Defining Oxidation and Reduction

10.1

The term *oxidation* can be used to describe the process in which certain fruits turn brown by reacting with oxygen. The original, historical definition of this term was "to combine with oxygen." Thus, oxidation occurred when iron rusted, and when magnesium was burned in oxygen gas. The term *reduction* was used historically to describe the opposite of oxidation, that is, the formation of a metal from its compounds. An **ore** is a naturally occurring solid compound or mixture of compounds from which a metal can be extracted. Thus, the process of obtaining a metal from an ore was known as a reduction. Copper ore was reduced to yield copper, and iron ore was reduced to yield iron.

As you will learn in this chapter, the modern definitions for oxidation and reduction are much broader. The current definitions are based on the idea of electron transfers, and can now be applied to numerous chemical reactions. In Unit 1, you saw the terms oxidation and reduction used to describe changes to carbon-hydrogen and carbon-oxygen bonds within organic compounds. These changes involve electron transfers, so the broader definitions that you will learn in this chapter still apply.

In your previous chemistry course, you compared the reactivities of metals. You may recall that, when a piece of zinc is placed in an aqueous solution of copper(II) sulfate, the zinc displaces the copper in a single displacement reaction. This reaction is shown in Figure 10.1. As the zinc dissolves, the zinc strip gets smaller. A dark red-brown layer of solid copper forms on the zinc strip, and some copper is deposited on the bottom of the beaker. The blue colour of the solution fades, as blue copper(II) ions are replaced by colourless zinc ions.

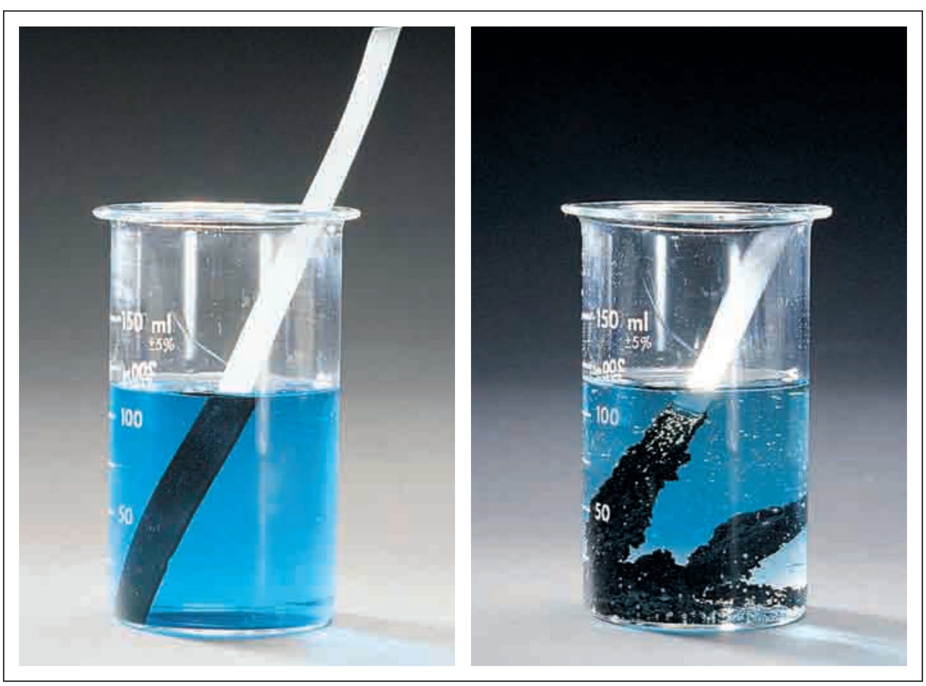

Figure 10.1 **A solid zinc strip reacts with a solution that contains blue copper(II) ions.**

Section Preview/ Specific Expectations

In this section, you will

- **describe** oxidation and reduction in terms of the loss and the gain of electrons
- **write** half-reactions from balanced chemical equations for oxidation-reduction systems
- **investigate** oxidation-reduction reactions by comparing the reactivities of some metals
- **communicate** your understanding of the terms *ore*, *oxidation*, *reduction*, *oxidation-reduction reaction*, *redox reaction*, *oxidizing agent*, *reducing agent*, *half-reaction*, *disproportionation*

CONCEPT CHECK

From your earlier work, you will recognize the sulfate ion, SO_4^{2-}, as a polyatomic ion. To review the names and formulas of common polyatomic ions, refer to Appendix E, Table E.5.

The reaction in Figure 10.1 is represented by the following equation.

$$Zn_{(s)} + CuSO_{4(aq)} \rightarrow Cu_{(s)} + ZnSO_{4(aq)}$$

This equation can be written as a total ionic equation.

$$Zn_{(s)} + Cu^{2+}_{(aq)} + SO_4{}^{2-}_{(aq)} \rightarrow Cu_{(s)} + Zn^{2+}_{(aq)} + SO_4{}^{2-}_{(aq)}$$

The sulfate ions are *spectator ions*, meaning ions that are not involved in the chemical reaction. By omitting the spectator ions, you obtain the following net ionic equation.

$$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Cu_{(s)} + Zn^{2+}_{(aq)}$$

Notice what happens to the reactants in this equation. The zinc atoms *lose* electrons to form zinc ions. The copper ions *gain* electrons to form copper atoms.

gains $2e^-$

$$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Cu_{(s)} + Zn^{2+}_{(aq)}$$

loses $2e^-$

The following chemical definitions describe these changes.

- **Oxidation** is the loss of electrons.
- **Reduction** is the gain of electrons.

CHEM FACT

Try using a mnemonic to remember the definitions for oxidation and reduction. For example, in "LEO the lion says GER," LEO stands for "Loss of Electrons is Oxidation." GER stands for "Gain of Electrons is Reduction." The mnemonic "OIL RIG" stands for "Oxidation Is Loss. Reduction Is Gain." Make up your own mnemonic to help you remember these definitions.

In the reaction of zinc atoms with copper(II) ions, the zinc atoms lose electrons and undergo oxidation. In other words, the zinc atoms are *oxidized*. The copper(II) ions gain electrons and undergo reduction. In other words, the copper(II) ions are *reduced*. Because oxidation and reduction both occur in the reaction, it is known as an **oxidation-reduction reaction** or **redox reaction**.

Notice that electrons are transferred from zinc atoms to copper(II) ions. The copper(II) ions are responsible for the oxidation of the zinc atoms. A reactant that oxidizes another reactant is called an **oxidizing agent**. The oxidizing agent accepts electrons in a redox reaction. In this reaction, copper(II) is the oxidizing agent. The zinc atoms are responsible for the reduction of the copper(II) ions. A reactant that reduces another reactant is called a **reducing agent**. The reducing agent gives or donates electrons in a redox reaction. In this reaction, zinc is the reducing agent.

A redox reaction can also be defined as a reaction between an oxidizing agent and a reducing agent, as illustrated in Figure 10.2.

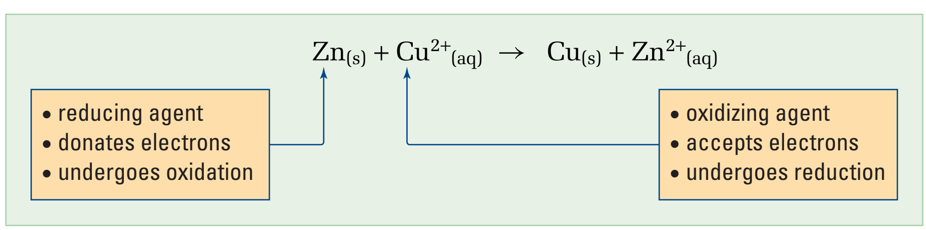

Figure 10.2 **In a redox reaction, the reducing agent is oxidized, and the oxidizing agent is reduced. Note that the oxidizing agent *does not* undergo oxidation, and that the reducing agent *does not* undergo reduction.**

Try the following practice problems to review your understanding of net ionic equations, and to work with the new concepts of oxidation and reduction.

Practice Problems

1. Write a balanced net ionic equation for the reaction of zinc with aqueous iron(II) chloride. Include the physical states of the reactants and products.
2. Write a balanced net ionic equation for each reaction, including physical states.
   (a) magnesium with aqueous aluminum sulfate
   (b) a solution of silver nitrate with metallic cadmium
3. Identify the reactant oxidized and the reactant reduced in each reaction in question 2.
4. Identify the oxidizing agent and the reducing agent in each reaction in question 2.

Half-Reactions

To monitor the transfer of electrons in a redox reaction, you can represent the oxidation and reduction separately. A **half-reaction** is a balanced equation that shows the number of electrons involved in either oxidation or reduction. Because a redox reaction involves both oxidation and reduction, two half-reactions are needed to represent a redox reaction. One half-reaction shows oxidation, and the other half-reaction shows reduction.

As you saw earlier, the reaction of zinc with aqueous copper(II) sulfate can be represented by the following net ionic equation.

$$Zn_{(s)} + Cu^{2+}{}_{(aq)} \rightarrow Cu_{(s)} + Zn^{2+}{}_{(aq)}$$

Each neutral Zn atom is oxidized to form a Zn^{2+} ion. Thus, each Zn atom must lose two electrons. You can write an oxidation half-reaction to show this change.

$$Zn_{(s)} \rightarrow Zn^{2+}{}_{(aq)} + 2e^-$$

Each Cu^{2+} ion is reduced to form a neutral Cu atom. Thus, each Cu^{2+} ion must gain two electrons. You can write a reduction half-reaction to show this change.

$$Cu^{2+}{}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$$

If you look again at each half-reaction above, you will notice that the atoms and the charges are balanced. Like other types of balanced equations, half-reactions are balanced using the smallest possible whole-number coefficients. In the following equation, the atoms and charges are balanced, but the coefficients can all be divided by 2 to give the usual form of the half-reaction.

$$2Cu^{2+}{}_{(aq)} + 4e^- \rightarrow 2Cu_{(s)}$$

CONCEPT CHECK

You can write separate oxidation and reduction half-reactions to represent a redox reaction, but one half-reaction cannot occur on its own. Explain why this statement must be true.

In most redox reactions, one substance is oxidized and a different substance is reduced. In a **disproportionation** reaction, however, a single element undergoes both oxidation and reduction in the same reaction. For example, a copper(I) solution undergoes disproportionation in the following reaction.

$$2Cu^{+}_{(aq)} \rightarrow Cu_{(s)} + Cu^{2+}_{(aq)}$$

In this reaction, some copper(I) ions gain electrons, while other copper(I) ions lose electrons.

gains $1e^-$

$$Cu^{+}_{(aq)} + Cu^{+}_{(aq)} \rightarrow Cu_{(s)} + Cu^{2+}_{(aq)}$$

loses $1e^-$

The two half-reactions are as follows.

Oxidation: $Cu^{+}_{(aq)} \rightarrow Cu^{2+}_{(aq)} + 1e^-$

Reduction: $Cu^{+}_{(aq)} + 1e^- \rightarrow Cu_{(s)}$

You have learned that half-reactions can be used to represent oxidation and reduction separately. Half-reactions always come in pairs: an oxidation half-reaction is always accompanied by a reduction half-reaction, and vice versa. Try writing and balancing half-reactions using the following practice problems.

Practice Problems

5. Write balanced half-reactions from the net ionic equation for the reaction between solid aluminum and aqueous iron(III) sulfate. The sulfate ions are spectator ions, and are not included.

$Al_{(s)} + Fe^{3+}_{(aq)} \rightarrow Al^{3+}_{(aq)} + Fe_{(s)}$

6. Write balanced half-reactions from the following net ionic equations.

(a) $Fe_{(s)} + Cu^{2+}_{(aq)} \rightarrow Fe^{2+}_{(aq)} + Cu_{(s)}$

(b) $Cd_{(s)} + 2Ag^{+}_{(aq)} \rightarrow Cd^{2+}_{(aq)} + 2Ag_{(s)}$

7. Write balanced half-reactions for each of the following reactions.

(a) $Sn_{(s)} + PbCl_{2(aq)} \rightarrow SnCl_{2(aq)} + Pb_{(s)}$

(b) $Au(NO_3)_{3(aq)} + 3Ag_{(s)} \rightarrow 3AgNO_{3(aq)} + Au_{(s)}$

(c) $3Zn_{(s)} + Fe_2(SO_4)_{3(aq)} \rightarrow 3ZnSO_{4(aq)} + 2Fe_{(s)}$

8. Write the net ionic equation and the half-reactions for the disproportionation of mercury(I) ions in aqueous solution to give liquid mercury and aqueous mercury(II) ions. Assume that mercury(I) ions exist in solution as Hg_2^{2+}.

COURSE CHALLENGE

The Chemistry Bulletin, on the next page, introduces you to the terms *oxidant* and *antioxidant*. How may oxidants and antioxidants affect human health? Consider this question to prepare for your Chemistry Course Challenge.

You already know that some metals are more reactive than others. You may also have carried out an investigation on the metal activity series in a previous course. In Investigation 10-A, located on page 470, you will discover how this series is related to oxidation and reduction. You will write chemical equations, ionic equations, and half-reactions for the single displacement reactions of several metals.

Section Summary

In this section, you learned to define and recognize redox reactions, and to write oxidation and reduction half-reactions. In Investigation 10-A, you observed the connection between the metal activity series and redox reactions. However, thus far, you have only worked with redox reactions that involve atoms and ions as reactants or products. In the next section, you will learn about redox reactions that involve covalent reactants or products.

Section Review

1 K/U Predict whether each of the following single displacement reactions will occur. If so, write a balanced chemical equation, a balanced net ionic equation, and two balanced half-reactions. Include the physical states of the reactants and products in each case.

(a) aqueous silver nitrate and metallic cadmium

(b) gold and aqueous copper(II) sulfate

(c) aluminum and aqueous mercury(II) chloride

2 **(a)** K/U On which side of an oxidation half-reaction are the electrons? Why?

(b) K/U On which side of a reduction half-reaction are the electrons? Why?

3 C Explain why, in a redox reaction, the oxidizing agent undergoes reduction.

4 C In a combination reaction, does metallic lithium act as an oxidizing agent or a reducing agent? Explain.

5 I Write a net ionic equation for a reaction in which

(a) Fe^{2+} acts as an oxidizing agent

(b) Al acts as a reducing agent

(c) Au^{3+} acts as an oxidizing agent

(d) Cu acts as a reducing agent

(e) Sn^{2+} acts as an oxidizing agent and as a reducing agent

6 MC The element potassium is made industrially by the single displacement reaction of molten sodium with molten potassium chloride.

(a) Write a net ionic equation for the reaction, assuming that all reactants and products are in the liquid state.

(b) Identify the oxidizing agent and the reducing agent in the reaction.

(c) Explain why the reaction is carried out in the liquid state and not in aqueous solution.

Unit Investigation Prep

In the end-of-unit investigation, you will be working with the metals zinc and copper. Which metal is more easily oxidized? Which is more easily reduced?

Oxidation Numbers

10.2

Redox reactions are very common. Some of them produce light in a process known as *chemiluminescence*. In living things, the production of light in redox reactions is known as *bioluminescence*. You can actually see the light from redox reactions occurring in some organisms, such as glowworms and fireflies, as shown in Figure 10.3.

Figure 10.3 **Fireflies use flashes of light produced by redox reactions to attract a mate.**

Section Preview/ Specific Expectations

In this section, you will

- **describe** oxidation and reduction in terms of changes in oxidation number
- **assign** oxidation numbers to elements in covalent molecules and polyatomic ions
- **identify** redox reactions using oxidation numbers
- **communicate** your understanding of the terms *oxidation numbers, oxidation, reduction*

Not all redox reactions give off light, however. How can you recognize a redox reaction, and how can you identify the oxidizing and reducing agents? In section 10.1, you saw net ionic equations with monatomic elements, such as Cu and Zn, and with ions containing a single element, such as Cu^{2+} and Zn^{2+}. In these cases, you could use ionic charges to describe the transfer of electrons. However, many redox reactions involve reactants or products with covalent bonds, including elements that exist as covalent molecules, such as oxygen, O_2; covalent compounds, such as water, H_2O; or polyatomic ions that are not spectator ions, such as permanganate, MnO_4^-. For reactions involving covalent reactants and products, you cannot use ionic charges to describe the transfer of electrons.

Oxidation numbers are actual or hypothetical charges, assigned using a set of rules. They are used to describe redox reactions with covalent reactants or products. They are also used to identify redox reactions, and to identify oxidizing and reducing agents. In this section, you will see how oxidation numbers were developed from Lewis structures, and then learn the rules to assign oxidation numbers.

CHEM FACT

Oxidation numbers are just a bookkeeping method used to keep track of electron transfers. In a covalent molecule or a polyatomic ion, the oxidation number of each element does *not* represent an ionic charge, because the elements are not present as ions. However, to assign oxidation numbers to the elements in a covalent molecule or polyatomic ion, you can *pretend* the bonds are ionic.

Oxidation Numbers from Lewis Structures

You are probably familiar with the Lewis structure of water, shown in Figure 10.4A. From the electronegativities on the periodic table in Figure 10.5, on the next page, you can see that oxygen (electronegativity 3.44) is more electronegative than hydrogen (electronegativity 2.20). The electronegativity difference is less than 1.7, so the two hydrogen-oxygen bonds are polar covalent, not ionic. In each bond, the electrons are more strongly attracted to the oxygen atom than to the hydrogen atom.

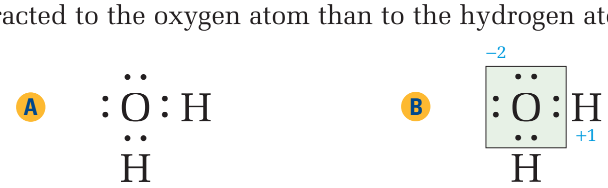

Figure 10.4 **(A) The Lewis structure of water; (B) The formal counting of electrons with the more electronegative element assigned a negative charge**

To assign oxidation numbers to the atoms in a water molecule, you can consider all the bonding electrons to be "owned" by the more electronegative oxygen atom, as shown in Figure 10.4B. Thus, each hydrogen atom in a water molecule is considered to have no electrons, as hydrogen would in a hydrogen ion, H^+. Therefore, the element hydrogen is assigned an oxidation number of +1 in water. On the other hand, the oxygen atom in a water molecule is considered to have a filled octet of electrons, as oxygen would in an oxide ion, O^{2-}. Therefore, the element oxygen is assigned an oxidation number of −2 in water. (**Note:** These are *not* ionic charges, since water is a covalent molecule. Also, note that the plus or minus sign in an oxidation number, such as −2, is written *before* the number. The plus or minus sign in an ionic charge, such as 2−, is written *after* the number.)

H 2.20																	He -
Li 0.98	Be 1.57											B 2.04	C 2.55	N 3.04	O 3.44	F 3.98	Ne -
Na 0.93	Mg 1.31											Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16	Ar -
K 0.82	Ca 1.00	Sc 1.36	Ti 1.54	V 1.63	Cr 1.66	Mn 1.55	Fe 1.83	Co 1.88	Ni 1.91	Cu 1.90	Zn 1.65	Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96	Kr -
Rb 0.82	Sr 0.95	Y 1.22	Zr 1.33	Nb 1.6	Mo 2.16	Tc 2.10	Ru 2.2	Rh 2.28	Pd 2.20	Ag 1.93	Cd 1.69	In 1.78	Sn 1.96	Sb 2.05	Te 2.1	I 2.66	Xe -
Cs 0.79	Ba 0.89	Lu 1.0	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2	Rn -
Fr 0.7	Ra 0.9	Lr -	Rf -	Db -	Sg -	Bh -	Hs -	Mt -	Uun -	Uuu -	Uub -	-	Uuq -	-	Uuh -	-	Uuo -

La 1.10	Ce 1.12	Pr 1.13	Nd 1.14	Pm -	Sm 1.17	Eu -	Gd 1.20	Tb -	Dy 1.22	Ho 1.23	Er 1.24	Tm 1.25	Yb -
Ac 1.1	Th 1.3	Pa 1.5	U 1.7	Np 1.3	Pu 1.3	Am -	Cm -	Bk -	Cf -	Es -	Fm -	Md -	No -

Figure 10.5 The periodic table, showing electronegativity values

In a chlorine molecule, Cl_2, each atom has the same electronegativity, so the bond is non-polar covalent. Because the electrons are equally shared, you can consider each chlorine atom to "own" one of the shared electrons, as shown in Figure 10.6. Thus, each chlorine atom in the molecule is considered to have the same number of electrons as a neutral chlorine atom. Each chlorine atom is therefore assigned an oxidation number of 0.

Figure 10.6 (A) The Lewis structure of a chlorine molecule; (B) The formal counting of electrons in a chlorine molecule for oxidation number purposes

Figure 10.7 shows how oxidation numbers are assigned for the polyatomic cyanide ion, CN^-. The electronegativity of nitrogen (3.04) is greater than the electronegativity of carbon (2.55). Thus, the three shared pairs of electrons are all considered to belong to the nitrogen atom. As a result, the carbon atom is considered to have two valence electrons, which is two electrons less than the four valence electrons of a neutral carbon atom. Therefore, the carbon atom in CN^- is assigned an oxidation number of +2. The nitrogen atom is considered to have eight valence electrons, which is three electrons more than the five valence electrons of a neutral nitrogen atom. Therefore, the nitrogen atom in CN^- is assigned an oxidation number of −3.

Figure 10.7 **(A) The Lewis structure of a cyanide ion; (B) The formal counting of electrons in a cyanide ion for oxidation number purposes**

You have seen examples of how Lewis structures can be used to assign oxidation numbers for polar molecules such as water, non-polar molecules such as chlorine, and polar polyatomic ions such as the cyanide ion. In the following ThoughtLab, you will use Lewis structures to assign oxidation number values, and then look for patterns in your results.

ThoughtLab Finding Rules for Oxidation Numbers

Procedure

1. Use Lewis structures to assign an oxidation number to each element in the following covalent molecules.
   (a) HI **(b)** O_2 **(c)** PCl_5 **(d)** BBr_3
2. Use Lewis structures to assign an oxidation number to each element in the following polyatomic ions.
   (a) OH^- **(b)** NH_4^+ **(c)** CO_3^{2-}
3. Assign an oxidation number to each of the following atoms or monatomic ions. Explain your reasoning.
   (a) Ne **(b)** K **(c)** I^- **(d)** Mg^{2+}

Analysis

1. For each molecule in question 1 of the procedure, find the sum of the oxidation numbers of all the atoms present. What do you notice? Explain why the observed sum must be true for a neutral molecule.
2. For each polyatomic ion in question 2 of the procedure, find the sum of the oxidation numbers of all the atoms present. Describe and explain any pattern you see.

Extension

3. Predict the sum of the oxidation numbers of the atoms in the hypochlorite ion, OCl^-.
4. Test your prediction from question 3.

Using Rules to Find Oxidation Numbers

Drawing Lewis structures to assign oxidation numbers can be a very time-consuming process for large molecules or large polyatomic ions. Instead, the results from Lewis structures have been summarized to produce a more convenient set of rules, which can be applied more quickly. Table 10.1 summarizes the rules used to assign oxidation numbers. You may have discovered some of these rules for yourself in the ThoughtLab you just completed.

Table 10.1 Oxidation Number Rules

Rules	Examples
1. A pure element has an oxidation number of 0.	Na in $Na_{(s)}$, Br in $Br_{2(\ell)}$, and P in $P_{4(s)}$ all have an oxidation number of 0.
2. The oxidation number of an element in a monatomic ion equals the charge of the ion.	The oxidation number of Al in Al^{3+} is +3. The oxidation number of Se in Se^{2-} is −2.
3. The oxidation number of hydrogen in its compounds is +1, except in metal hydrides, where the oxidation number of hydrogen is −1.	The oxidation number of H in H_2S or CH_4 is +1. The oxidation number of H in NaH or in CaH_2 is −1.
4. The oxidation number of oxygen in its compounds is usually −2, but there are exceptions. These include peroxides, such as H_2O_2, and the compound OF_2.	The oxidation number of O in Li_2O or in KNO_3 is −2.
5. In covalent compounds that do not contain hydrogen or oxygen, the more electronegative element is assigned an oxidation number that equals the negative charge it usually has in its ionic compounds.	The oxidation number of Cl in PCl_3 is −1. The oxidation number of S in CS_2 is −2.
6. The sum of the oxidation numbers of all the elements in a compound is 0.	In CF_4, the oxidation number of F is −1, and the oxidation number of C is +4. $(+4) + 4(-1) = 0$
7. The sum of the oxidation numbers of all the elements in a polyatomic ion equals the charge on the ion.	In NO_2^-, the oxidation number of O is −2, and the oxidation number of N is +3. $(+3) + 2(-2) = -1$

Some oxidation numbers found using these rules are not integers. For example, an important iron ore called magnetite has the formula Fe_3O_4. Using the oxidation number rules, you can assign oxygen an oxidation number of −2, and calculate an oxidation number of $+\frac{8}{3}$ for iron. However, magnetite contains no iron atoms with this oxidation number. It actually contains iron(III) ions and iron(II) ions in a 2:1 ratio. The formula of magnetite is sometimes written as $Fe_2O_3 \bullet FeO$ to indicate that there are two different oxidation numbers. The value $+\frac{8}{3}$ for the oxidation number of iron is an average value.

$$\frac{2(+3) + (+2)}{3} = +\frac{8}{3}$$

Even though some oxidation numbers found using these rules are averages, the rules are still useful for monitoring electron transfers in redox reactions.

In the following Sample Problem, you will find out how to apply these rules to covalent molecules and polyatomic ions.

Sample Problem

Assigning Oxidation Numbers

Problem

Assign an oxidation number to each element.

(a) $SiBr_4$ **(b)** $HClO_4$ **(c)** $Cr_2O_7^{2-}$

Solution

(a)
- Because the compound $SiBr_4$ does not contain hydrogen or oxygen, rule 5 applies. Because $SiBr_4$ is a compound, rule 6 also applies.
- Silicon has an electronegativity of 1.90. Bromine has an electronegativity of 2.96. From rule 5, therefore, you can assign bromine an oxidation number of −1.
- The oxidation number of silicon is unknown, so let it be x. You know from rule 6 that the sum of the oxidation numbers is 0. Then,

$$x + 4(-1) = 0$$
$$x - 4 = 0$$
$$x = 4$$

The oxidation number of silicon is +4. The oxidation number of bromine is −1.

(b)
- Because the compound $HClO_4$ contains hydrogen and oxygen, rules 3 and 4 apply. Because $HClO_4$ is a compound, rule 6 also applies.
- Hydrogen has its usual oxidation number of +1. Oxygen has its usual oxidation number of −2. The oxidation number of chlorine is unknown, so let it be x. You know from rule 6 that the sum of the oxidation numbers is 0. Then,

$$(+1) + x + 4(-2) = 0$$
$$x - 7 = 0$$
$$x = 7$$

The oxidation number of hydrogen is +1. The oxidation number of chlorine is +7. The oxidation number of oxygen is −2.

(c)
- Because the polyatomic ion $Cr_2O_7^{2-}$ contains oxygen, rule 4 applies. Because $Cr_2O_7^{2-}$ is a polyatomic ion, rule 7 also applies.
- Oxygen has its usual oxidation number of −2.
- The oxidation number of chromium is unknown, so let it be x. You know from rule 7 that the sum of the oxidation numbers is −2. Then,

$$2x + 7(-2) = -2$$
$$2x - 14 = -2$$
$$2x = 12$$
$$x = 6$$

The oxidation number of chromium is +6. The oxidation number of oxygen is −2.

PROBLEM TIP

When finding the oxidation numbers of elements in ionic compounds, you can work with the ions separately. For example, $Na_2Cr_2O_7$ contains two Na^+ ions, and so sodium has an oxidation number of +1. The oxidation numbers of Cr and O can then be calculated as shown in part (c) of the Sample Problem.

Practice Problems

9. Determine the oxidation number of the specified element in each of the following.

(a) N in NF_3 **(b)** S in S_8 **(c)** Cr in CrO_4^{2-}

(d) P in P_2O_5 **(e)** C in $C_{12}H_{22}O_{11}$ **(f)** C in $CHCl_3$

10. Determine the oxidation number of each element in each of the following.

(a) H_2SO_3 **(b)** OH^- **(c)** HPO_4^{2-}

11. As stated in rule 4, oxygen does not always have its usual oxidation number of –2. Determine the oxidation number of oxygen in each of the following.

(a) the compound oxygen difluoride, OF_2 **(b)** the peroxide ion, O_2^{2-}

12. Determine the oxidation number of each element in each of the following ionic compounds by considering the ions separately. **Hint:** One formula unit of the compound in part (c) contains two identical monatomic ions and one polyatomic ion.

(a) $Al(HCO_3)_3$ **(b)** $(NH_4)_3PO_4$ **(c)** $K_2H_3IO_6$

Applying Oxidation Numbers to Redox Reactions

You have seen that the single displacement reaction of zinc with copper(II) sulfate is a redox reaction, represented by the following chemical equation and net ionic equation.

$$Zn_{(s)} + CuSO_{4(aq)} \rightarrow Cu_{(s)} + ZnSO_{4(aq)}$$
$$Zn_{(s)} + Cu^{2+}{}_{(aq)} \rightarrow Cu_{(s)} + Zn^{2+}{}_{(aq)}$$

Each atom or ion shown in the net ionic equation can be assigned an oxidation number. Zn has an oxidation number of 0; Cu^{2+} has an oxidation number of +2; Cu has an oxidation number of 0; and Zn^{2+} has an oxidation number of +2. Thus, there are changes in oxidation numbers in this reaction. The oxidation number of zinc increases, while the oxidation number of copper decreases.

oxidation number increases
(loss of electrons)

$$\underset{0}{Zn} + \underset{+2}{Cu^{2+}} \rightarrow \underset{+2}{Zn^{2+}} + \underset{0}{Cu}$$

oxidation number decreases
(gain of electrons)

In the oxidation half-reaction, the element zinc undergoes an increase in its oxidation number from 0 to +2.

$$\underset{0}{Zn} \rightarrow \underset{+2}{Zn^{2+}} + 2e^-$$

In the reduction half-reaction, the element copper undergoes a decrease in its oxidation number from +2 to 0.

$$\underset{+2}{Cu^{2+}} + 2e^- \rightarrow \underset{0}{Cu}$$

Therefore, you can describe oxidation and reduction as follows. (Also see Figure 10.8.)

- **Oxidation** is an increase in oxidation number.
- **Reduction** is a decrease in oxidation number.

You can also monitor changes in oxidation numbers in reactions that involve covalent molecules. For example, oxidation number changes occur in the reaction of hydrogen and oxygen to form water.

$$2\underset{0}{H}_{2(g)} + \underset{0}{O}_{2(g)} \rightarrow 2\underset{+1}{H}_2\underset{-2}{O}_{(\ell)}$$

Because hydrogen combines with oxygen in this reaction, hydrogen undergoes oxidation, according to the historical definition given at the beginning of section 10.1. Hydrogen also undergoes oxidation according to the modern definition, because the oxidation number of hydrogen increases from 0 to +1. Hydrogen is the reducing agent in this reaction. The oxygen undergoes reduction, because its oxidation number decreases from 0 to −2. Oxygen is the oxidizing agent in this reaction.

The following Sample Problem illustrates how to use oxidation numbers to identify redox reactions, oxidizing agents, and reducing agents.

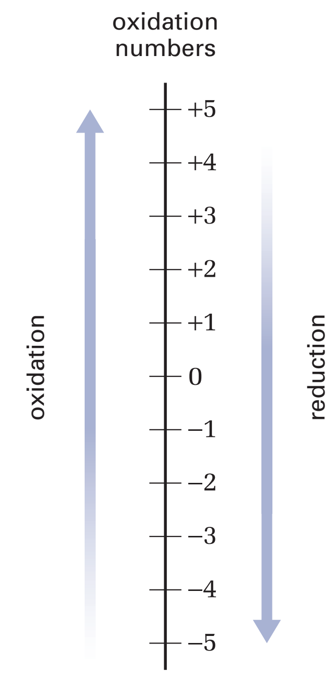

Figure 10.8 Oxidation and reduction are directly related to changes in oxidation numbers.

Sample Problem

Identifying Redox Reactions

Problem

Determine whether each of the following reactions is a redox reaction. If so, identify the oxidizing agent and the reducing agent.

(a) $CH_{4(g)} + Cl_{2(g)} \rightarrow CH_3Cl_{(g)} + HCl_{(g)}$

(b) $CaCO_{3(s)} + 2HCl_{(aq)} \rightarrow CaCl_{2(aq)} + H_2O_{(\ell)} + CO_{2(g)}$

Solution

Find the oxidation number of each element in the reactants and products. Identify any elements that undergo an increase or a decrease in oxidation number during the reaction.

(a) The oxidation number of each element in the reactants and products is as shown.

$$\underset{-4}{C}\underset{+1}{H}_{4(g)} + \underset{0}{Cl}_{2(g)} \rightarrow \underset{-2}{C}\underset{+1}{H}_3\underset{-1}{Cl}_{(g)} + \underset{+1}{H}\underset{-1}{Cl}_{(g)}$$

- The oxidation number of hydrogen is +1 on both sides of the equation, so hydrogen is neither oxidized nor reduced.
- Both carbon and chlorine undergo changes in oxidation number, so the reaction is a redox reaction.
- The oxidation number of carbon increases from −4 to −2. The carbon atoms on the reactant side exist in methane molecules, $CH_{4(g)}$, so methane is oxidized. Therefore, methane is the reducing agent.
- The oxidation number of chlorine decreases from 0 to −1, so elemental chlorine, $Cl_{2(g)}$, is reduced. Therefore, elemental chlorine is the oxidizing agent.

(b) Because this reaction involves ions, write the equation in its total ionic form.

$$CaCO_{3(s)} + 2H^+_{(aq)} + 2Cl^-_{(aq)} \rightarrow Ca^{2+}_{(aq)} + 2Cl^-_{(aq)} + H_2O_{(\ell)} + CO_{2(g)}$$

Continued ...

PROBLEM TIPS

- Use the fact that the sum of the oxidation numbers in a molecule is zero to check the assignment of the oxidation numbers.
- Make sure that a reaction does not include only a reduction or only an oxidation. Oxidation and reduction must occur together in a redox reaction.

CONCEPT CHECK

In part (b) of the Sample Problem, you can assign oxidation numbers to each element in the given chemical equation *or* in the net ionic equation. What are the advantages and the disadvantages of each method?

CONCEPT CHECK

In your previous chemistry course, you classified reactions into four main types: synthesis, decomposition, single displacement, and double displacement. You also learned to recognize combustion reactions and neutralization reactions. You have now learned to classify redox reactions. In addition, you have also learned about a special type of redox reaction known as a disproportionation reaction.

1. Classify each reaction in two ways.
   - **(a)** magnesium reacting with a solution of iron(II) nitrate
     $Mg + Fe(NO_3)_2 \rightarrow Fe + Mg(NO_3)_2$
   - **(b)** hydrogen sulfide burning in oxygen
     $2H_2S + 3O_2 \rightarrow 2SO_2 + 2H_2O$
   - **(c)** calcium reacting with chlorine
     $Ca + Cl_2 \rightarrow CaCl_2$
2. Classify the formation of water and oxygen from hydrogen peroxide in three ways.
   $2H_2O_2 \rightarrow 2H_2O + O_2$

Continued ...

The chloride ions are spectator ions, which do not undergo oxidation or reduction. The net ionic equation is as follows.

$$CaCO_{3(s)} + 2H^+_{(aq)} \rightarrow Ca^{2+}_{(aq)} + H_2O_{(\ell)} + CO_{2(g)}$$

For the net ionic equation, the oxidation number of each element in the reactants and products is as shown.

$$\underset{+2\ +4\ -2}{CaCO_{3(s)}} + \underset{+1}{2H^+_{(aq)}} \rightarrow \underset{+2}{Ca^{2+}_{(aq)}} + \underset{+1\ -2}{H_2O_{(\ell)}} + \underset{+4\ -2}{CO_{2(g)}}$$

No elements undergo changes in oxidation numbers, so the reaction is not a redox reaction.

Practice Problems

13. Determine whether each reaction is a redox reaction.

(a) $H_2O_2 + 2Fe(OH)_2 \rightarrow 2Fe(OH)_3$

(b) $PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$

14. Identify the oxidizing agent and the reducing agent for the redox reaction(s) in the previous question.

15. For the following balanced net ionic equation, identify the reactant that undergoes oxidation and the reactant that undergoes reduction.

$Br_2 + 2ClO_2^- \rightarrow 2Br^- + 2ClO_2$

16. Nickel and copper are two metals that are important to the Ontario economy, particularly in the Sudbury area. Nickel and copper ores usually contain the metals as sulfides, such as NiS and Cu_2S. Do the extractions of these pure elemental metals from their ores involve redox reactions? Explain your reasoning.

Section Summary

In this section, you extended your knowledge of redox reactions to include covalent reactants and products. You did this by learning how to assign oxidation numbers and how to use them to recognize redox reactions, oxidizing agents, and reducing agents. In the next section, you will extend your knowledge further by learning how to write balanced equations that represent redox reactions.

Section Review

1 C At the beginning of section 10.1, it was stated that oxidation originally meant "to combine with oxygen." Explain why a metal that combines with the element oxygen undergoes oxidation as we now define it. What happens to the oxygen in this reaction? Write a balanced chemical equation for a reaction that illustrates your answer.

2 K/U Determine whether each of the following reactions is a redox reaction.

(a) $H_2 + I_2 \rightarrow 2HI$

(b) $2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2$