

5

OXIDATION-REDUCTION
REACTIONS

This athlete is able to perform because her body derives energy from food she consumed. The metabolism of foods provides the energy we need for all sorts of activities, from simply thinking to participating in sports. The chemical reactions involved can be viewed as occurring by electron transfer. In this chapter we study such reactions, how to balance equations that describe them, and how these reactions are useful for laboratory work.
(Tim Pannell/Corbis)

CHAPTER OUTLINE

5.1 Oxidation–reduction reactions involve electron transfer

5.2 The ion–electron method creates balanced net ionic equations for redox reactions

5.3 Metals are oxidized when they react with acids

5.4 A more active metal will displace a less active one from its compounds

5.5 Molecular oxygen is a powerful oxidizing agent

5.6 Redox reactions follow the same stoichiometric principles as other reactions

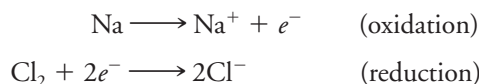
THIS CHAPTER IN CONTEXT In the preceding chapter you learned about some important reactions that take place in aqueous solutions. This chapter expands on that knowledge with a discussion of a class of reactions that can be viewed as involving the transfer of one or more electrons from one reactant to another. Our goal is to teach you how to recognize and analyze the changes that occur in these reactions and how to balance equations for reactions that involve electron transfer. You will also learn how to apply the principles of stoichiometry to these reactions and how to predict a type of reaction called single replacement. The reactions discussed here constitute a very broad class with many practical examples that range from combustion to batteries to the metabolism of foods by our bodies. Although we will introduce you to some of those reactions in this chapter, we will have to wait until a later time to discuss some of the others.

5.1 OXIDATION-REDUCTION REACTIONS INVOLVE ELECTRON TRANSFER

Among the first reactions studied by early scientists were those that involved oxygen. The combustion of fuels and the reactions of metals with oxygen to give oxides were described by the word *oxidation*. The removal of oxygen from metal oxides to give the metals in their elemental forms was described as *reduction*.

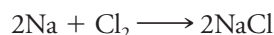
In 1789, the French chemist Antoine Lavoisier discovered that *combustion* involves the reaction of chemicals in various fuels, like wood and coal, not just with air but specifically with the oxygen in air. Over time, scientists came to realize that such reactions were actually special cases of a much more general phenomenon, one in which electrons are transferred from one substance to another. Collectively, electron transfer reactions came to be called **oxidation–reduction reactions**, or simply **redox reactions**. The term **oxidation** was used to describe the loss of electrons by one reactant, and **reduction** was used to describe the gain of electrons by another. For example, the reaction between sodium and chlorine to yield sodium chloride involves a loss of electrons by sodium (*oxidation* of sodium) and a gain of electrons by chlorine (*reduction* of chlorine). We can write these changes in equation form including the electrons, which we represent by the symbol e^- .

□ Notice that when we write equations of this type, the electron appears as a “product” if the process is oxidation and as a “reactant” if the process is reduction.



We say that sodium (Na) is oxidized and chlorine (Cl_2) is reduced.

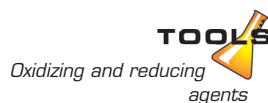
Oxidation and reduction always occur together. No substance is ever oxidized unless something else is reduced, and the total number of electrons lost by one substance is always the same as the total number gained by the other. If this were not true, electrons would appear as a product of the overall reaction, and this is never observed.¹ In the reaction of sodium with chlorine, for example, the overall reaction is



When two sodium atoms are oxidized, two electrons are lost, which is exactly the number of electrons gained when one Cl_2 molecule is reduced.

For a redox reaction to occur, one substance must accept electrons from the other. The substance that accepts the electrons is called the **oxidizing agent**; it is the agent that allows the other substance to lose electrons and be oxidized. Similarly, the substance that supplies the electrons is called the **reducing agent** because it helps something else to be reduced. In our example above, sodium is serving as a reducing agent when it supplies electrons to chlorine. In the process, sodium is oxidized. Chlorine is an oxidizing agent when it accepts electrons from the sodium, and when that happens, chlorine is reduced to chloride ion. One way to remember this is by the following summary:

□ The *oxidizing agent* causes oxidation to occur by accepting electrons (it gets reduced). The *reducing agent* causes reduction by supplying electrons (it gets oxidized).



The reducing agent is the substance that is oxidized.
The oxidizing agent is the substance that is reduced.

Redox reactions are very common. They occur in batteries, which are built so that the electrons transferred can pass through some external circuit where they are able to light a flashlight or power an iPod. The metabolism of foods, which supplies our bodies with energy, also occurs by a series of redox reactions. And ordinary household bleach works by oxidizing substances that stain fabrics, making them colorless or easier to remove from the fabric (see Figure 5.1).

¹ If electron loss didn't equal electron gain, it would also violate the law of conservation of mass, and that doesn't happen in chemical reactions.



FIG. 5.1 “Chlorine” bleach. This common household product is a dilute aqueous solution of sodium hypochlorite, NaOCl, which destroys fabric stains by oxidizing them to colorless products. (OPC, Inc.)

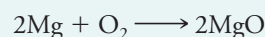
EXAMPLE 5.1

Identifying Oxidation–Reduction

The bright light produced by the reaction between magnesium and oxygen often is used in fireworks displays. The product of the reaction is magnesium oxide, an ionic compound. Which element is oxidized and which is reduced? What are the oxidizing and reducing agents?

ANALYSIS: This example asks us to apply the definitions presented above, so we need to know how the electrons are transferred in the reaction. As a first step, let’s write the chemical equation for the reaction.

Magnesium oxide is a compound of a metal and a nonmetal, so it’s an ionic substance. The locations of the elements in the periodic table tell us that the ions are Mg^{2+} and O^{2-} , so the formula for magnesium oxide is MgO. (You probably already knew the formulas of these ions, but we’re showing how you can apply previous knowledge to the problem at hand.) The reactants are magnesium, Mg, and molecular oxygen, O_2 . The equation for the reaction is therefore



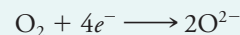
Now that we have the equation and the formulas of the ions we can determine how electrons are exchanged.

SOLUTION: When a magnesium atom becomes a magnesium ion, it must lose two electrons. Because electrons are lost in this process, they appear on the right when we express it as an equation.



By losing electrons, *magnesium is oxidized*. This also means that *Mg must be the reducing agent*.

When oxygen reacts to yield O^{2-} ions, each oxygen atom must gain two electrons, so an O_2 molecule must gain four electrons. Because electrons are gained, they appear on the left in the equation.



By gaining electrons, *O_2 is reduced and must be the oxidizing agent*.

ARE THE ANSWERS REASONABLE? There are two things we can do to check our answers. First, we can check to be sure that we’ve placed electrons on the correct sides of the equations. As with ionic equations, *the number of atoms of each kind and the net charge must be the same on both sides*. We see that this is true for both equations. (If we had placed the electrons on the wrong side, the charges would not balance.) By observing the locations of the electrons in the equations (on the right for oxidation; on the left for reduction), we come to the same conclusions that Mg is oxidized and O_2 is reduced.

Another check is noting that we’ve identified one substance as being oxidized and the other as being reduced. If we had made a mistake, we might have concluded that both were oxidized, or both were reduced. But that’s impossible, because in every reaction in which there is oxidation, there must also be reduction.



Fireworks display over Washington, D.C. (Pete Saloutos/Corbis Images.)

178 Chapter 5 Oxidation-Reduction Reactions

Practice Exercise 1: When sodium reacts with molecular oxygen, O_2 , the product is sodium peroxide, Na_2O_2 , which contains the peroxide ion, O_2^{2-} . In this reaction, is O_2 oxidized or reduced? (Hint: Which reactant gains electrons, and which loses electrons?)

Practice Exercise 2: Identify the substances oxidized and reduced and the oxidizing and reducing agents in the reaction of aluminum and chlorine to form aluminum chloride.

Oxidation numbers are used to follow redox changes

Unlike the reaction of magnesium with oxygen, not all reactions with oxygen produce ionic products. For example, sulfur reacts with oxygen to give sulfur dioxide, SO_2 , which is molecular. Nevertheless, it is convenient to also view this as a redox reaction, but this requires that we change the way we define oxidation and reduction. To do this, chemists developed a bookkeeping system called **oxidation numbers**, which provides a way to keep tabs on electron transfers.

The oxidation number of an element in a particular compound is assigned according to a set of rules, which are described below. For simple, monatomic ions in a compound such as $NaCl$, the oxidation numbers are the same as the charges on the ions, so in $NaCl$ the oxidation number of Na^+ is $+1$ and the oxidation number of Cl^- is -1 . The real value of oxidation numbers is that they can also be assigned to atoms in molecular compounds. In such cases, it is important to realize that the oxidation number does not actually equal a charge on an atom. To be sure to differentiate oxidation numbers from actual electrical charges, we will specify the sign *before* the number when writing oxidation numbers, and *after* the number when writing electrical charges. Thus, a sodium ion has a charge of $1+$ and an oxidation number of $+1$.

A term that is frequently used interchangeably with *oxidation number* is **oxidation state**. In $NaCl$, sodium has an oxidation number of $+1$ and is said to be “in the $+1$ oxidation state.” Similarly, the chlorine in $NaCl$ is said to be in the -1 oxidation state. There are times when it is convenient to specify the oxidation state of an element when its name is written out. This is done by writing the oxidation number as a Roman numeral in parentheses after the name of the element. For example, “iron(III)” means iron in the $+3$ oxidation state.

We can use these new terms now to redefine a redox reaction.

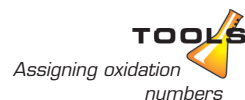
A **redox reaction** is a chemical reaction in which changes in oxidation numbers occur.

We will find it easy to follow redox reactions by taking note of the changes in oxidation numbers. To do this, however, we must be able to assign oxidation numbers to atoms in a quick and simple way.

Rules permit assignment of oxidation numbers to almost any atom

We can use some basic knowledge learned earlier plus the set of rules below to determine the oxidation numbers of the atoms in almost any compound.

▣ Oxidation numbers are sometimes written as a superscript using Roman numerals. Thus S^{VI} stands for sulfur in the $+6$ oxidation state.



Rules for Assigning Oxidation Numbers

1. The oxidation number of any *free element* (an element not combined chemically with a different element) is zero, regardless of how complex its molecules are.
2. The oxidation number for any simple, monatomic ion (e.g., Na^+ or Cl^-) is equal to the charge on the ion. The charge on a polyatomic ion can be viewed as the *net* oxidation number of the ion.
3. The sum of all the oxidation numbers of the atoms in a molecule or polyatomic ion must equal the charge on the particle.
4. In its compounds, fluorine has an oxidation number of -1 .
5. In its compounds, hydrogen has an oxidation number of $+1$.
6. In its compounds, oxygen has an oxidation number of -2 .

▣ Rule 1 means that O in O_2 , P in P_4 , and S in S_8 all have oxidation numbers of zero.

5.1 Oxidation–Reduction Reactions Involve Electron Transfer 179

As you will see shortly, occasionally there is a conflict between two of these rules. When this happens, *we apply the rule with the lower number and ignore the conflicting rule.*

In addition to these basic rules, there is some other chemical knowledge you will need to remember. Recall that we can use the periodic table to help us remember the charges on certain ions of the elements. For instance, all the metals in Group IA form ions with a 1+ charge, and all those in Group IIA form ions with a 2+ charge. This means that when we find sodium in a compound, we can assign it an oxidation number of +1 because its simple ion, Na^+ , has a charge of 1+. (We have applied Rule 2.) Similarly, calcium in a compound exists as Ca^{2+} and has an oxidation number of +2.

In binary ionic compounds with metals, the nonmetals have oxidation numbers equal to the charges on their anions (Table 2.6 on page 65). For example, the compound Fe_2O_3 contains the oxide ion, O^{2-} , which is assigned an oxidation number of -2 . Similarly, Mg_3P_2 contains the phosphide ion, P^{3-} , which has an oxidation number of -3 .

The numbered rules given above usually come into play when an element is capable of having more than one oxidation state. For example, you learned that transition metals can form more than one ion. Iron, for example, forms Fe^{2+} and Fe^{3+} ions, so in an iron compound we have to use the rules to figure out which iron ion is present. Similarly, when nonmetals are combined with hydrogen and oxygen in compounds or polyatomic ions, their oxidation numbers can vary and must be calculated using the rules.

With this as background, let's look at some examples that illustrate how we apply the rules, especially when they don't explicitly cover all the atoms in a formula.

EXAMPLE 5.2
 Assigning Oxidation Numbers

Titanium dioxide, TiO_2 , is a white pigment used in making paint. A now outmoded process of making TiO_2 from its ore involved $\text{Ti}(\text{SO}_4)_2$ as an intermediate. What is the oxidation number of titanium in $\text{Ti}(\text{SO}_4)_2$?

ANALYSIS: The key here is recognizing SO_4 as the sulfate ion, SO_4^{2-} . Once we know this, the rest is straightforward. Because we're only interested in the oxidation number of titanium, we use the charge on SO_4^{2-} to equal the net oxidation number of the ion (Rule 2).

SOLUTION: The sulfate ion has a charge of $2-$, which we can take to be its net oxidation number. Then we apply the summation rule (Rule 3) to find the oxidation number of titanium, which we will represent by x .

$$\begin{array}{rcl} \text{Ti} & (1 \text{ atom}) \times (x) & = x \\ \text{SO}_4^{2-} & (2 \text{ ions}) \times (-2) & = -4 \\ \hline & \text{Sum} & = 0 \quad (\text{Rule 3}) \end{array}$$

Obviously, the oxidation number of titanium is $+4$ so that the sum can be zero.

IS THE ANSWER REASONABLE? We have the sum of oxidation numbers adding up to zero, the charge on $\text{Ti}(\text{SO}_4)_2$, so our answer is okay.

EXAMPLE 5.3
 Assigning Oxidation Numbers

Determine the oxidation numbers of the atoms in hydrogen peroxide, H_2O_2 , a common antiseptic purchased in pharmacies.

ANALYSIS: The compound is molecular, so there are no ions to work with. Scanning the rules, we see we have one for hydrogen and another for oxygen. However, we begin to see we have a conflict between two of the rules. Rule 5 tells us to assign an oxidation number of $+1$

180 Chapter 5 Oxidation-Reduction Reactions



Hydrogen peroxide destroys bacteria by oxidizing them. (Robert Capece.)

to hydrogen, and Rule 6 tells us to give oxygen an oxidation number of -2 . Both of these can't be correct because the sum must be zero (Rule 3).

$$\begin{array}{rcl} \text{H} & (2 \text{ atoms}) \times (+1) = & +2 \quad (\text{Rule 5}) \\ \text{O} & (2 \text{ atoms}) \times (-2) = & -4 \quad (\text{Rule 6}) \\ \hline & \text{Sum} \neq & 0 \quad (\text{violates Rule 3}) \end{array}$$

As mentioned above, when there is a conflict between the rules, we ignore the higher numbered rule that causes the conflict.

SOLUTION: Rule 6 is the higher numbered rule causing the conflict, so we have to ignore it this time and just apply Rules 3 (the sum rule) and 5 (the rule that tells us the oxidation number of hydrogen is $+1$). Because we don't have a rule that applies to oxygen in this case, we'll represent the oxidation number of O by x .

$$\begin{array}{rcl} \text{H} & (2 \text{ atoms}) \times (+1) = & +2 \quad (\text{Rule 5}) \\ \text{O} & (2 \text{ atoms}) \times (x) = & 2x \\ \hline & \text{Sum} = & 0 \quad (\text{Rule 3}) \end{array}$$

For the sum to be zero, $2x = -2$, so $x = -1$. Therefore, in this compound, oxygen has an oxidation number of -1 .

$$\text{H} = +1 \quad \text{O} = -1$$

IS THE ANSWER REASONABLE? A conflict between the rules occurs only rarely, but when it happens the conflict becomes apparent because it causes a violation of the sum rule. However, *the sum rule always applies*, so the answer is reasonable.

Sometimes, oxidation numbers calculated by the rules have fractional values, as illustrated in the next example.

EXAMPLE 5.4 Assigning Oxidation Numbers



The explosive decomposition of sodium azide releases nitrogen gas, which rapidly inflates an air bag during a crash. (Corbis-Bettmann.)

The air bags used as safety devices in modern autos are inflated by the very rapid decomposition of the ionic compound sodium azide, NaN_3 . The reaction gives elemental sodium and gaseous nitrogen. What is the average oxidation number of the nitrogen in sodium azide?

ANALYSIS: We're told that NaN_3 is ionic, so we know there is a cation and an anion. The cation is the sodium ion, Na^+ , which means that the remainder of the formula unit, " N_3 ," must carry one unit of negative charge. However, there could not be three nitrogen anions each with a charge of $-\frac{1}{3}$ because it would mean that each nitrogen atom had acquired one-third of an electron. Whole numbers of electrons are always involved in electron transfers. Therefore, the anion must be a single particle with a negative one charge, namely, N_3^- . For this anion, the sum of the oxidation numbers of the three nitrogens must be -1 . We can use this information, now, to solve the problem.

SOLUTION: The sum of the oxidation numbers of the nitrogen must be equal to -1 . If we let x stand for the oxidation number of just one of the nitrogens, then

$$\begin{aligned} (3 \text{ atoms}) \times (x) &= 3x = -1 \\ x &= -\frac{1}{3} \end{aligned}$$

We could have also tackled the problem just using the rules for assigning oxidation numbers. We know that sodium exists as the ion Na^+ and that the compound is neutral overall. Therefore,

$$\begin{array}{rcl} \text{Na} & (1 \text{ atom}) \times (+1) = & +1 \quad (\text{Rule 2}) \\ \text{N} & (3 \text{ atoms}) \times (x) = & 3x \\ \hline & \text{Sum} = & 0 \quad (\text{Rule 3}) \end{array}$$

5.1 Oxidation–Reduction Reactions Involve Electron Transfer 181

The sum of the oxidation numbers of the three nitrogen atoms in this ion must add up to -1 , so each nitrogen must have an oxidation number of $-\frac{1}{3}$.

IS THE ANSWER REASONABLE? We've solved this example two ways, so we can certainly feel confident the answer is correct.

Practice Exercise 3: Chlorite ion, ClO_2^- , has been shown to be a potent disinfectant, and solutions of it are sometimes used to disinfect air-conditioning systems in cars. What is the oxidation number of chlorine in this ion? (Hint: The sum of the oxidation numbers is not zero.)

Practice Exercise 4: Assign oxidation numbers to each atom in (a) NiCl_2 , (b) Mg_2TiO_4 , (c) $\text{K}_2\text{Cr}_2\text{O}_7$, (d) HPO_4^{2-} , and (e) $\text{V}(\text{C}_2\text{H}_3\text{O}_2)_3$.

Practice Exercise 5: Iron forms a magnetic oxide with the formula Fe_3O_4 that contains both Fe^{2+} and Fe^{3+} ions. What is the *average* oxidation number of iron in this oxide?

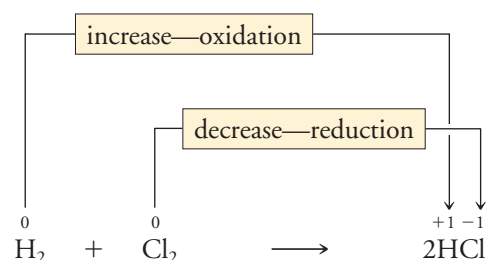
Oxidation numbers are used to identify oxidation and reduction

Oxidation numbers can be used in several ways. One is to define oxidation and reduction in the most comprehensive manner, as follows:

Oxidation is an increase in oxidation number.

Reduction is a decrease in oxidation number.

Let's see how these definitions apply to the reaction of hydrogen with chlorine. To avoid ever confusing oxidation numbers with actual electrical charges, we will write oxidation numbers directly above the chemical symbols of the elements.

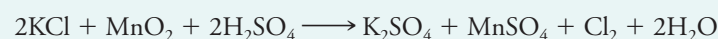


Notice that we have assigned the atoms in H_2 and Cl_2 oxidation numbers of zero, in accord with Rule 1. The changes in oxidation number tell us that hydrogen is oxidized and chlorine is reduced.

EXAMPLE 5.5

Using Oxidation Numbers to Follow Redox Reactions

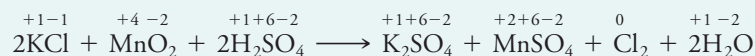
Is the following a redox reaction? If so, identify the substance oxidized and the substance reduced as well as the oxidizing and reducing agents.



ANALYSIS: To determine whether the reaction is redox and to give the specific answers requested, our tools will be the rules for assigning oxidation numbers and the revised definitions of oxidation and reduction. This will tell us whether redox is occurring, and if so, what is oxidized and reduced. Then we recall that the substance oxidized is the reducing agent, and the substance reduced is the oxidizing agent.

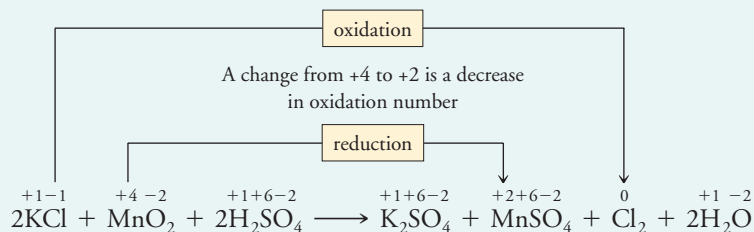
182 Chapter 5 Oxidation-Reduction Reactions

SOLUTION: To determine whether redox is occurring here, we first must assign oxidation numbers to each atom on both sides of the equation. Following the rules, we get



Next we look for changes, keeping in mind that an increase in oxidation number is oxidation and a decrease is reduction.

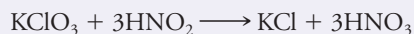
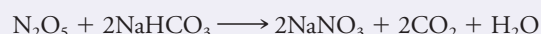
A change from -1 to 0 is going up the number scale, so it's an increase in oxidation number



Thus the Cl in KCl is oxidized and the Mn in MnO_2 is reduced. The reducing agent is KCl and the oxidizing agent is MnO_2 . (Notice that when we identify the oxidizing and reducing agents, we give the entire formulas for the substances that contain the atoms with oxidation numbers that change.)

IS THE ANSWER REASONABLE? There are lots of things we could check here. We have found changes that lead us to conclude that redox is happening. Assigning oxidation numbers also allows us to identify one change as oxidation and the other as reduction, which gives us confidence that we've done the rest of the work correctly.

Practice Exercise 6: Consider the following reactions:



Which one is a redox reaction? For the redox reaction, which compound is oxidized and which is reduced? (Hint: How is redox defined using oxidation numbers?)

Practice Exercise 7: Chlorine dioxide, ClO_2 , is used to kill bacteria in the dairy industry, meat industry, and other food and beverage industry applications. It is unstable, but can be made by the following reaction.



Identify the substances oxidized and reduced as well as the oxidizing and reducing agents in the reaction.

Practice Exercise 8: When hydrogen peroxide is used as an antiseptic, it kills bacteria by oxidizing them. When the H_2O_2 serves as an oxidizing agent, which product might be formed from it, O_2 or H_2O ? Why?

5.2 THE ION-ELECTRON METHOD CREATES BALANCED NET IONIC EQUATIONS FOR REDOX REACTIONS

Many redox reactions take place in aqueous solution and many of these involve ions; they are ionic reactions. An example is the reaction of laundry bleach with substances in the wash water. The active ingredient in the bleach is hypochlorite ion, OCl^- , which is the oxidizing agent in these reactions. To study redox reactions, it is often helpful to write ionic and net ionic equations, just as we did in our analysis of metathesis reactions earlier in Chapter 4. Balancing net ionic equations for redox reactions is especially easy if we follow a procedure called the ion–electron method.

5.2 The Ion–Electron Method Creates Balanced Net Ionic Equations for Redox Reactions 183

The ion–electron method uses a divide and conquer approach

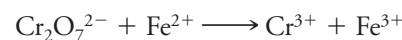
In the **ion–electron method**, we divide the oxidation and reduction processes into individual equations called **half-reactions** that are balanced separately. Each half-reaction is made to obey *both* criteria for a balanced ionic equation: *both atoms and charge have to balance*. Then we combine the balanced half-reactions to obtain the fully balanced net ionic equation.

In balancing the half-reactions, we must take into account that for many redox reactions in aqueous solutions, H^+ or OH^- ions play an important role, as do water molecules. For example, when solutions of $\text{K}_2\text{Cr}_2\text{O}_7$ and FeSO_4 are mixed, the acidity of the mixture decreases as dichromate ion, $\text{Cr}_2\text{O}_7^{2-}$, oxidizes Fe^{2+} (Figure 5.2). This is because the reaction uses up H^+ as a reactant and produces H_2O as a product. In other reactions, OH^- is consumed, while in still others H_2O is a reactant. Another fact is that in many cases the products (or even the reactants) of a redox reaction will differ depending on the acidity of the solution. For example, in an acidic solution MnO_4^- is reduced to Mn^{2+} ion, but in a neutral or slightly basic solution, the reduction product is insoluble MnO_2 .

Because of these factors, redox reactions are generally carried out in solutions containing a substantial excess of either acid or base, so before we can apply the ion–electron method, we have to know whether the reaction occurs in an acidic or a basic solution. (This information will always be given to you in this book.)

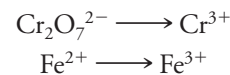
 H^+ and H_2O help balance redox equations for acidic solutions

As you just learned, $\text{Cr}_2\text{O}_7^{2-}$ reacts with Fe^{2+} in an acidic solution to give Cr^{3+} and Fe^{3+} as products. This information permits us to write the **skeleton equation**, which shows only the ions (or sometimes molecules, too) involved in the redox changes.

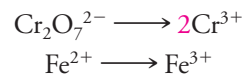


We then proceed through the steps described below to find the balanced equation. As you will see, the ion–electron method will tell us how H^+ and H_2O are involved in the reaction; we don't need to know this in advance.

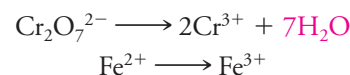
Step 1. Divide the skeleton equation into half-reactions. We choose one of the reactants, let's say $\text{Cr}_2\text{O}_7^{2-}$, and write it at the left of an arrow. On the right, we write what $\text{Cr}_2\text{O}_7^{2-}$ changes to, which is Cr^{3+} . This gives us the beginnings of one half-reaction. For the second half-reaction, we write the other reactant, Fe^{2+} , on the left and the other product, Fe^{3+} , on the right. *Notice we are careful to use the complete formulas for the ions that appear in the skeleton equation.* Except for hydrogen and oxygen, the same elements must appear on both sides of a given half-reaction.



Step 2. Balance atoms other than H and O. There are two Cr atoms on the left and only one on the right, so we place a coefficient of 2 in front of Cr^{3+} . The second half-reaction is already balanced in terms of atoms, so we leave it “as is.”



Step 3. Balance oxygen by adding H_2O to the side that needs O. There are seven oxygen atoms on the left of the first half-reaction and none on the right. Therefore, we add $7\text{H}_2\text{O}$ to the right side of the first half-reaction to balance the oxygens. (There is no oxygen imbalance in the second half-reaction, so there's nothing to do there.)



The oxygen atoms now balance, but we've created an imbalance in hydrogen. That issue is addressed next.

Equations for redox reactions are often more complex than those for metathesis reactions and can be difficult to balance by inspection. The ion–electron method is a systematic procedure for balancing redox equations.



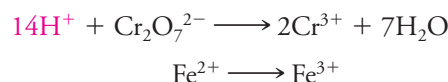
FIG. 5.2 A redox reaction taking place in an acidic solution. A solution of $\text{K}_2\text{Cr}_2\text{O}_7$ oxidizes Fe^{2+} to Fe^{3+} in an acidic solution. At the same time, the orange dichromate ion is reduced to Cr^{3+} . (Peter Lerman.)

Many students tend to forget this step. If you do, you may end up in trouble later on.

We use H_2O , not O or O_2 , to balance oxygen atoms because H_2O is what is actually present in the solution.

184 Chapter 5 Oxidation-Reduction Reactions

Step 4. Balance hydrogen by adding H^+ to the side that needs H. After adding the water, we see that the first half-reaction has 14 hydrogens on the right and none on the left. To balance hydrogen, we add $14H^+$ to the left side of the half-reaction. When you do this step (or others) *be careful to write the charges on the ions*. If they are omitted, you will not obtain a balanced equation in the end.

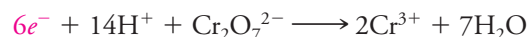


Now each half-reaction is balanced in terms of atoms. Next we will balance the charge.

Step 5. Balance the charge by adding electrons. First we compute the net electrical charge on each side. For the first half-reaction we have

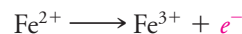


The algebraic difference between the net charges on the two sides equals the number of electrons that must be added to the more positive (or less negative) side. In this instance, we must add $6e^-$ to the left side of the half-reaction.

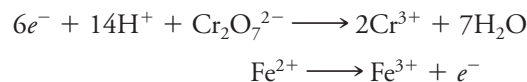


This half-reaction is now complete; it is balanced in terms of both atoms and charge. (We can check this by recalculating the charge on both sides.)

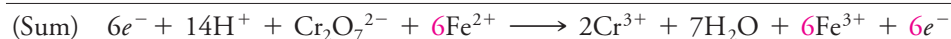
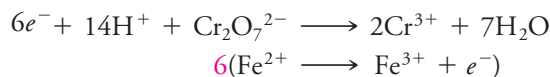
To balance the other half-reaction, we add one electron to the right.



Step 6. Make the number of electrons gained equal to the number lost and then add the two half-reactions. At this point we have the two balanced half-reactions



Six electrons are gained in the first, but only one is lost in the second. Therefore, before combining the two equations we multiply all of the coefficients of the second half-reaction by 6.



Step 7. Cancel anything that is the same on both sides. This is the final step. Six electrons cancel from both sides to give the final balanced equation.



Notice that both the charge and the atoms balance.

In some reactions, after adding the two half-reactions you may have H_2O or H^+ on both sides—for example, $6H_2O$ on the left and $2H_2O$ on the right. Cancel as many as you can. Thus,



reduces to



The following is a summary of the steps we've followed for balancing an equation for a redox reaction in an acidic solution. If you don't skip any steps and you perform them in the order given, you will always obtain a properly balanced equation.

■ Because we know the electrons will cancel, we really don't have to carry them down into the combined equation. We've done so here just for emphasis.

5.2 The Ion–Electron Method Creates Balanced Net Ionic Equations for Redox Reactions 185

Ion–Electron Method—Acidic Solution

- Step 1. Divide the equation into two half-reactions.
 Step 2. Balance atoms other than H and O.
 Step 3. Balance O by adding H₂O.
 Step 4. Balance H by adding H⁺.
 Step 5. Balance net charge by adding e⁻.
 Step 6. Make e⁻ gain equal e⁻ loss; then add half-reactions.
 Step 7. Cancel anything that's the same on both sides.

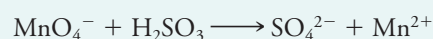


TOOLS
 Ion–electron method for
 acidic solutions

EXAMPLE 5.6

Using the Ion–Electron Method

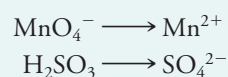
Balance the following equation. The reaction occurs in an acidic solution.



ANALYSIS: In using the ion–electron method, there's not much to analyze. It's necessary to know the steps and to follow them in sequence.

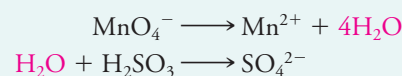
SOLUTION: We follow the steps given above.

Step 1. Divide the skeleton equation into half-reactions.

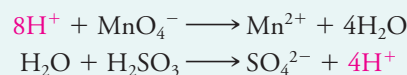


Step 2. There is nothing to do for this step. All the atoms except H and O are already in balance.

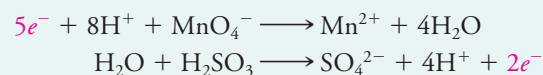
Step 3. Add H₂O to balance oxygens.



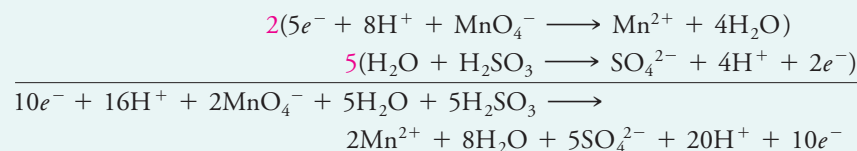
Step 4. Add H⁺ to balance H.



Step 5. Balance charge by adding electrons to the more positive side.



Step 6. Make electron loss equal to electron gain, then add half-reactions



Step 7. Cancel 10e⁻, 16H⁺, and 5H₂O from both sides. The final equation is



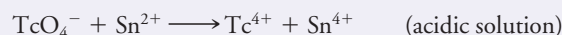
IS THE ANSWER REASONABLE? The check involves *two* steps. First, we check that each side of the equation has the same number of atoms of each element, which it does. Second, we check to be sure that the net charge is the same on both sides. On the left we have 2MnO₄⁻ with a net charge of 2-. On the right we have 2Mn²⁺ and 4H⁺ (total charge = 8+) along with 5SO₄²⁻ (total charge = 10-), so the net charge is also 2-. Having both atoms *and* charge in balance makes it a balanced equation and confirms that we've worked the problem correctly.

186 Chapter 5 Oxidation-Reduction Reactions

Practice Exercise 9: Explain why the following equation is not balanced. Balance it using the ion–electron method. (Hint: What are the criteria for a balanced ionic equation?)



Practice Exercise 10: The element technetium (atomic number 43) is radioactive and one of its isotopes, ^{99}Tc , is used in medicine for diagnostic imaging. The isotope is usually obtained in the form of the pertechnetate anion, TcO_4^- , but its use sometimes requires the technetium to be in a lower oxidation state. Reduction can be carried out using Sn^{2+} in an acidic solution. The skeleton equation is



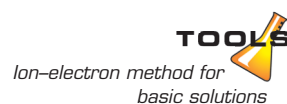
Balance the equation by the ion–electron method.

Practice Exercise 11: What is the balanced net ionic equation for the following reaction in an acidic solution?



Additional steps produce balanced equations for basic solutions

In a basic solution, the concentration of H^+ is very small; the dominant species are H_2O and OH^- . Strictly speaking, these should be used to balance the half-reactions. However, the simplest way to obtain a balanced equation for a basic solution is to first *pretend* that the solution is acidic. We balance the equation using the seven steps just described, and then we use a simple three-step procedure described below to convert the equation to the correct form for a basic solution. The conversion uses the fact that H^+ and OH^- react in a 1-to-1 ratio to give H_2O .



Additional Steps in the Ion–Electron Method for Basic Solutions

Step 8. Add to *both* sides of the equation the same number of OH^- as there are H^+ .

Step 9. Combine H^+ and OH^- to form H_2O .

Step 10. Cancel any H_2O that you can.

As an example, suppose we wanted to balance the following equation for a basic solution.



Following Steps 1 through 7 for acidic solutions gives



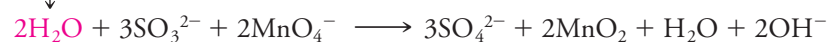
Conversion of this equation to one appropriate for a basic solution proceeds as follows.

Step 8. Add to *both* sides of the equation the same number of OH^- as there are H^+ .

The equation for acidic solution has 2H^+ on the left, so we add 2OH^- to *each* side. This gives



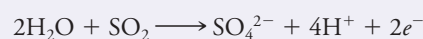
Step 9. Combine H^+ and OH^- to form H_2O . The left side has 2OH^- and 2H^+ , which become $2\text{H}_2\text{O}$. So in place of $2\text{OH}^- + 2\text{H}^+$ we write $2\text{H}_2\text{O}$.



Step 10. Cancel any H_2O that you can. In this equation, one H_2O can be eliminated from both sides. The final equation, balanced for basic solution, is



Practice Exercise 12: Consider the following half-reaction balanced for an acidic solution:



What is the balanced half-reaction for a basic solution? (Hint: Remember that H^+ and OH^- react to form H_2O .)

Practice Exercise 13: Balance the following equation for a basic solution.



5.3 METALS ARE OXIDIZED WHEN THEY REACT WITH ACIDS

Earlier you learned that one of the properties of acids is that they react with bases. Another important property is their ability to react with certain metals. These are redox reactions in which the metal is oxidized and the acid is reduced. But in these reactions, the part of the acid that's reduced depends on the composition of the acid itself as well as on the metal.

When a piece of zinc is placed into a solution of hydrochloric acid, bubbling is observed and the zinc gradually dissolves (Figure 5.3). The chemical reaction is



for which the net ionic equation is



In this reaction, zinc is oxidized and hydrogen ions are reduced. Stated another way, *the H^+ of the acid is the oxidizing agent.*

Many metals react with acids just as zinc does—by being oxidized by hydrogen ions. In these reactions a metal salt and gaseous hydrogen are the products.

Metals that are able to react with acids such as HCl and H_2SO_4 to give hydrogen gas are said to be *more active* than hydrogen (H_2). For other metals, however, hydrogen ions are not powerful enough to cause their oxidation. Copper, for example, is significantly less reactive than zinc or iron, and H^+ cannot oxidize it. Copper is an example of a metal that is *less active* than H_2 .

The oxidizing power of an acid depends on the nature of the anion

Hydrochloric acid contains H_3O^+ ions (which we abbreviate as H^+) and Cl^- ions. The hydrogen ion in hydrochloric acid is able to be an oxidizing agent by being reduced to H_2 . However, the Cl^- ion in the solution has no tendency at all to be an oxidizing agent, so in a solution of HCl the only oxidizing agent is H^+ . The same applies to dilute solutions of sulfuric acid, H_2SO_4 .

The hydrogen ion in water is actually a rather poor oxidizing agent, so hydrochloric acid and sulfuric acid have rather poor oxidizing abilities. They are often called **nonoxidizing acids**, even though their hydrogen ions are able to oxidize certain metals. (When we call something a nonoxidizing acid, we mean the *anion* of the acid is a weaker oxidizing agent than H^+ and that the anion of the acid is more difficult to reduce than H^+ .) Some acids contain anions that are stronger oxidizing agents than H^+ and are called **oxidizing acids**. (See Table 5.1.)

Nitric acid is a powerful oxidizing agent

Nitric acid, HNO_3 , ionizes in water to give H^+ and NO_3^- ions. In this solution the nitrate ion is a more powerful oxidizing agent than the hydrogen ion. This makes it able to oxidize metals that H^+ cannot, such as copper and silver. For example, the molecular equation for the reaction of concentrated HNO_3 with copper, shown in Figure 5.4, is

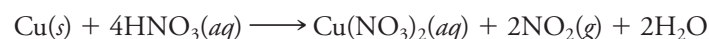


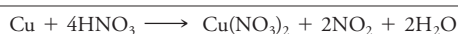
FIG. 5.3 Zinc reacts with hydrochloric acid. Bubbles of hydrogen are formed when a solution of hydrochloric acid comes in contact with metallic zinc. The same reaction takes place if hydrochloric acid is spilled on galvanized (zinc coated) steel. (Andy Washmik.)

■ The strongest oxidizing agent in a solution of a “nonoxidizing” acid is H^+ .

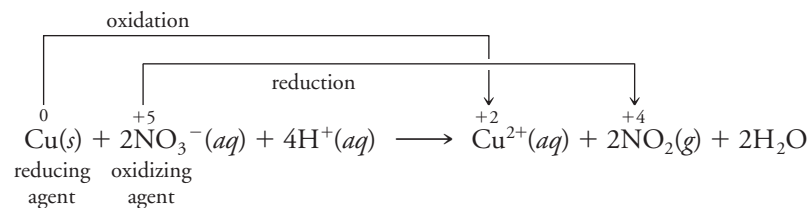
188 Chapter 5 Oxidation-Reduction Reactions

**TABLE 5.1** Nonoxidizing and Oxidizing Acids

Nonoxidizing Acids	
HCl(aq)	
H ₂ SO ₄ (aq) ^a	
H ₃ PO ₄ (aq)	
Most organic acids (e.g., HC ₂ H ₃ O ₂)	
Oxidizing Acids	Reduction reaction
HNO ₃	(conc.) NO ₃ ⁻ + 2H ⁺ + e ⁻ → NO ₂ (g) + H ₂ O
	(dilute) NO ₃ ⁻ + 4H ⁺ + 3e ⁻ → NO(g) + 2H ₂ O
	(very dilute, with strong reducing agent) NO ₃ ⁻ + 10H ⁺ + 8e ⁻ → NH ₄ ⁺ + 3H ₂ O
H ₂ SO ₄	(hot, conc.) SO ₄ ²⁻ + 4H ⁺ + 2e ⁻ → SO ₂ (g) + 2H ₂ O
	(hot, conc., with strong reducing agent) SO ₄ ²⁻ + 10H ⁺ + 8e ⁻ → H ₂ S(g) + 4H ₂ O

^aH₂SO₄ is a nonoxidizing acid when cold and dilute.**FIG. 5.4** The reaction of copper with concentrated nitric acid. A copper penny reacts vigorously with concentrated nitric acid, as this sequence of photographs shows. The dark red brown vapors are nitrogen dioxide, the same gas that gives smog its characteristic color. (Michael Watson.)

If we convert this to a net ionic equation and then assign oxidation numbers, we can see that NO₃⁻ is the oxidizing agent and Cu is the reducing agent.



Notice that in this reaction, *no hydrogen gas is formed*. The H⁺ ions of the HNO₃ are an essential part of the reaction, but they just become part of water molecules without a change in oxidation number.

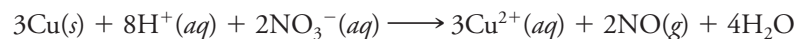
The nitrogen-containing product formed in the reduction of nitric acid depends on the concentration of the acid and the reducing power of the metal. With *concentrated* nitric acid, nitrogen dioxide, NO₂, is often the reduction product. With *dilute* nitric acid the product is often nitrogen monoxide (also called nitric oxide), NO, instead. Copper, for example, reacts as follows:

Concentrated HNO₃



5.4 A More Active Metal Will Displace a Less Active One from Its Compounds 189

Dilute HNO_3



Nitric acid is a very effective oxidizing acid. All metals except the most unreactive ones, such as platinum and gold, are attacked by it. Nitric acid also does a good job of oxidizing organic compounds, so it is wise to be especially careful when working with this acid in the laboratory. Very serious accidents have occurred when inexperienced people have used concentrated nitric acid around organic substances.

■ Nitric acid causes severe skin burns, so be careful when you work with it in the laboratory. If you spill any on your skin, wash it off immediately and seek the help of your lab teacher.

Hot concentrated sulfuric acid is an oxidizing acid

In a dilute solution, the sulfate ion of sulfuric acid has little tendency to serve as an oxidizing agent. However, if the sulfuric acid is both concentrated and hot, it becomes a fairly potent oxidizer. For example, copper is not bothered by cool dilute H_2SO_4 , but it is attacked by hot concentrated H_2SO_4 according to the following equation:



Because of this oxidizing ability, hot concentrated sulfuric acid can be very dangerous. The liquid is viscous and can stick to the skin, causing severe burns.

Practice Exercise 14: Write the balanced half-reactions for the reaction of zinc with hydrogen ions. (Hint: Be sure to place the electrons on the correct sides of the half-reactions.)

Practice Exercise 15: When very dilute nitric acid reacts with a strong oxidizing agent such as magnesium, the nitrate ion is reduced to ammonium ion. Write a balanced net ionic equation for the reaction.

Practice Exercise 16: Write balanced molecular, ionic, and net ionic equations for the reaction of hydrochloric acid with (a) magnesium and (b) aluminum. (Both metals are oxidized by hydrogen ions.)

5.4

A MORE ACTIVE METAL WILL DISPLACE A LESS ACTIVE ONE FROM ITS COMPOUNDS

The formation of hydrogen gas in the reaction of a metal with an acid is a special case of a more general phenomenon—one element displacing (pushing out) another element from a compound by means of a redox reaction. In the case of a metal–acid reaction, it is the metal that displaces hydrogen from the acid, changing 2H^+ to H_2 .

Another reaction of this same general type occurs when one metal displaces another metal from its compounds, and is illustrated by the experiment shown in Figure 5.5. Here we see a brightly polished strip of metallic zinc that is dipped into a solution of copper sulfate. After the zinc is in the solution for a while, a reddish brown deposit of metallic copper forms on the zinc, and if the solution were analyzed, we would find that it now contains zinc ions, as well as some remaining unreacted copper ions.

The results of this experiment can be summarized by the following net ionic equation.



Metallic zinc is oxidized as copper ion is reduced. In the process, Zn^{2+} ions have taken the place of the Cu^{2+} ions, so a solution of copper sulfate is changed to a solution of zinc sulfate. An atomic-level view of what's happening at the surface of the zinc during the reaction is depicted in Figure 5.6. A reaction such as this, in which one element replaces another in a compound, is sometimes called a **single replacement reaction**.

■ Sulfate ion is a spectator ion in this reaction.

The activity series arranges metals according to their ease of oxidation

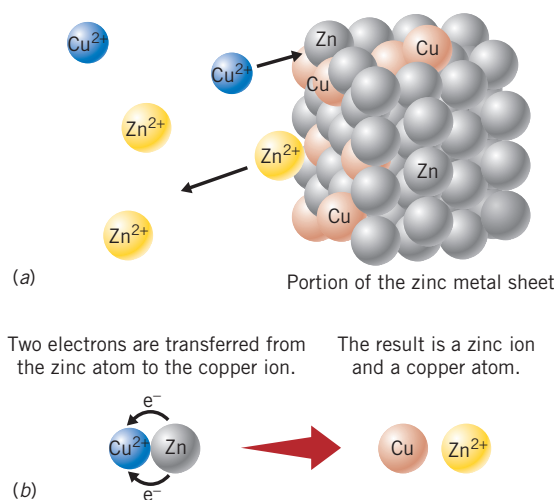
In the reaction of zinc with copper ion, the more “active” zinc displaces the less “active” copper in a compound, where we have used the word *active* to mean “easily oxidized.” This is actually a general phenomenon: *an element that is more easily oxidized will displace one that is less*

190 Chapter 5 Oxidation-Reduction Reactions



FIG. 5.5 The reaction of zinc with copper ion. (*Left*) A piece of shiny zinc next to a beaker containing a copper sulfate solution. (*Center*) When the zinc is placed in the solution, copper ions are reduced to the free metal while the zinc dissolves. (*Right*) After a while the zinc becomes coated with a red-brown layer of copper. Notice that the solution is a lighter blue than before, showing that some of the copper ions have left the solution. (*Michael Watson.*)

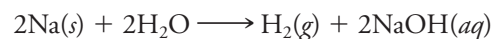
FIG. 5.6 The reaction of copper ions with zinc, viewed at the atomic level. (a) Copper ions (blue) collide with the zinc surface where they pick up electrons from zinc atoms (gray). The zinc atoms become zinc ions (yellow) and enter the solution. The copper ions become copper atoms (red-brown) and stick to the surface of the zinc. (For clarity, the water molecules of the solution and the sulfate ions are not shown.) (b) A close-up view of the exchange of electrons that leads to the reaction.



easily oxidized from its compounds. By comparing the relative ease of oxidation of various metals using experiments like the one pictured in Figure 5.5, we can arrange metals in order of their ease of oxidation. This yields the **activity series** shown in Table 5.2. In this table, metals at the bottom are more easily oxidized (are more active) than those at the top. *This means that a given element will be displaced from its compounds by any metal below it in the table.*

Notice that we have included hydrogen in the activity series. Metals below hydrogen in the series can displace hydrogen from solutions containing H^+ . These are the metals that are capable of reacting with nonoxidizing acids. On the other hand, metals above hydrogen in the table do not react with acids having H^+ as the strongest oxidizing agent.

Metals at the very bottom of the table are very easily oxidized and are extremely strong reducing agents. They are so reactive, in fact, that they are able to reduce the hydrogen in water molecules. Sodium, for example, reacts vigorously (see Figure 5.7).



For metals below hydrogen in the activity series, there's a parallel between the ease of oxidation of the metal and the speed with which it reacts with H^+ . For example, in

5.4 A More Active Metal Will Displace a Less Active One from Its Compounds 191

TABLE 5.2 Activity Series for Some Metals (and Hydrogen)

	Element	Oxidation Product
Least Active	Gold	Au^{3+}
	Mercury	Hg^{2+}
	Silver	Ag^+
	Copper	Cu^{2+}
	HYDROGEN	H^+
	Lead	Pb^{2+}
	Tin	Sn^{2+}
	Cobalt	Co^{2+}
	Cadmium	Cd^{2+}
	Iron	Fe^{2+}
	Chromium	Cr^{3+}
	Zinc	Zn^{2+}
	Manganese	Mn^{2+}
	Aluminum	Al^{3+}
	Magnesium	Mg^{2+}
	Sodium	Na^+
	Calcium	Ca^{2+}
Strontium	Sr^{2+}	
Barium	Ba^{2+}	
Potassium	K^+	
Rubidium	Rb^+	
Most Active	Cesium	Cs^+

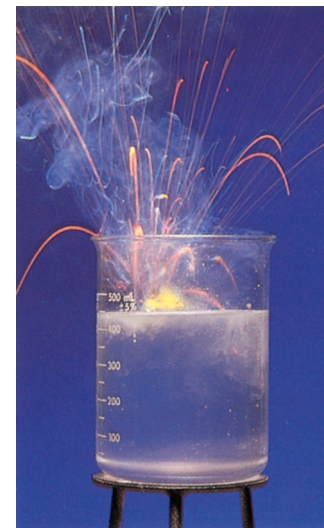


FIG. 5.7 Metallic sodium reacts violently with water.

The heat of the reaction ignites the sodium metal, which can be seen burning and sending sparks from the surface of the water. In the reaction, sodium is oxidized to Na^+ and water molecules are reduced to give hydrogen gas and hydroxide ions. When the reaction is over, the solution contains sodium hydroxide. (OPC, Inc.)

Figure 5.8, we see samples of iron, zinc, and magnesium reacting with solutions of hydrochloric acid. In each test tube the initial HCl concentration is the same, but we see that the magnesium reacts more rapidly than zinc, which reacts more rapidly than iron. You can see that the order of reactivity in Table 5.2 is the same; magnesium is more easily oxidized than zinc, which is more easily oxidized than iron.

The activity series can be used to predict reactions

The activity series in Table 5.2 permits us to make predictions of the outcome of single replacement redox reactions, as illustrated in the following examples.

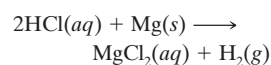
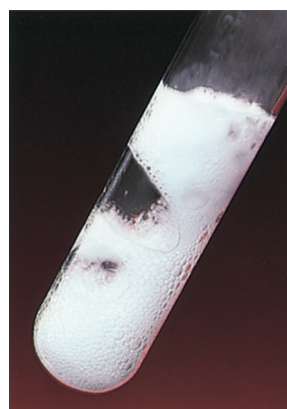
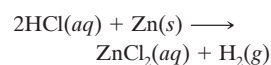
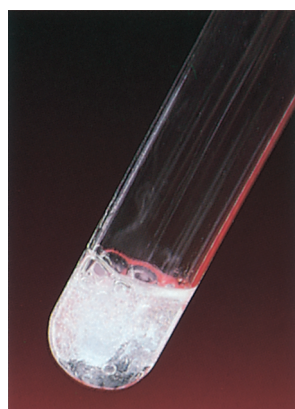
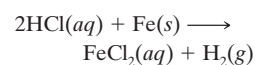
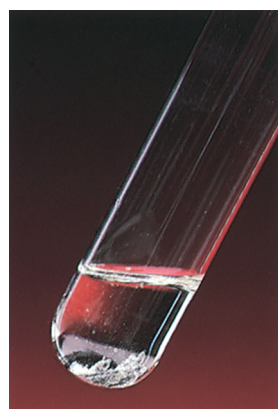


FIG. 5.8 The relative ease of oxidation of metals parallels their rates of reaction with hydrogen ions of an acid. The products are hydrogen gas and the metal ion in solution. All three test tubes contain $\text{HCl}(aq)$ at the same concentration. The first also contains pieces of iron, the second, pieces of zinc, and the third, pieces of magnesium. Among these three metals, the ease of oxidation increases from iron to zinc to magnesium. (OPC, Inc.)

192 Chapter 5 Oxidation-Reduction Reactions

EXAMPLE 5.7
Using the Activity Series

What will happen if an iron nail is dipped into a solution containing copper(II) sulfate? If a reaction occurs, write its molecular equation.

ANALYSIS: Reading the question, we have to ask, what *could* happen? If a chemical reaction were to occur, iron would have to react with the copper sulfate. A *metal* possibly reacting with the *salt of another metal*? This suggests the possibility of a single replacement reaction. The tool we use to predict such reactions is the activity series.

Examining Table 5.2 we see that iron is below copper. This means iron is more easily oxidized than copper, so we expect metallic iron to displace copper ions from the solution. *A reaction will occur.* (We've answered one part of the question.) The formula for copper(II) sulfate is CuSO_4 . To write an equation for the reaction, we have to know the final oxidation state of the iron. In the table, this is indicated as +2, so the Fe atoms change to Fe^{2+} ions. To write the formula of the salt in the solution we pair Fe^{2+} with SO_4^{2-} to give FeSO_4 . Copper(II) ions are reduced to copper atoms.

SOLUTION: Our analysis told us that a reaction *will* occur and it also gave us the products, so the equation is



IS THE ANSWER REASONABLE? We can check the activity series again to be sure we've reached the correct conclusion, and we can check to be sure the equation we've written has the correct formulas and is balanced correctly. Doing this confirms that we've got the right answers.

EXAMPLE 5.8
Using the Activity Series

What happens if an iron nail is dipped into a solution of aluminum sulfate? If a reaction occurs, write the molecular equation.

ANALYSIS: Once again, we have to realize that we're looking for a potential single replacement reaction. Scanning the activity series, we see that aluminum metal is *more* easily oxidized than iron metal. This means that aluminum atoms would be able to displace iron ions from an iron compound. But it also means that iron atoms cannot displace aluminum ions from its compounds, and iron *atoms* plus aluminum *ions* are what we're given.

SOLUTION: Our analysis has told us that iron atoms will not reduce aluminum ions, so we must conclude that no reaction can occur.



IS THE ANSWER REASONABLE? Checking the activity series again, we are confident we've come to the correct answer. In writing the equation, we've also been careful to correctly write the formula of aluminum sulfate.

Practice Exercise 17: Suppose a mixture is prepared containing magnesium sulfate (MgSO_4), copper(II) sulfate (CuSO_4), metallic magnesium, and metallic copper. What reaction, if any, will occur? (Hint: What reactions could occur?)

Practice Exercise 18: Write a chemical equation for the reaction that will occur, if any, when (a) aluminum metal is added to a solution of copper(II) chloride and (b) silver metal is added to a solution of magnesium sulfate. If no reaction will occur, write "no reaction" in place of the products.

5.5 MOLECULAR OXYGEN IS A POWERFUL OXIDIZING AGENT

Oxygen is a plentiful chemical; it's in the air and available to anyone who wants to use it, chemist or not. Furthermore, O_2 is a very reactive oxidizing agent, so its reactions have been well studied. When they are rapid, with the evolution of light and heat, we call them **combustion**. The products of reactions with oxygen are generally oxides, *molecular oxides* when oxygen reacts with nonmetals and *ionic oxides* when oxygen reacts with metals.

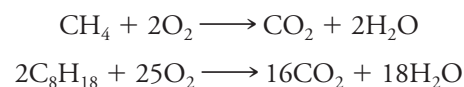
Organic compounds burn in oxygen

Experience has taught you that certain materials burn. For example, if you had to build a fire to keep warm, you no doubt would look for combustible materials like twigs, logs, or other pieces of wood to use as fuel. When you drive a car, it is probably powered by the combustion of gasoline. Wood and gasoline are examples of substances or mixtures of substances that chemists call *organic compounds*—compounds whose structures are determined primarily by the linking together of carbon atoms. When organic compounds burn, the products of the reactions are usually easy to predict.

Hydrocarbons are important fuels

Fuels such as natural gas, gasoline, kerosene, heating oil, and diesel fuel are examples of *hydrocarbons*—compounds containing only the elements carbon and hydrogen. Natural gas is composed principally of methane, CH_4 . Gasoline is a mixture of hydrocarbons, the most familiar of which is octane, C_8H_{18} . Kerosene, heating oil, and diesel fuel are mixtures of hydrocarbons in which the molecules contain even more atoms of carbon and hydrogen.

When hydrocarbons burn in a *plentiful* supply of oxygen, the products of combustion are always carbon dioxide and water. Thus, methane and octane combine with oxygen according to the equations



Many people don't realize that water is one of the products of the combustion of hydrocarbons, even though they have seen evidence for it. Perhaps you've seen clouds of condensed water vapor coming from the exhaust pipes of automobiles on cold winter days, or you may have noticed that shortly after you first start a car, drops of water fall from the exhaust pipe. This is water that has been formed during the combustion of the gasoline. Similarly, the "smokestacks" of power stations release clouds of condensed water vapor (Figure 5.9), which is often mistaken for smoke from fires used to generate power to make electricity. Actually, many of today's power stations produce very little smoke because they burn clean natural gas instead of coal.



FIG. 5.9 Water is a product of the combustion of hydrocarbons. Here we see clouds of condensed water vapor coming from the stacks of an oil-fired electric generating plant during the winter. (Sandra Baker/Liaison Agency, Inc./Getty Images.)



TOOLS
Hydrocarbon combustion
with plentiful supply of O_2

194 Chapter 5 Oxidation-Reduction Reactions

TOOLS
Hydrocarbon combustion
with limited supply of O₂

TOOLS
Hydrocarbon combustion
with extremely limited supply
of O₂

When the supply of oxygen is somewhat restricted during the combustion of a hydrocarbon, some of the carbon is converted to carbon monoxide. The formation of CO is a pollution problem associated with the use of gasoline engines, as you may know.



When the oxygen supply is extremely limited, only the hydrogen of a hydrocarbon mixture is converted to the oxide (water). The carbon atoms emerge as elemental carbon. For example, when a candle burns, the fuel is a high-molecular-weight hydrocarbon (e.g., C₂₀H₄₂) and incomplete combustion forms tiny particles of carbon that glow brightly. If a cold surface is held in the flame, the unburned carbon deposits, as seen in Figure 5.10.

An important commercial reaction is the incomplete combustion of methane in a very limited oxygen supply, which follows the equation



The carbon that forms is very finely divided and would be called *soot* by almost anyone observing the reaction. Nevertheless, such soot has considerable commercial value when collected and marketed under the name *lampblack*. This sooty form of carbon is used to manufacture inks and much of it is used in the production of rubber tires, where it serves as a binder and a filler. When soot from incomplete combustion is released into air, its tiny particles constitute a component of air pollution referred to as *particulates*, which contribute to the haziness of smog.

▣ This finely divided form of carbon is also called *carbon black*.

▣ The formula for cellulose can be expressed as (C₆H₁₀O₅)_n, which indicates that the molecule contains the C₆H₁₀O₅ unit repeated some large number *n* times.

TOOLS
Combustion of organic
compounds containing C, H,
and O

TOOLS
Combustion of organic
compounds containing sulfur

Combustion of organic compounds that contain oxygen also produces CO₂ and H₂O

Earlier we mentioned that you might choose wood to build a fire. The chief combustible ingredient in wood is cellulose, a fibrous material that gives plants their structural strength. Cellulose is composed of the elements carbon, hydrogen, and oxygen. Each cellulose molecule consists of many small, identical groups of atoms that are linked together to form a very long molecule, although the lengths of the molecules differ. For this reason we cannot specify a molecular formula for cellulose. Instead, we use the empirical formula, C₆H₁₀O₅, which represents the small, repeating “building block” units in large cellulose molecules. When cellulose burns, the products are also carbon dioxide and water. The only difference between its reaction and the reaction of a hydrocarbon with oxygen is that some of the oxygen in the products comes from the cellulose.



The complete combustion of all other organic compounds containing only carbon, hydrogen, and oxygen produces the same products, CO₂ and H₂O, and follows similar equations.

Burning organic compounds that contain sulfur gives SO₂ as one of the products

A major pollution problem in industrialized countries is caused by the release into the atmosphere of sulfur dioxide formed by the combustion of fuels that contain sulfur or its compounds. The products of the combustion of organic compounds of sulfur are carbon dioxide, water, and sulfur dioxide. A typical reaction is

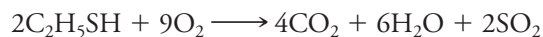


FIG. 5.10 Incomplete combustion of a hydrocarbon. The bright yellow color of a candle flame is caused by glowing particles of elemental carbon. Here we see that a black deposit of carbon is formed when the flame contacts a cold porcelain surface. (Andy Washnik.)



5.5 Molecular Oxygen Is a Powerful Oxidizing Agent 195

A solution of sulfur dioxide in water is acidic, and when rain falls through polluted air it picks up SO_2 and becomes “acid rain.” Some SO_2 is also oxidized to SO_3 , which reacts with moisture to give H_2SO_4 , making the acid rain even more acidic.

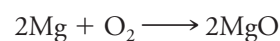
Practice Exercise 19: Write a balanced chemical equation for the combustion of candle wax, $\text{C}_{20}\text{H}_{42}$, in a very limited supply of oxygen. (Hint: What happens to methane under these conditions?)

Practice Exercise 20: Write a balanced equation for the combustion of butane, C_4H_{10} , in an abundant supply of oxygen. Butane is the fuel used in disposable cigarette lighters.

Practice Exercise 21: Ethanol, $\text{C}_2\text{H}_5\text{OH}$, is now mixed with gasoline, and the mixture is sold under the name *gasohol*. Write a chemical equation for the combustion of ethanol.

Many metals react with oxygen

We don't often think of metals as undergoing combustion, but have you ever seen an old-fashioned flashbulb fired to take a photograph? The source of light is the reaction of the metal magnesium with oxygen (see Figure 5.11). A close look at a fresh flashbulb reveals a fine web of thin magnesium wire within the glass envelope. The wire is surrounded by an atmosphere of oxygen, a colorless gas. When the flashbulb is used, a small electric current surges through the thin wire, causing it to become hot enough to ignite, and it burns rapidly in the oxygen atmosphere. The equation for the reaction is



Most metals react directly with oxygen, although not so spectacularly, and usually we refer to the reaction as **corrosion** or **tarnishing** because the oxidation products dull the shiny metal surface. Iron, for example, is oxidized fairly easily, especially in the presence of moisture. As you know, under these conditions the iron corrodes—it rusts. Rust is a form of iron(III) oxide, Fe_2O_3 , that also contains an appreciable amount of absorbed water. The formula for rust is therefore normally given as $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ to indicate its somewhat variable composition. Although the rusting of iron is a slow reaction, the combination of iron with oxygen can be speeded up if the metal is heated to a very high temperature under a stream of pure O_2 (see Figure 5.12).

An aluminum surface, unlike that of iron, is not noticeably dulled by the reaction of aluminum with oxygen. Aluminum is a common metal found around the home in uses ranging from aluminum foil to aluminum window frames, and it surely appears shiny. Yet, aluminum is a rather easily oxidized metal, as can be seen from its position in the activity series (Table 5.2). A *freshly* exposed surface of the metal does react very quickly with oxygen and becomes coated with a very thin film of aluminum oxide, Al_2O_3 , so thin that it doesn't obscure the shininess of the metal beneath. Fortunately, the oxide coating adheres very tightly to the surface of the metal and makes it very difficult for additional oxygen to combine with the aluminum. Therefore, further oxidation of aluminum occurs very slowly.

Practice Exercise 22: Write a balanced chemical equation for the reaction of molecular oxygen with strontium metal to form the oxide. (Hint: Strontium, Sr, is in the same group in the periodic table as calcium.)

Practice Exercise 23: The oxide formed in the reaction shown in Figure 5.12 is iron(III) oxide. Write a balanced chemical equation for the reaction.

Most nonmetals react with oxygen directly

Most nonmetals combine as readily with oxygen as do the metals, and their reactions usually occur rapidly enough to be described as combustion. To most people, the most important nonmetal combustion reaction is that of carbon because the reaction is a source of heat. Coal and charcoal, for example, are common carbon fuels. Coal is used worldwide in large amounts to generate electricity, and charcoal is a popular fuel for broiling hamburgers. If plenty of oxygen is available, the combustion of carbon gives CO_2 , but when the supply



FIG. 5.11 A flashbulb, before and after firing. Fine magnesium wire in an atmosphere of oxygen fills the flashbulb at the left. After being used (*right*), the interior of the bulb is coated with a white film of magnesium oxide. (Robert Capecce.)



FIG. 5.12 Cutting steel with an oxyacetylene torch. An oxygen–acetylene flame is used to heat steel until its glowing red hot. Then the acetylene is turned off and the steel is cut by a stream of pure oxygen whose reaction with the hot metal produces enough heat to melt the steel and send a shower of burning steel sparks flying. (Scott T. Smith/Corbis Images.)

196 Chapter 5 Oxidation-Reduction Reactions



The label on a bag of charcoal displays a warning about carbon monoxide. (Andy Washnik.)

of O_2 is limited, some CO forms as well. Manufacturers that package charcoal briquettes, therefore, print a warning on the bag that the charcoal shouldn't be used indoors for cooking or heating.

Sulfur is another nonmetal that burns readily in oxygen. In the manufacture of sulfuric acid, the first step is the combustion of sulfur to produce sulfur dioxide. As mentioned earlier, sulfur dioxide also forms when sulfur compounds burn, and the presence of sulfur and sulfur compounds as impurities in coal and petroleum is a major source of air pollution. Power plants that burn coal are making strides to remove the SO_2 from their exhausts and it is being used to make sulfuric acid. As we noted earlier, when SO_2 does enter the atmosphere, it can dissolve in rainwater and become one of the components of acid rain. Some SO_2 is also oxidized slowly to SO_3 , which gives the strong acid H_2SO_4 when it dissolves in rainwater.

5.6 REDOX REACTIONS FOLLOW THE SAME STOICHIOMETRIC PRINCIPLES AS OTHER REACTIONS

In general, working stoichiometry problems involving redox reactions follows the same principles we've applied to other reactions. The principal difference is that the chemical equations are more complex. Nevertheless, once we have a balanced equation, moles of substances involved in the reaction are related by the coefficients in the balanced equation.

Because so many reactions involve oxidation and reduction, it should not be surprising that they have useful applications in the lab. Some redox reactions are especially useful in chemical analyses, particularly in titrations. Unlike in acid–base titrations, however, there are no simple indicators that can be used to conveniently detect the end points in redox titrations, so we have to rely on color changes among the reactants themselves.

One of the most useful reactants for redox titrations is potassium permanganate, $KMnO_4$, especially when the reaction can be carried out in an acidic solution. Permanganate ion is a powerful oxidizing agent, so it oxidizes most substances that are capable of being oxidized. That's one reason why it is used. Especially important, though, is the fact that the MnO_4^- ion has an intense purple color and its reduction product in acidic solution is the almost colorless Mn^{2+} ion. Therefore, when a solution of $KMnO_4$ is added from a buret to a solution of a reducing agent, the chemical reaction that occurs forms a nearly colorless product. This is illustrated in Figure 5.13, where we see a solution of $KMnO_4$ being poured into an acidic solution containing Fe^{2+} . As the $KMnO_4$ solution is added, the purple color continues to be destroyed as long as there is any reducing agent left. In a titration, after the last trace of the reducing agent has been consumed, the MnO_4^- ion in the next drop of titrant has nothing to react with, so it colors the solution pink. This signals the end of the titration. In this way, permanganate ion serves as its own indicator in redox titrations. The next example illustrates a typical analysis using $KMnO_4$ in a redox titration.

■ In concentrated solutions, MnO_4^- is purple, but dilute solutions of the ion appear pink.

FIG. 5.13 Reduction of MnO_4^- by Fe^{2+} .

A solution of $KMnO_4$ is added to a stirred acidic solution containing Fe^{2+} . The reaction oxidizes the pale blue-green Fe^{2+} to Fe^{3+} while the MnO_4^- is reduced to the almost colorless Mn^{2+} ion. The purple color of the permanganate will continue to be destroyed until all of the Fe^{2+} has reacted. Only then will the iron-containing solution take on a pink or purple color. This ability of MnO_4^- to signal the completion of the reaction makes it especially useful in redox titrations, where it serves as its own indicator. (Andy Washnik.)



5.6 Redox Reactions Follow the Same Stoichiometric Principles as Other Reactions 197

EXAMPLE 5.9

Redox Titrations in Chemical Analysis

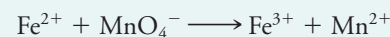
All the iron in a 2.000 g sample of an iron ore was dissolved in an acidic solution and converted to Fe^{2+} , which was then titrated with 0.1000 M KMnO_4 solution. In the titration the iron was oxidized to Fe^{3+} . The titration required 27.45 mL of the KMnO_4 solution to reach the end point.

- How many grams of iron were in the sample?
- What was the percentage iron in the sample?
- If the iron was present in the sample as Fe_2O_3 , what was the percentage by mass of Fe_2O_3 in the sample?

ANALYSIS: We're dealing with a chemical reaction, so the first step will be to write the balanced equation using the ion–electron method covered earlier in this chapter. With this as a start, let's look over the tools we'll use to answer the first two questions. We'll tackle the last part afterward.

- Molarity and volume of the KMnO_4 : These will give us moles of KMnO_4 used in the titration (remember: volume (L) \times molarity = moles).
- Coefficients of the equation: These permit us to find moles of iron from the moles of KMnO_4 used.
- Molar mass of iron: This lets us calculate the mass of iron in the sample from moles of iron.
- Equation to calculate the percentage of iron: $\% \text{ Fe} = \frac{\text{g Fe}}{\text{g sample}} \times 100\%$.

SOLUTION: The skeleton equation for the reaction is



Balancing it by the ion–electron method for acidic solutions gives



The number of moles of KMnO_4 consumed in the reaction is calculated from the volume of the solution used in the titration and its concentration.

$$0.02745 \text{ L } \cancel{\text{KMnO}_4 \text{ soln}} \times \frac{0.1000 \text{ mol } \text{KMnO}_4}{1.000 \text{ L } \cancel{\text{KMnO}_4 \text{ soln}}} \Leftrightarrow 0.002745 \text{ mol } \text{KMnO}_4$$

Next, we use the coefficients of the equation to calculate the number of moles of Fe^{2+} that reacted. The chemical equation tells us five moles of Fe^{2+} react per mole of MnO_4^- consumed.

$$0.002745 \text{ mol } \cancel{\text{KMnO}_4} \times \frac{5 \text{ mol } \text{Fe}^{2+}}{1 \text{ mol } \cancel{\text{KMnO}_4}} \Leftrightarrow 0.01372 \text{ mol } \text{Fe}^{2+}$$

This is the number of moles of iron in the ore sample, so the mass of iron in the sample is

$$0.01372 \text{ mol } \cancel{\text{Fe}} \times \frac{55.845 \text{ g Fe}}{1 \text{ mol } \cancel{\text{Fe}}} = 0.7662 \text{ g Fe}$$

This is the answer to part (a) of the problem. Next we calculate the percentage of iron in the sample, which is the mass of iron divided by the mass of the sample, all multiplied by 100%.

$$\% \text{ Fe} = \frac{\text{mass of Fe}}{\text{mass of sample}} \times 100\%$$

Substituting gives

$$\% \text{ Fe} = \frac{0.7662 \text{ g Fe}}{2.000 \text{ g sample}} \times 100\% = 38.31\% \text{ Fe}$$

The answer to part (b) is that the sample is 38.31% iron.

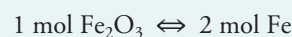
198 Chapter 5 Oxidation-Reduction Reactions

ARE THE ANSWERS REASONABLE? We can use some approximate arithmetic to estimate the answer. In the titration we used approximately 30 mL, or 0.030 L, of the KMnO_4 solution, which is 0.10 M . Multiplying these tells us we've used approximately 0.003 mol of KMnO_4 . From the coefficients of the equation, five times as many moles of Fe^{2+} react, so the amount of Fe in the sample is approximately $5 \times 0.003 = 0.015$ mol. The atomic mass of Fe is about 55 g/mol, so the mass of Fe in the sample is approximately $0.015 \times 55 \approx 0.8$ g. Our answer (0.7662 g) is reasonable. Calculating % Fe is then straightforward.

ANALYSIS CONTINUED: Now we can work on the last part of the question. Earlier in the problem we determined the number of moles of iron that reacted, 0.01372 mol Fe. How many moles of Fe_2O_3 would have contained that number of moles of iron? That's the critical question we have to answer. Once we know this, we can calculate the mass of the Fe_2O_3 and the percentage of Fe_2O_3 in the original sample. The tools we'll use in solving this part of the problem are

- The chemical formula, Fe_2O_3 : The formula relates moles of iron to moles Fe_2O_3 .
- Molar mass of Fe_2O_3 : This lets us calculate the mass of Fe_2O_3 .
- Formula for calculating percentage of Fe_2O_3 : $\% \text{Fe}_2\text{O}_3 = \frac{\text{g Fe}_2\text{O}_3}{\text{g sample}} \times 100\%$.

SOLUTION CONTINUED: The chemical formula for the iron oxide gives us



This provides the conversion factor we need to determine how many moles of Fe_2O_3 were present in the sample. Working with the number of moles of Fe,

$$0.01372 \text{ mol Fe} \times \frac{1 \text{ mol Fe}_2\text{O}_3}{2 \text{ mol Fe}} \Leftrightarrow 0.006860 \text{ mol Fe}_2\text{O}_3$$

This is the number of moles of Fe_2O_3 in the sample. The formula mass of Fe_2O_3 is 159.69 g mol^{-1} , so the mass of Fe_2O_3 in the sample was

$$0.006860 \text{ mol Fe}_2\text{O}_3 \times \frac{159.69 \text{ g Fe}_2\text{O}_3}{1 \text{ mol Fe}_2\text{O}_3} = 1.095 \text{ g Fe}_2\text{O}_3$$

Finally, the percentage of Fe_2O_3 in the sample was

$$\% \text{Fe}_2\text{O}_3 = \frac{1.095 \text{ g Fe}_2\text{O}_3}{2.000 \text{ g sample}} \times 100\% = 54.75\% \text{ Fe}_2\text{O}_3$$

The ore sample contained 54.75% Fe_2O_3 .

IS THE ANSWER REASONABLE? We've noted that the amount of Fe in the sample is approximately 0.015 mol. The amount of Fe_2O_3 that contains this much Fe is 0.0075 mol. The formula mass of Fe_2O_3 is about 160, so the mass of Fe_2O_3 in the sample was approximately $0.0075 \times 160 = 1.2$ g, which isn't too far from the mass we obtained (1.095 g). Since 1.095 g is about half of the total sample mass of 2.000 g, the sample was approximately 50% Fe_2O_3 , in agreement with the answer we obtained.

Practice Exercise 24: A 15.00 mL sample of a solution containing oxalic acid, $\text{H}_2\text{C}_2\text{O}_4$, was titrated with 0.02000 M KMnO_4 . The titration required 18.30 mL of the KMnO_4 solution. What was the molarity of the $\text{H}_2\text{C}_2\text{O}_4$ solution? In the reaction, oxalate ion ($\text{C}_2\text{O}_4^{2-}$) is oxidized to CO_2 and MnO_4^- is reduced to Mn^{2+} . (Hint: You will need to calculate number of moles of $\text{H}_2\text{C}_2\text{O}_4$ in the sample and then apply the definition of molarity.)

Practice Exercise 25: A researcher planned to use chlorine gas in an experiment and wished to trap excess chlorine to prevent it from escaping into the atmosphere. To accomplish this, the reaction of sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) with chlorine gas in an acidic aqueous solution to give sulfate ion and chloride ion would be used. How many grams of $\text{Na}_2\text{S}_2\text{O}_3$ are needed to trap 4.25 g of chlorine?

Practice Exercise 26: A sample of a tin ore weighing 0.3000 g was dissolved in an acid solution and all the tin in the sample was changed to tin(II). In a titration, 8.08 mL of 0.0500 M KMnO_4 solution was required to oxidize the tin(II) to tin(IV).

- What is the balanced equation for the reaction in the titration?
- How many grams of tin were in the sample?
- What was the percentage by mass of tin in the sample?
- If the tin in the sample had been present in the compound SnO_2 , what would have been the percentage by mass of SnO_2 in the sample?

SUMMARY

Oxidation–Reduction. **Oxidation** is the loss of electrons or an algebraic increase in oxidation number; **reduction** is the gain of electrons or an algebraic decrease in oxidation number. Both always occur together in **redox reactions**. The substance oxidized is the **reducing agent**; the substance reduced is the **oxidizing agent**. **Oxidation numbers** are a bookkeeping device that we use to follow changes in redox reactions. They are assigned according to the rules on page 178. The term **oxidation state** is equivalent to oxidation number.

Ion–Electron Method. In a balanced redox equation, the number of electrons gained by one substance is always equal to the number lost by another substance. This fact forms the basis for the **ion–electron method** (page 183), which provides a systematic method for deriving a net ionic equation for a redox reaction in aqueous solution. According to this method the *skeleton* net ionic equation is divided into two **half-reactions**, which are balanced separately before being recombined to give the final balanced net ionic equation. For reactions in basic solution, the equation is balanced as if it occurred in an acidic solution, and then the balanced equation is converted to its proper form for basic solution by adding an appropriate number of OH^- .

Metal–Acid Reactions. In **nonoxidizing acids**, the strongest oxidizing agent is H^+ (Table 5.1). The reaction of a metal with a nonoxidizing acid gives hydrogen gas and a salt of the acid. Only metals more active than hydrogen react this way. These are metals that are located below hydrogen in the **activity series** (Table 5.2). **Oxidizing acids**, like HNO_3 , contain an anion that is a stronger

oxidizing agent than H^+ , and they are able to oxidize many metals that nonoxidizing acids cannot.

Metal-Displacement Reactions. If one metal is more easily oxidized than another, it can displace the other metal from its compounds by a redox reaction. Such reactions are sometimes called **single replacement reactions**. Atoms of the more active metal become ions; ions of the less active metal generally become atoms. In this manner, any metal in the **activity series** can displace any of the others above it in the series from their compounds.

Oxidations by Molecular Oxygen. **Combustion** is the rapid reaction of a substance with oxygen accompanied by the evolution of heat and light. Combustion of a hydrocarbon in the presence of excess oxygen gives CO_2 and H_2O , two molecular oxides. When the supply of oxygen is limited, some CO also forms, and in a very limited supply of oxygen the products are H_2O and very finely divided, elemental carbon (as soot or lampblack). The combustion of organic compounds containing only carbon, hydrogen, and oxygen also gives the same products, CO_2 and H_2O . Sulfur burns to give SO_2 , which also forms when sulfur-containing fuels burn. Most nonmetals also burn in oxygen to give molecular oxides.

Many metals combine with oxygen in a process often called **corrosion**, but only sometimes is the reaction rapid enough to be considered combustion. The products are ionic metal oxides.

Redox Titrations. Potassium permanganate is often used in redox titrations because it is a powerful oxidizing agent and serves as its own indicator. In acidic solutions, the purple MnO_4^- ion is reduced to the nearly colorless Mn^{2+} ion.

200 Chapter 5 Oxidation-Reduction Reactions



TOOLS FOR PROBLEM SOLVING

In this chapter you learned to apply the following concepts as tools in solving problems. Study each one carefully so that you know what each is used for. When faced with solving a problem, recall what each tool does and consider whether it will be helpful in finding a solution. This will aid you in selecting the tools you need.

Identifying oxidizing and reducing agents (page 176) The substance reduced is the oxidizing agent; the substance oxidized is the reducing agent.

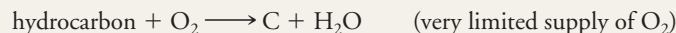
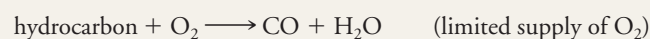
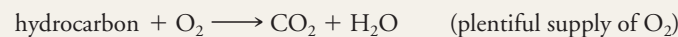
Rules for assigning oxidation numbers (page 178) The rules permit us to assign oxidation numbers to elements in compounds and ions. You use changes in oxidation numbers to identify oxidation and reduction. Remember that when there is a conflict between two rules, the rule with the lower number is followed and the rule with the higher number is ignored.

Ion-electron method (For acidic solutions, page 185; for basic solutions, page 186) Use this method when you need to obtain a balanced net ionic equation for a redox reaction. Be sure to follow the steps in the order given and do not skip steps. Also, be sure to include charges on all ions.

Table of oxidizing and nonoxidizing acids (Table 5.1, page 188) Refer to this table to identify oxidizing and nonoxidizing acids, which enables you to anticipate the products of reactions of metals with acids. Nonoxidizing acids will react with metals below hydrogen in Table 5.2 to give H_2 and the metal ion.

Activity series of metals (Table 5.2, page 191) When a question deals with the possible reaction of one metal with the salt of another, refer to the activity series to determine the outcome. A metal in the table will reduce the ion of any metal above it in the table, leading to a single replacement reaction.

Combustion reactions of hydrocarbons with oxygen (pages 193 and 194) The products of the reaction do not depend on the identity of the hydrocarbon, but they do depend on the availability of oxygen.



Combustion of compounds containing C, H, and O (page 194) Complete combustion gives CO_2 and H_2O .



Organic compounds containing sulfur give SO_2 when burned (page 194) If an organic compound contains sulfur, SO_2 is formed in addition to CO_2 and H_2O when the compound is burned.

QUESTIONS, PROBLEMS, AND EXERCISES

Answers to problems whose numbers are printed in color are given in Appendix B. More challenging problems are marked with asterisks. ILW = Interactive Learningware solution is available at www.wiley.com/college/brady. OH = an Office Hours video is available for this problem.

REVIEW QUESTIONS

Oxidation-Reduction

5.1 Define *oxidation* and *reduction* (a) in terms of electron transfer and (b) in terms of oxidation numbers.

5.2 In the reaction $2Mg + O_2 \longrightarrow 2MgO$, which substance is the oxidizing agent and which is the reducing agent? Which substance is oxidized and which is reduced?

5.3 Why must both oxidation and reduction occur simultaneously during a redox reaction? What is an oxidizing agent? What happens to it in a redox reaction? What is a reducing agent? What happens to it in a redox reaction?

5.4 In the compound As_4O_6 , arsenic has an *oxidation number* of +3. What is the *oxidation state* of arsenic in this compound?

5.5 Is the following a redox reaction? Explain.



5.6 Is the following a redox reaction? Explain.



5.7 If the oxidation number of nitrogen in a certain molecule changes from +3 to -2 during a reaction, is the nitrogen oxidized or reduced? How many electrons are gained (or lost) by each nitrogen atom?

Ion-Electron Method

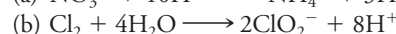
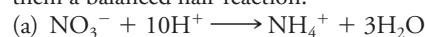
5.8 The following equation is not balanced. Why? Use the ion-electron method to balance it.



5.9 Use the ion-electron method to balance the following equation.



5.10 What are the net charges on the left and right sides of the following equations? Add electrons as necessary to make each of them a balanced half-reaction.



5.11 In the preceding question, which half-reaction represents oxidation? Which represents reduction?

Reactions of Metals with Acids and the Activity Series

5.12 What is a *single replacement reaction*?

5.13 What is a nonoxidizing acid? Give two examples. What is the oxidizing agent in a nonoxidizing acid?

5.14 What is the strongest oxidizing agent in an aqueous solution of nitric acid?

5.15 If a metal is able to react with a solution of HCl, where must the metal stand relative to hydrogen in the activity series?

5.16 Where in the activity series (Table 5.2) do we find the best reducing agents? Where do we find the best oxidizing agents?

5.17 Which metals in Table 5.2 will not react with nonoxidizing acids?

5.18 Which metals in Table 5.2 will react with water? Write chemical equations for each of these reactions.

5.19 When manganese reacts with silver ion, is manganese oxidized or reduced? Is it an oxidizing agent or a reducing agent?

Oxygen as an Oxidizing Agent

5.20 Define *combustion*.

5.21 Why is “loss of electrons” described as oxidation?

5.22 What products are produced in the combustion of $\text{C}_{10}\text{H}_{22}$ (a) if there is an excess of oxygen available? (b) If there is a slightly limited oxygen supply? (c) If there is a very limited supply of oxygen?

5.23 If one of the impurities in diesel fuel has the formula $\text{C}_2\text{H}_6\text{S}$, what products will be formed when it burns? Write a balanced chemical equation for the reaction.

5.24 Burning ammonia in an atmosphere of oxygen produces stable N_2 molecules as one of the products. What is the other product? Write the balanced equation for the reaction.

REVIEW PROBLEMS**Oxidation-Reduction; Oxidation Numbers**

5.25 Assign oxidation numbers to the atoms in the following: (a) S^{2-} , (b) SO_2 , (c) P_4 , and (d) PH_3 .

OH 5.26 Assign oxidation numbers to the atoms in the following: (a) ClO_4^- , (b) CrCl_3 , (c) SnS_2 , and (d) $\text{Au}(\text{NO}_3)_3$.

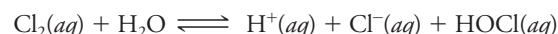
5.27 Assign oxidation numbers to each atom in the following: (a) NaOCl , (b) NaClO_2 , (c) NaClO_3 , and (d) NaClO_4 .

5.28 Assign oxidation numbers to the elements in the following. (a) $\text{Ca}(\text{VO}_3)_2$, (b) SnCl_4 , (c) MnO_4^{2-} , (d) MnO_2

5.29 Assign oxidation numbers to the elements in the following. (a) PbS , (b) TiCl_4 , (c) CsO_2 , (d) O_2F_2

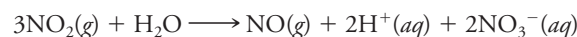
5.30 Assign oxidation numbers to the elements in the following. (a) $\text{Sr}(\text{IO}_3)_2$, (b) Cr_2S_3 , (c) OF_2 , (d) HOF

5.31 When chlorine is added to drinking water to kill bacteria, some of the chlorine is changed into ions by the following equilibrium:



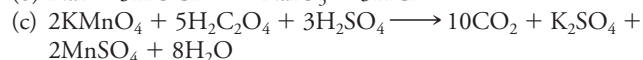
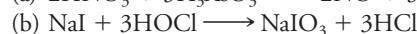
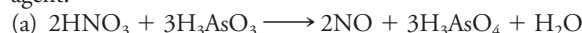
In the forward reaction (the reaction going from left to right), which substance is oxidized and which is reduced? In the reverse reaction, which is the oxidizing agent and which is the reducing agent?

5.32 A pollutant in smog is nitrogen dioxide, NO_2 . The gas has a reddish brown color and is responsible for the red-brown color associated with this type of air pollution. Nitrogen dioxide is also a contributor to acid rain because when rain passes through air contaminated with NO_2 , it dissolves and undergoes the following reaction:

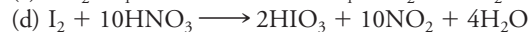
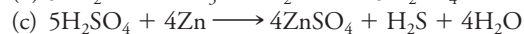
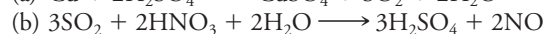
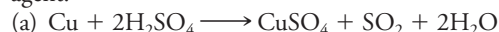


In this reaction, which element is reduced and which is oxidized?

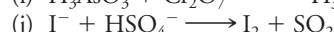
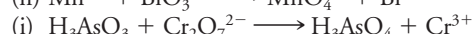
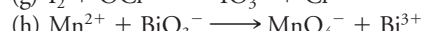
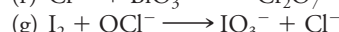
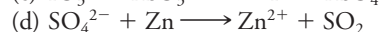
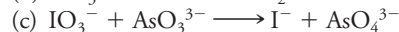
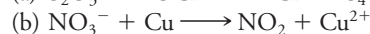
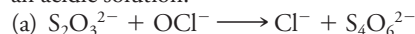
5.33 For the following reactions, identify the substance oxidized, the substance reduced, the oxidizing agent, and the reducing agent.



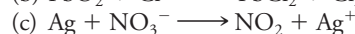
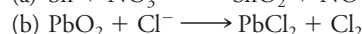
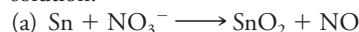
5.34 For the following reactions, identify the substance oxidized, the substance reduced, the oxidizing agent, and the reducing agent.

**Ion-Electron Method**

HW 5.35 Balance the following equations for reactions occurring in an acidic solution.



5.36 Balance these equations for reactions occurring in an acidic solution.



202 Chapter 5 Oxidation-Reduction Reactions

- (d) $\text{Fe}^{3+} + \text{NH}_3\text{OH}^+ \longrightarrow \text{Fe}^{2+} + \text{N}_2\text{O}$
 (e) $\text{HNO}_2 + \text{I}^- \longrightarrow \text{I}_2 + \text{NO}$
 (f) $\text{C}_2\text{O}_4^{2-} + \text{HNO}_2 \longrightarrow \text{CO}_2 + \text{NO}$
 (g) $\text{HNO}_2 + \text{MnO}_4^- \longrightarrow \text{Mn}^{2+} + \text{NO}_3^-$
 (h) $\text{H}_3\text{PO}_2 + \text{Cr}_2\text{O}_7^{2-} \longrightarrow \text{H}_3\text{PO}_4 + \text{Cr}^{3+}$
 (i) $\text{VO}_2^+ + \text{Sn}^{2+} \longrightarrow \text{VO}^{2+} + \text{Sn}^{4+}$
 (j) $\text{XeF}_2 + \text{Cl}^- \longrightarrow \text{Xe} + \text{F}^- + \text{Cl}_2$

5.37 Balance equations for these reactions occurring in a basic solution.

- (a) $\text{CrO}_4^{2-} + \text{S}^{2-} \longrightarrow \text{S} + \text{CrO}_2^-$
 (b) $\text{MnO}_4^- + \text{C}_2\text{O}_4^{2-} \longrightarrow \text{CO}_2 + \text{MnO}_2$
 (c) $\text{ClO}_3^- + \text{N}_2\text{H}_4 \longrightarrow \text{NO} + \text{Cl}^-$
 (d) $\text{NiO}_2 + \text{Mn}(\text{OH})_2 \longrightarrow \text{Mn}_2\text{O}_3 + \text{Ni}(\text{OH})_2$
 (e) $\text{SO}_3^{2-} + \text{MnO}_4^- \longrightarrow \text{SO}_4^{2-} + \text{MnO}_2$

5.38 Balance equations for these reactions occurring in a basic solution.

- (a) $\text{CrO}_2^- + \text{S}_2\text{O}_8^{2-} \longrightarrow \text{CrO}_4^{2-} + \text{SO}_4^{2-}$
 (b) $\text{SO}_3^{2-} + \text{CrO}_4^{2-} \longrightarrow \text{SO}_4^{2-} + \text{CrO}_2^-$
 (c) $\text{O}_2 + \text{N}_2\text{H}_4 \longrightarrow \text{H}_2\text{O}_2 + \text{N}_2$
 (d) $\text{Fe}(\text{OH})_2 + \text{O}_2 \longrightarrow \text{Fe}(\text{OH})_3 + \text{OH}^-$
 (e) $\text{Au} + \text{CN}^- + \text{O}_2 \longrightarrow \text{Au}(\text{CN})_4^- + \text{OH}^-$

5.39 Laundry bleach such as Clorox is a dilute solution of sodium hypochlorite, NaOCl. Write a balanced net ionic equation for the reaction of NaOCl with $\text{Na}_2\text{S}_2\text{O}_3$. The OCl^- is reduced to chloride ion and the $\text{S}_2\text{O}_3^{2-}$ is oxidized to sulfate ion.

OH 5.40 Calcium oxalate is one of the minerals found in kidney stones. If a strong acid is added to calcium oxalate, the compound will dissolve and the oxalate ion will be changed to oxalic acid (a weak acid). Oxalate ion is a moderately strong reducing agent. Write a balanced net ionic equation for the oxidation of $\text{H}_2\text{C}_2\text{O}_4$ by $\text{K}_2\text{Cr}_2\text{O}_7$ in an acidic solution. The reaction yields Cr^{3+} and CO_2 among the products.

5.41 Ozone, O_3 , is a very powerful oxidizing agent, and in some places ozone is used to treat water to kill bacteria and make it safe to drink. One of the problems with this method of purifying water is that if there is any bromide ion in the water, it becomes oxidized to bromate ion, which has shown evidence of causing cancer in test animals. Assuming that ozone is reduced to water, write a balanced chemical equation for the reaction. (Assume an acidic solution.)

5.42 Chlorine is a good bleaching agent because it is able to oxidize substances that are colored to give colorless reaction products. It is used in the pulp and paper industry as a bleach, but after it has done its work, residual chlorine must be removed. This is accomplished using sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3$, which reacts with the chlorine, reducing it to chloride ion. The thiosulfate ion is changed to sulfate ion, which is easily removed by washing with water. Write a balanced chemical equation for the reaction of chlorine with thiosulfate ion, assuming an acidic solution.

Reactions of Metals with Acids

5.43 Write balanced molecular, ionic, and net ionic equations for the reactions of the following metals with hydrochloric acid to give hydrogen plus the metal ion in solution.

- (a) Manganese (gives Mn^{2+})
 (b) Cadmium (gives Cd^{2+})
 (c) Tin (gives Sn^{2+})

5.44 Write balanced molecular, ionic, and net ionic equations for the reaction of each of the following metals with dilute sulfuric acid.

- (a) Nickel (gives Ni^{2+})
 (b) Chromium (gives Cr^{3+})
 (c) Aluminum (gives Al^{3+})

5.45 On the basis of the discussions in this chapter, suggest chemical equations for the oxidation of metallic silver to Ag^+ ion with (a) dilute HNO_3 and (b) concentrated HNO_3 .

OH 5.46 When hot and concentrated, sulfuric acid is a fairly strong oxidizing agent. Write a balanced net ionic equation for the oxidation of metallic copper to copper(II) ion by hot concentrated H_2SO_4 , in which the sulfur is reduced to SO_2 . Write a balanced molecular equation for the reaction.

Single Replacement Reactions and the Activity Series

5.47 Use Table 5.2 to predict the outcome of the following reactions. If no reaction occurs, write N.R. If a reaction occurs, write a balanced chemical equation for it.

- (a) $\text{Fe} + \text{Mg}^{2+} \longrightarrow$
 (b) $\text{Cr} + \text{Pb}^{2+} \longrightarrow$
 (c) $\text{Ag}^+ + \text{Fe} \longrightarrow$
 (d) $\text{Ag} + \text{Au}^{3+} \longrightarrow$

OH 5.48 Use Table 5.2 to predict the outcome of the following reactions. If no reaction occurs, write N.R. If a reaction occurs, write a balanced chemical equation for it.

- (a) $\text{Mn} + \text{Fe}^{2+} \longrightarrow$
 (b) $\text{Cd} + \text{Zn}^{2+} \longrightarrow$
 (c) $\text{Mg} + \text{Co}^{2+} \longrightarrow$
 (d) $\text{Cr} + \text{Sn}^{2+} \longrightarrow$

5.49 The following reactions occur spontaneously.



List the metals Pu, Pt, and Tl in order of increasing ease of oxidation.

5.50 The following reactions occur spontaneously.



List the metals Y, Ni, and Mo in order of increasing ease of oxidation.

5.51 It is found that the following reaction occurs spontaneously.



What reaction will occur if a mixture is prepared containing the following: $\text{Cd}(\text{s})$, $\text{Cd}(\text{NO}_3)_2(\text{aq})$, $\text{Tl}(\text{s})$, $\text{TlCl}(\text{aq})$? (Refer to the information in Problem 5.49 above.)

5.52 It is observed that when magnesium metal is dipped into a solution of nickel(II) chloride, some of the magnesium dissolves and nickel metal is deposited on the surface of the magnesium. Referring to Problem 5.50, can you tell which of the following reactions will occur spontaneously? Explain the reason for your answer.

- (a) $2\text{Mo}^{3+} + 3\text{Mg} \longrightarrow 3\text{Mg}^{2+} + 2\text{Mo}$
 (b) $2\text{Mo} + 3\text{Mg}^{2+} \longrightarrow 2\text{Mo}^{3+} + 3\text{Mg}$

Reactions of Oxygen

5.53 Write balanced chemical equations for the complete combustion (in the presence of excess oxygen) of the following:

- C_6H_6 (benzene, an important industrial chemical and solvent)
- C_3H_8 (propane, a gaseous fuel used in many stoves)
- $C_{21}H_{44}$ (a component of paraffin wax)

5.54 Write balanced chemical equations for the complete combustion (in the presence of excess oxygen) of the following:

- $C_{12}H_{26}$ (a component of kerosene)
- $C_{18}H_{36}$ (a component of diesel fuel)
- C_7H_8 (toluene, a raw material in the production of TNT)

5.55 Write balanced equations for the combustion of the hydrocarbons in Problem 5.53 in (a) a slightly limited supply of oxygen and (b) a very limited supply of oxygen.

5.56 Write balanced equations for the combustion of the hydrocarbons in Problem 5.54 in (a) a slightly limited supply of oxygen and (b) a very limited supply of oxygen.

5.57 Methanol, CH_3OH , has been suggested as an alternative to gasoline as an automotive fuel. Write a balanced chemical equation for its complete combustion.

OH 5.58 Metabolism of carbohydrates such as glucose, $C_6H_{12}O_6$, produces the same products as complete combustion. Write a chemical equation representing the metabolism (combustion) of glucose.

5.59 Write the balanced equation for the combustion of dimethylsulfide, $(CH_3)_2S$, in an abundant supply of oxygen.

5.60 Thiophene, C_4H_4S , is an impurity in crude oil and is a source of pollution if not removed. Write an equation for the combustion of thiophene.

5.61 Write chemical equations for the reaction of oxygen with (a) zinc, (b) aluminum, (c) magnesium, and (d) iron to form iron(III) oxide.

5.62 Write chemical equations for the reaction of oxygen with (a) beryllium, (b) lithium, (c) barium, and (d) bismuth to form bismuth(III) oxide.

Redox Reactions and Stoichiometry

5.63 Iodate ion reacts with sulfite ion to give sulfate ion and iodide ion.

- Write a balanced net ionic equation for the reaction.
- How many grams of sodium sulfite are needed to react with 5.00 g of sodium iodate?

5.64 Potable water (drinking water) should not have manganese concentrations in excess of 0.05 mg/mL. If the manganese concentration is greater than 0.1 mg/mL, it imparts a foul taste to the water and discolors laundry and porcelain surfaces. Manganese(II) ion is oxidized to permanganate ion by bismuthate ion, BiO_3^- , in an acidic solution. In the reaction, BiO_3^- is reduced to Bi^{3+} .

- Write a balanced net ionic equation for the reaction.
- How many milligrams of $NaBiO_3$ are needed to oxidize the manganese in 18.5 mg of manganese(II) sulfate?

OH 5.65 How many grams of copper must react to displace 12.0 g of silver from a solution of silver nitrate?

5.66 How many grams of aluminum must react to displace all the silver from 25.0 g of silver nitrate? The reaction occurs in aqueous solution.

5.67 In an acidic solution, permanganate ion reacts with tin(II) ion to give manganese(II) ion and tin(IV) ion.

- Write a balanced net ionic equation for the reaction.
- How many milliliters of 0.230 M potassium permanganate solution are needed to react completely with 40.0 mL of 0.250 M tin(II) chloride solution?

5.68 In an acidic solution, bisulfite ion reacts with chlorate ion to give sulfate ion and chloride ion.

- Write a balanced net ionic equation for the reaction.
- How many milliliters of 0.150 M sodium chlorate solution are needed to react completely with 30.0 mL of 0.450 M sodium bisulfite solution?

5.69 Sulfites are used worldwide in the wine industry as antioxidant and antimicrobial agents. However, sulfites have also been identified as causing certain allergic reactions suffered by asthmatics, and the FDA mandates that sulfites be identified on the label if they are present at levels of 10 ppm (parts per million) or higher. The analysis of sulfites in wine uses the “Ripper method” in which a standard iodine solution, prepared by the reaction of iodate and iodide ions, is used to titrate a sample of the wine. The iodine is formed in the reaction



The iodine is held in solution by adding an excess of I^- which combines with I_2 to give I_3^- . In the titration, the SO_3^{2-} is converted to SO_2 by acidification and the reaction during the titration is



Starch is added to the wine sample to detect the end point, which is signaled by the formation of a dark blue color when excess iodine binds to the starch molecules. In a certain analysis, 0.0421 g of $NaIO_3$ was dissolved in dilute acid and excess NaI was added to the solution, which was then diluted to a total volume of 100.0 mL. A 50.0 mL sample of wine was then acidified and titrated with the iodine-containing solution. In the titration, 2.47 mL of the iodine solution was required.

- What was the molarity of the iodine (actually, I_3^-) in the standard solution?
- How many grams of SO_2 were in the wine sample?
- If the density of the wine was 0.96 g/mL, what was the percentage of SO_2 in the wine?
- Parts per million (ppm) is calculated in a manner similar to percent (which is equivalent to *parts per hundred*).

$$\text{ppm} = \frac{\text{grams of component}}{\text{grams of sample}} \times 10^6 \text{ ppm}$$

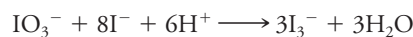
What was the concentration of sulfite in the wine, expressed as parts per million SO_2 ?

5.70 Methylbromide, CH_3Br , is used in agriculture to fumigate soil to rid it of pests such as nematodes. It is injected directly into the soil, but over time it has a tendency to escape before it can undergo natural degradation to innocuous products. Soil chemists have found that ammonium thiosulfate, $(NH_4)_2S_2O_3$, a nitrogen and sulfur fertilizer, drastically reduces methylbromide emissions by causing it to degrade.

In a chemical analysis to determine the purity of a batch of commercial ammonium thiosulfate, a chemist first prepared a standard solution of iodine following the procedure in the preceding

204 Chapter 5 Oxidation-Reduction Reactions

problem. First, 0.462 g of KIO_3 was dissolved in 100 mL of water. The solution was made acidic and treated with excess potassium iodide, which caused the following reaction to take place:



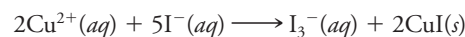
The solution containing the I_3^- was then diluted to exactly 250 mL in a volumetric flask. Next, the chemist dissolved 0.218 g of the fertilizer in water, added starch indicator, and titrated it with the standard I_3^- solution. The reaction was



The titration required 27.99 mL of the I_3^- solution.

- What was the molarity of the I_3^- solution used in the titration?
- How many grams of $(\text{NH}_4)_2\text{S}_2\text{O}_3$ were in the fertilizer sample?
- What was the percentage by mass of $(\text{NH}_4)_2\text{S}_2\text{O}_3$ in the fertilizer?

||W 5.71 A sample of a copper ore with a mass of 0.4225 g was dissolved in acid. A solution of potassium iodide was added, which caused the reaction



The I_3^- that formed reacted quantitatively with exactly 29.96 mL of 0.02100 M $\text{Na}_2\text{S}_2\text{O}_3$ according to the following equation.



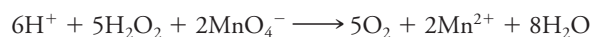
- What was the percentage by mass of copper in the ore?
- If the ore contained CuCO_3 , what was the percentage by mass of CuCO_3 in the ore?

5.72 A 1.362 g sample of an iron ore that contained Fe_3O_4 was dissolved in acid and all the iron was reduced to Fe^{2+} . The solution was then acidified with H_2SO_4 and titrated with 39.42 mL of 0.0281 M KMnO_4 , which oxidized the iron to Fe^{3+} . The net ionic equation for the reaction is



- What was the percentage by mass of iron in the ore?
- What was the percentage by mass of Fe_3O_4 in the ore?

5.73 Hydrogen peroxide (H_2O_2) solution can be purchased in drug stores for use as an antiseptic. A sample of such a solution weighing 1.000 g was acidified with H_2SO_4 and titrated with a 0.02000 M solution of KMnO_4 . The net ionic equation for the reaction is



The titration required 17.60 mL of KMnO_4 solution.

- How many grams of H_2O_2 reacted?
- What is the percentage by mass of the H_2O_2 in the original antiseptic solution?

5.74 Sodium nitrite, NaNO_2 , is used as a preservative in meat products such as frankfurters and bologna. In an acidic solution, nitrite ion is converted to nitrous acid, HNO_2 , which reacts with permanganate ion according to the equation



A 1.000 g sample of a water-soluble solid containing NaNO_2 was dissolved in dilute H_2SO_4 and titrated with 0.01000 M KMnO_4

solution. The titration required 12.15 mL of the KMnO_4 solution. What was the percentage by mass of NaNO_2 in the original 1.000 g sample?

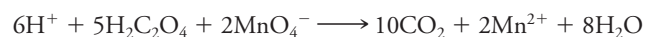
5.75 A sample of a chromium-containing alloy weighing 3.450 g was dissolved in acid, and all the chromium in the sample was oxidized to CrO_4^{2-} . It was then found that 3.18 g of Na_2SO_3 was required to reduce the CrO_4^{2-} to CrO_2^- in a basic solution, with the SO_3^{2-} being oxidized to SO_4^{2-} .

- Write a balanced equation for the reaction of CrO_4^{2-} with SO_3^{2-} in a basic solution.
- How many grams of chromium were in the alloy sample?
- What was the percentage by mass of chromium in the alloy?

5.76 Solder is an alloy containing the metals tin and lead. A particular sample of the alloy weighing 1.50 g was dissolved in acid. All the tin was then converted to the +2 oxidation state. Next, it was found that 0.368 g of $\text{Na}_2\text{Cr}_2\text{O}_7$ was required to oxidize the Sn^{2+} to Sn^{4+} in an acidic solution. In the reaction the chromium was reduced to Cr^{3+} ion.

- Write a balanced net ionic equation for the reaction between Sn^{2+} and $\text{Cr}_2\text{O}_7^{2-}$ in an acidic solution.
- Calculate the number of grams of tin that were in the sample of solder.
- What was the percentage by mass of tin in the solder?

5.77 Both calcium chloride and sodium chloride are used to melt ice and snow on roads in the winter. A certain company was marketing a mixture of these two compounds for this purpose. A chemist, wishing to analyze the mixture, dissolved 2.463 g of it in water and precipitated calcium oxalate by adding sodium oxalate, $\text{Na}_2\text{C}_2\text{O}_4$. The calcium oxalate was carefully filtered from the solution, dissolved in sulfuric acid, and titrated with 0.1000 M KMnO_4 solution. The reaction that occurred was



The titration required 21.62 mL of the KMnO_4 solution.

- How many moles of $\text{C}_2\text{O}_4^{2-}$ were present in the calcium oxalate precipitate?
- How many grams of calcium chloride were in the original 2.463 g sample?
- What was the percentage by mass of calcium chloride in the sample?

5.78 A way to analyze a sample for nitrite ion is to acidify a solution containing NO_2^- and then allow the HNO_2 that is formed to react with iodide ion in the presence of excess I^- . The reaction is



Then the I_3^- is titrated with $\text{Na}_2\text{S}_2\text{O}_3$ solution using starch as an indicator.



In a typical analysis, a 1.104 g sample that was known to contain NaNO_2 was treated as described above. The titration required 29.25 mL of 0.3000 M $\text{Na}_2\text{S}_2\text{O}_3$ solution to reach the end point.

- How many moles of I_3^- had been produced in the first reaction?
- How many moles of NO_2^- had been in the original 1.104 g sample?
- What was the percentage by mass of NaNO_2 in the original sample?

ADDITIONAL EXERCISES

5.79 What is the oxidation number of sulfur in the tetrathionate ion, $S_4O_6^{2-}$?

***5.80** In Practice Exercise 7 (page 182), some of the uses of chlorine dioxide were described along with a reaction that could be used to make ClO_2 . Another reaction that is used to make this substance is



Which element is oxidized? Which element is reduced? Which substance is the oxidizing agent and which is the reducing agent?

5.81 What is the average oxidation number of carbon in (a) C_2H_5OH (grain alcohol), (b) $C_{12}H_{22}O_{11}$ (sucrose—table sugar), (c) $CaCO_3$ (limestone), and (d) $NaHCO_3$ (baking soda)?

5.82 The following chemical reactions are *observed to occur* in aqueous solution.



Arrange the metals Al, Pb, Fe, and Cu in order of increasing ease of oxidation.

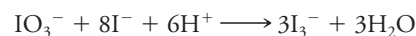
5.83 In the preceding problem, were all the experiments described actually necessary to establish the order?

5.84 According to the activity series in Table 5.2, which of the following metals react with nonoxidizing acids? (a) silver, (b) gold, (c) zinc, (d) magnesium

5.85 In each pair below, choose the metal that would most likely react more rapidly with a nonoxidizing acid such as HCl. (a) aluminum or iron, (b) zinc or nickel, (c) cadmium or magnesium

5.86 In June 2002, the Department of Health and Children in Ireland began a program to distribute tablets of potassium iodate to households as part of Ireland's National Emergency Plan for Nuclear Accidents. Potassium iodate provides iodine, which when taken during a nuclear emergency, works by "topping off" the thyroid gland to prevent the uptake of radioactive iodine that might be released into the environment by a nuclear accident.

To test the potency of the tablets, a chemist dissolved one in 100 mL of water, made the solution acidic, and then added excess potassium iodide, which caused the following reaction to occur.

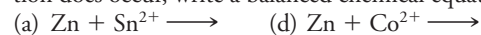


The resulting solution containing I_3^- was titrated with 0.0500 M $Na_2S_2O_3$ solution, using starch indicator to detect the end point. (In the presence of iodine, starch turns dark blue. When the $S_2O_3^{2-}$ has consumed all the iodine, the solution becomes colorless.) The titration required 22.61 mL of the thiosulfate solution to reach the end point. The reaction during the titration was



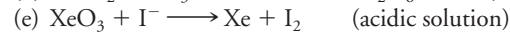
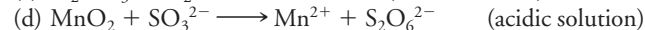
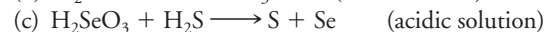
How many milligrams of KIO_3 were in the tablet?

5.87 Use Table 5.2 to predict whether the following displacement reactions should occur. If no reaction occurs, write N.R. If a reaction does occur, write a balanced chemical equation for it.



5.88 Sucrose, $C_{12}H_{22}O_{11}$, is ordinary table sugar. Write a balanced chemical equation representing the metabolism of sucrose. (See Review Problem 5.58.)

***5.89** Balance the following equations by the ion–electron method.



5.90 Lead(IV) oxide reacts with hydrochloric acid to give chlorine. The unbalanced equation for the reaction is



How many grams of PbO_2 must react to give 15.0 g of Cl_2 ?

***5.91** A solution contains $Ce(SO_4)_3^{2-}$ at a concentration of 0.0150 M . It was found that in a titration, 25.00 mL of this solution reacted completely with 23.44 mL of 0.032 M $FeSO_4$ solution. The reaction gave Fe^{3+} as a product in the solution. In this reaction, what is the final oxidation state of the Ce?

***5.92** A copper bar with a mass of 12.340 g is dipped into 255 mL of 0.125 M $AgNO_3$ solution. When the reaction that occurs has finally ceased, what will be the mass of unreacted copper in the bar? If all the silver that forms adheres to the copper bar, what will be the total mass of the bar after the reaction?

5.93 A solution containing 0.1244 g of $K_2C_2O_4$ was acidified, changing the $C_2O_4^{2-}$ ions to $H_2C_2O_4$. The solution was then titrated with 13.93 mL of a $KMnO_4$ solution to reach a faint pink end point. In the reaction, $H_2C_2O_4$ was oxidized to CO_2 and MnO_4^- was reduced to Mn^{2+} . What was the molarity of the $KMnO_4$ solution used in the titration?

***5.94** It was found that a 20.0 mL portion of a solution of oxalic acid, $H_2C_2O_4$, requires 6.25 mL of 0.200 M $K_2Cr_2O_7$ for complete reaction in an acidic solution. In the reaction, the oxidation product is CO_2 and the reduction product is Cr^{3+} . How many milliliters of 0.450 M $NaOH$ are required to completely neutralize the $H_2C_2O_4$ in a separate 20.00 mL sample of the same oxalic acid solution?

***5.95** A mixture is made by combining 300 mL of 0.0200 M $Na_2Cr_2O_7$ with 400 mL of 0.060 M $Fe(NO_3)_2$. Initially, the H^+ concentration in the mixture is 0.400 M . Dichromate ion oxidizes Fe^{2+} to Fe^{3+} and is reduced to Cr^{3+} . After the reaction in the mixture has ceased, how many milliliters of 0.0100 M $NaOH$ will be required to neutralize the remaining H^+ ?

***5.96** A solution with a volume of 500.0 mL contained a mixture of SO_3^{2-} and $S_2O_3^{2-}$. A 100.0 mL portion of the solution was found to react with 80.00 mL of 0.0500 M CrO_4^{2-} in a basic solution to give CrO_2^- . The only sulfur-containing product was SO_4^{2-} . After the reaction, the solution was treated with excess 0.200 M $BaCl_2$ solution, which precipitated $BaSO_4$. This solid was filtered from the solution, dried, and found to weigh 0.9336 g.

206 Chapter 5 Oxidation-Reduction Reactions

Explain in detail how you can determine the molar concentrations of SO_3^{2-} and $\text{S}_2\text{O}_3^{2-}$ in the original solution.

***5.97** An organic compound contains carbon, hydrogen, and sulfur. A sample of it with a mass of 1.045 g was burned in oxygen to give gaseous CO_2 , H_2O , and SO_2 . These gases were passed through 500.0 mL of an acidified 0.0200 M KMnO_4 solution, which caused the SO_2 to be oxidized to SO_4^{2-} . Only part of the available KMnO_4 was reduced to Mn^{2+} . Next, 50.00 mL of 0.0300 M SnCl_2 was added to a 50.00 mL portion of this solution, which still contained unreduced KMnO_4 . There was more than enough added SnCl_2 to cause all of the remaining MnO_4^- in the 50 mL portion to be reduced to Mn^{2+} . The excess Sn^{2+} that still remained after the reaction was then titrated with 0.0100 M KMnO_4 , requiring 27.28 mL of the KMnO_4 solution to reach the end point. What was the percentage of sulfur in the original sample of the organic compound that had been burned?

***5.98** A bar of copper weighing 32.00 g was dipped into 50.0 mL of 0.250 M AgNO_3 solution. If all the silver that deposits adheres to the copper bar, how much will the bar weigh after the reaction is complete? Write and balance any necessary chemical equations.

**EXERCISES IN
CRITICAL THINKING**

5.99 The ion OSCN^- is found in human saliva. Discuss the problems in assigning oxidation numbers to the atoms in this ion. Suggest a reasonable set of oxidation numbers for the atoms in OSCN^- .

5.100 We described the ion–electron method for balancing redox equations. Can you devise an alternate method using oxidation numbers?

5.101 Assuming that a chemical reaction with DNA could lead to damage causing cancer, would a very strong or a weak oxidizing agent have a better chance of being a carcinogen? Justify your answer.

5.102 Would you expect atomic oxygen and chlorine to be better or worse oxidizing agents than molecular oxygen and molecular chlorine? Justify your answer.

5.103 Do we live in an oxidizing or reducing environment? What effect might our environment have on chemistry we do in the laboratory? What effect might the environment have on the nature of the chemicals (minerals, etc.) we find on earth?