation state. Although this seems unusual, it is accepted because oxidation states are merely an imposed electron bookkeeping scheme, not an actual physical quantity.

Conceptual Connection 8.5 **Oxidation Numbers in Polyatomic Ions**

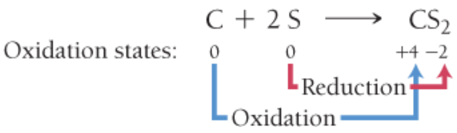
Identifying Redox Reactions

We can use oxidation states to identify redox reactions, even between nonmetals. For example, is the following reaction between carbon and sulfur a redox reaction?

$$C + 2\ S \rightarrow CS_2$$

> We discuss how to balance redox reactions in Section 19.2.

If it is a redox reaction, which element is oxidized? Which element is reduced? We use the oxidation state rules to assign oxidation states to all elements on both sides of the equation:



Carbon changes from an oxidation state of 0 to an oxidation state of +4. In terms of our electron bookkeeping scheme (the assigned oxidation state), carbon *loses electrons* and is *oxidized.* Sulfur changes from an oxidation state of 0 to an oxidation state of −2. In terms of our electron bookkeeping scheme, sulfur *gains electrons* and is *reduced.* In terms of oxidation states, oxidation and reduction are defined as follows.

- Oxidation: An increase in oxidation state
- Reduction: A decrease in oxidation state

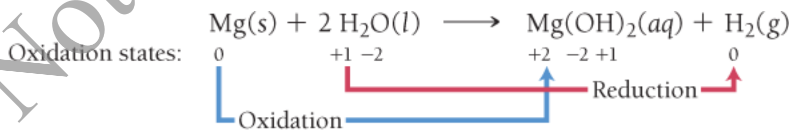
> Remember that a reduction is a *reduction* in oxidation state.

Example 8.16 Using Oxidation States to Identify Oxidation and Reduction

Use oxidation states to identify the element that is oxidized and the element that is reduced in the redox reaction.

$$Mg(s) + 2\ H_2O(l) \rightarrow Mg(OH)_2(aq) + H_2(g)$$

SOLUTION Begin by assigning an oxidation state to each atom in the reaction.



Since Mg increases in the oxidation state, it is oxidized. Since H decreases in the oxidation state, it is reduced.

FOR PRACTICE 8.16 Use oxidation states to identify the element that is oxidized and the element that is reduced in the redox reaction.

$$Sn(s) + 4\ HNO_3(aq) \rightarrow SnO_2(s) + 4\ NO_2(g) + 2\ H_2O(g)$$

FOR MORE PRACTICE 8.16 Determine whether or not each reaction is a redox reaction. If the reaction is a redox reaction, identify which element is oxidized and which is reduced.

a. $Hg_2(NO_3)_2(aq) + 2\ KBr(aq) \rightarrow Hgr_2Br_2(s) + 2\ KNO_3(aq)$

b. $4\ Al(s) + 3\ O_2(g) \rightarrow 2\ Al_2O_3(s)$

c. $CaO(s) + CO_2(g) \rightarrow CaCO_3(s)$

Notice that *oxidation and reduction must occur together.* If one substance loses electrons (oxidation), then another substance must gain electrons (reduction). A substance that causes the oxidation of another substance is an **oxidizing agent**. Oxygen, for example, is an excellent oxidizing agent because it causes the oxidation of many substances. In a redox reaction, *the oxidizing agent is always reduced.* A substance that causes the reduction of another substance is a **reducing agent**. Hydrogen, for example, as well as the group 1A and group 2A metals (because of their tendency to lose electrons) are excellent reducing agents. In a redox reaction, *the reducing agent is always oxidized.*

In Section 19.2, we will further discuss redox reactions, including how to balance them. For now, you need to be able to identify redox reactions, as well as oxidizing and reducing agents, according to the following guidelines.

Redox reactions

- Any reaction in which there is a change in the oxidation states of atoms in going from reactants to products.

In a redox reaction

- The oxidizing agent oxidizes another substance (and is itself reduced).
- The reducing agent reduces another substance (and is itself oxidized).

Example 8.17 Identifying Redox Reactions, Oxidizing Agents, and Reducing Agents

Determine whether or not each reaction is an oxidation–reduction reaction. For each oxidation–reduction reaction, identify the oxidizing agent and the reducing agent.

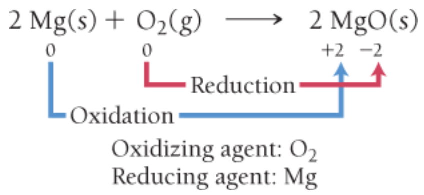
a. $2\ Mg(s) + O_2(g) \rightarrow 2\ MgO(s)$

b. $2\ HBr(aq) + Ca(OH)_2(aq) \rightarrow 2\ H_2O(l) + CaBr_2(aq)$

c. $Zn(s) + Fe^{2+}(aq) \rightarrow Zn^{2+}(aq) + Fe(s)$

SOLUTION *This is a redox reaction* because magnesium increases in oxidation number (oxidation) and oxygen decreases in oxidation number (reduction).

a.

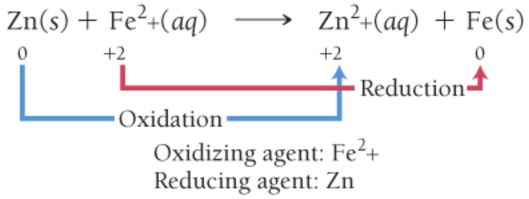


This is not a redox reaction because none of the atoms undergoes a change in oxidation number.

b. $2\ HBr(aq)_{+1\,-1} + Ca(OH)_2(aq)_{+2\,-2\,+1} \rightarrow 2\ H_2O(l)_{+1\,-2} + CaBr_2(aq)_{+2\,-1}$

This is a redox reaction because zinc increases in oxidation number (oxidation) and iron decreases in oxidation number (reduction).

c.



$$\mathrm{Zn}(s) + \mathrm{Fe}^{2+}(aq) \longrightarrow \mathrm{Zn}^{2+}(aq) + \mathrm{Fe}(s)$$

FOR PRACTICE 8.17 Determine whether or not each reaction is a redox reaction. For redox reactions, identify the oxidizing agent and the reducing agent.

a. $2\,\mathrm{Li}(s) + \mathrm{Cl}_2(g) \rightarrow 2\,\mathrm{LiCl}(s)$

b. $2\,\mathrm{Al}(s) + 3\,\mathrm{Sn}^{2+}(aq) \rightarrow 2\,\mathrm{Al}^{3+}(aq) + 3\,\mathrm{Sn}(s)$

c. $\mathrm{Pb}\left(\mathrm{NO}_3\right)_2(aq) + 2\,\mathrm{LiCl}(aq) \rightarrow \mathrm{PbCl}_2(s) + 2\,\mathrm{LiNO}_3(aq)$

d. $\mathrm{C}(s) + \mathrm{O}_2(g) \rightarrow \mathrm{CO}_2(g)$

Conceptual Connection 8.6 Oxidation and Reduction

Interactive

The Activity Series: Predicting Whether a Redox Reaction Is Spontaneous

Is there a way to predict whether a particular redox reaction will spontaneously occur? Suppose we knew that substance A has a greater tendency to lose electrons than substance B. (In other words, A is more easily oxidized than B.) Then we could predict that if we mix A with cations of B, a redox reaction would occur in which A loses its electrons (A is oxidized) to the cations of B (B cations are reduced). For example, Mg has a greater tendency to lose electrons than Cu. Consequently, if we put solid Mg into a solution containing Cu^{2+} ions, Mg is oxidized and Cu^{2+} is reduced.

$$\mathrm{Mg}(s) + \mathrm{Cu}^{2+}(aq) \rightarrow \mathrm{Mg}^{2+}(aq) + \mathrm{Cu}(s)$$

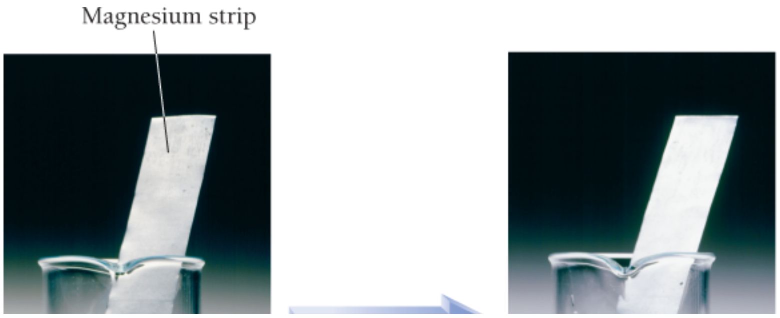
We see this as the fading of blue (the color of the Cu^{2+} ions in solution), the dissolving of the solid magnesium, and the appearance of solid copper on the remaining magnesium surface (Figure 8.24). This reaction is spontaneous—it occurs on its own when $\mathrm{Mg}(s)$ and $\mathrm{Cu}^{2+}(aq)$ come into contact. On the other hand, if we put $\mathrm{Cu}(s)$ in a solution containing $\mathrm{Mg}^{2+}(aq)$ ions, no reaction occurs (Figure 8.25).

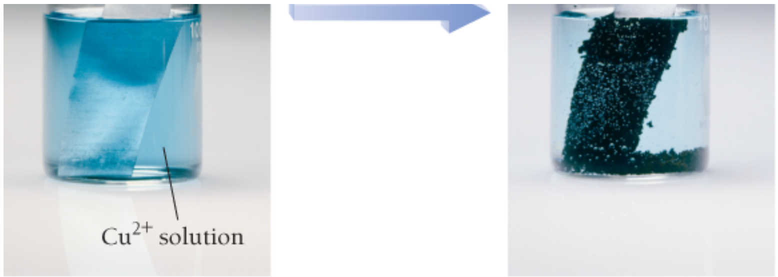
$$\mathrm{Cu}(s) + \mathrm{Mg}^{2+}(aq) \rightarrow \text{NO REACTION}$$

No reaction occurs because, as noted previously, Mg atoms have a greater tendency to lose electrons than do Cu atoms; Cu atoms will therefore not lose electrons to Mg^{2+} ions.

Figure 8.24 $\mathbf{Cu}^{2+}$ **Oxidizes Magnesium**

When we put a magnesium strip into a Cu^{2+} solution, the magnesium is oxidized to Mg^{2+} and the copper ion is reduced to $\mathrm{Cu}(s)$. Notice the fading of the blue color (due to Cu^{2+} ions) in solution and the appearance of solid copper on the magnesium strip.





$$Mg(s) + Cu^{2+}(aq) \longrightarrow Mg^{2+}(aq) + Cu(s)$$

Figure 8.25 Mg^{2+} **Does Not Oxidize Copper**

When we place solid copper in a solution containing Mg^{2+} ions, no reaction occurs.

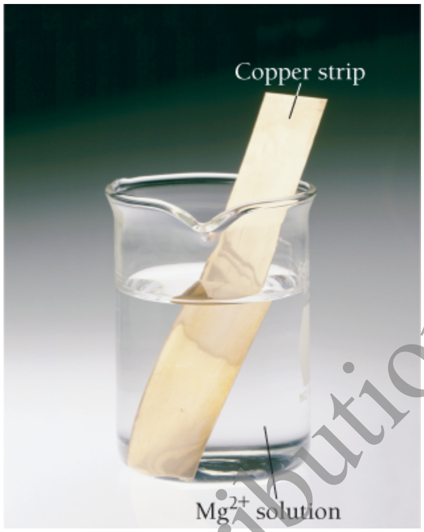


Table 8.4 shows the **activity series of metals**. This table lists metals in order of decreasing tendency to lose electrons. The metals at the top of the list have the greatest tendency to lose electrons—they are most easily oxidized and therefore the most reactive. The metals at the bottom of the list have the lowest tendency to lose electrons—they are the most difficult to oxidize and therefore the least reactive. It is not a coincidence that the metals used for jewelry, such as silver and gold, are near the bottom of the list. They are among the least reactive metals and therefore do not form compounds easily. Instead, they tend to remain as solid silver and solid gold rather than being oxidized to silver and gold cations by elements in the environment (such as the oxygen in the air).

Table 8.4 **Activity Series of Metals**

$Li(s) \longrightarrow Li^{+}(aq) + e^{-}$	Most reactive
$K(s) \longrightarrow K^{+}(aq) + e^{-}$	Most easily oxidized
$Ca(s) \longrightarrow Ca^{2+}(aq) + 2\,e^{-}$	Strongest tendency to lose electrons
$Na(s) \longrightarrow Na^{+}(aq) + e^{-}$	
$Mg(s) \longrightarrow Mg^{2+}(aq) + 2\,e^{-}$	
$Al(s) \longrightarrow Al^{3+}(aq) + 3\,e^{-}$	
$Mn(s) \longrightarrow Mn^{2+}(aq) + 2\,e^{-}$	
$Zn(s) \longrightarrow Zn^{2+}(aq) + 2\,e^{-}$	
$Cr(s) \longrightarrow Cr^{3+}(aq) + 3\,e^{-}$	
$Fe(s) \longrightarrow Fe^{2+}(aq) + 2\,e^{-}$	
$Ni(s) \longrightarrow Ni^{2+}(aq) + 2\,e^{-}$	
$Sn(s) \longrightarrow Sn^{2+}(aq) + 2\,e^{-}$	

$Pb(s) \longrightarrow Pb^{2+}(aq) + 2\,e^-$	
$H_2(g) \longrightarrow 2\,H^+(aq) + 2\,e^-$	
$Cu(s) \longrightarrow Cu^{2+}(aq) + 2\,e^-$	Least reactive
$Ag(s) \longrightarrow Ag^+(aq) + e^-$	Most difficult to oxidize
$Au(s) \longrightarrow Au^{3+}(aq) + 3\,e^-$	Least tendency to lose electrons

Each reaction in the activity series is an oxidation *half-reaction.* The half-reactions at the top are most likely to occur in the *forward* direction, and the half-reactions at the bottom are most likely to occur in the *reverse* direction. Consequently, if we pair a half-reaction from the top of the list with the reverse of a half-reaction from the bottom of the list, we get a spontaneous reaction. More specifically, any half-reaction on the list is spontaneous when paired with the reverse of any half-reaction below it on the list.

Gold is very low on the activity series. Because it is so difficult to oxidize, it resists the tarnishing and corrosion that more active metals undergo.

Conceptual Connection 8.7 **Activity Series**

Example 8.18 Predicting Spontaneous Redox Reactions

Determine whether each redox reaction is spontaneous:

a. $Fe(s) + Mg^{2+}(aq) \rightarrow Fe^{2+}(aq) + Mg(s)$

b. $Fe(s) + Pb^{2+}(aq) \rightarrow Fe^{2+}(aq) + Pb(s)$

SOLUTION

a. $Fe(s) + Mg^{2+}(aq) \rightarrow Fe^{2+}(aq) + Mg(s)$

This reaction involves the oxidation of Fe:

$$Fe(s) \rightarrow Fe^{2+}(aq) + 2\,e^-$$

with the reverse of a half-reaction *above it* in the activity series:

$$Mg^{2+}(aq) + 2\,e^- \rightarrow Mg(s)$$

Therefore, the reaction *is not* spontaneous.

b. $Fe(s) + Pb^{2+}(aq) \rightarrow Fe^{2+}(aq) + Pb(s)$

This reaction involves the oxidation of Fe:

$$Fe(s) \rightarrow Fe^{2+}(aq) + 2\ e^-$$

with the reverse of a half-reaction *below it* in the activity series:

$$Pb^{2+}(aq) + 2\ e^- \rightarrow Pb(s)$$

Therefore, the reaction *is* spontaneous.

FOR PRACTICE 8.18 Determine whether each redox reaction is spontaneous.

a. $Zn(s) + Ni^{2+}(aq) \rightarrow Zn^{2+}(aq) + Ni(s)$

b. $Zn(s) + Ca^{2+}(aq) \rightarrow Zn^{2+}(aq) + Ca(s)$