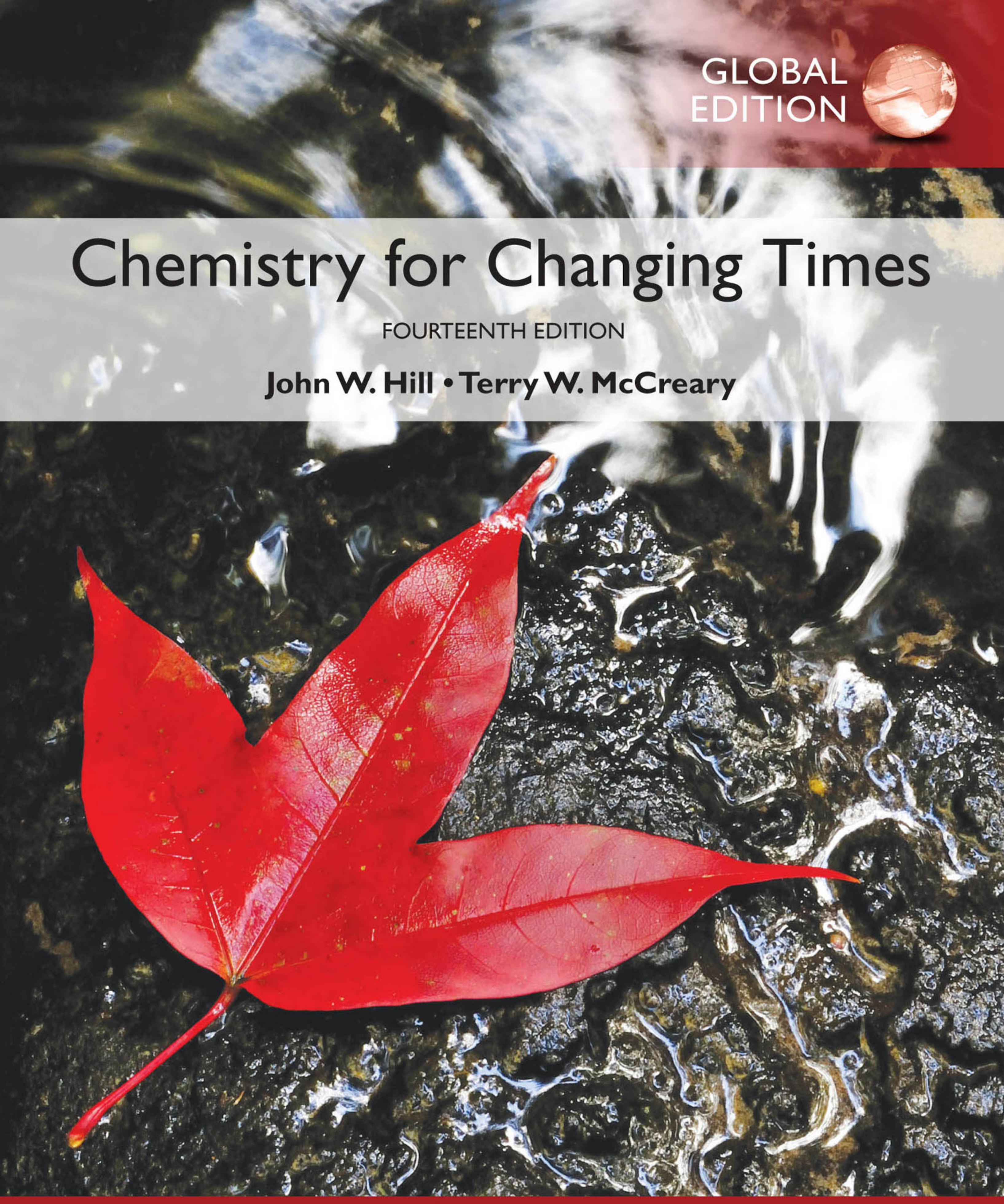


GLOBAL EDITION

Chemistry for Changing Times

FOURTEENTH EDITION

John W. Hill • Terry W. McCreary

ALWAYS LEARNING

PEARSON

PERIODIC TABLE OF THE ELEMENTS

Metals | Nonmetals | Noble gases

Period	Main groups		Transition metals										Main groups					
	1[a] 1A[b]	2 2A	3 3B	4 4B	5 5B	6 6B	7 7B	8 8B	9 8B	10 8B	11 1B	12 2B	13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
1	1 **H** Hydrogen 1.00794																	2 **He** Helium 4.002602
2	3 **Li** Lithium 6.941	4 **Be** Beryllium 9.012182											5 **B** Boron 10.811	6 **C** Carbon 12.0107	7 **N** Nitrogen 14.00674	8 **O** Oxygen 15.9994	9 **F** Fluorine 18.998403	10 **Ne** Neon 20.1797
3	11 **Na** Sodium 22.989770	12 **Mg** Magnesium 24.3050											13 **Al** Aluminum 26.981538	14 **Si** Silicon 28.0855	15 **P** Phosphorus 30.973762	16 **S** Sulfur 32.066	17 **Cl** Chlorine 35.4527	18 **Ar** Argon 39.948
4	19 **K** Potassium 39.0983	20 **Ca** Calcium 40.078	21 **Sc** Scandium 44.95591	22 **Ti** Titanium 47.867	23 **V** Vanadium 50.9415	24 **Cr** Chromium 51.9961	25 **Mn** Manganese 54.938049	26 **Fe** Iron 55.845	27 **Co** Cobalt 58.933200	28 **Ni** Nickel 58.6934	29 **Cu** Copper 63.546	30 **Zn** Zinc 65.39	31 **Ga** Gallium 69.723	32 **Ge** Germanium 72.61	33 **As** Arsenic 74.92160	34 **Se** Selenium 78.96	35 **Br** Bromine 79.904	36 **Kr** Krypton 83.80
5	37 **Rb** Rubidium 85.4678	38 **Sr** Strontium 87.62	39 **Y** Yttrium 88.90585	40 **Zr** Zirconium 91.224	41 **Nb** Niobium 92.90638	42 **Mo** Molybdenum 95.94	43 **Tc** Technetium [98]	44 **Ru** Ruthenium 101.07	45 **Rh** Rhodium 102.90550	46 **Pd** Palladium 106.42	47 **Ag** Silver 107.8682	48 **Cd** Cadmium 112.411	49 **In** Indium 114.818	50 **Sn** Tin 118.710	51 **Sb** Antimony 121.760	52 **Te** Tellurium 127.60	53 **I** Iodine 126.90447	54 **Xe** Xenon 131.29
6	55 **Cs** Cesium 132.90545	56 **Ba** Barium 137.327	57 ***La** Lanthanum 138.9055	72 **Hf** Hafnium 178.49	73 **Ta** Tantalum 180.9479	74 **W** Tungsten 183.84	75 **Re** Rhenium 186.207	76 **Os** Osmium 190.23	77 **Ir** Iridium 192.217	78 **Pt** Platinum 195.078	79 **Au** Gold 196.96655	80 **Hg** Mercury 200.59	81 **Tl** Thallium 204.3833	82 **Pb** Lead 207.2	83 **Bi** Bismuth 208.98038	84 **Po** Polonium [209]	85 **At** Astatine [210]	86 **Rn** Radon [222]
7	87 **Fr** Francium [223]	88 **Ra** Radium 226.025	89 **†Ac** Actinium 227.028	104 **Rf** Rutherfordium [261]	105 **Db** Dubnium [262]	106 **Sg** Seaborgium [266]	107 **Bh** Bohrium [267]	108 **Hs** Hassium [269]	109 **Mt** Meitnerium [268]	110 **Ds** Darmstadtium [281]	111 **Rg** Roentgenium [272]	112 **Cn** Copernicum [285]	113[c] [286]	114 **Fl** [289]	115 [288]	116 **Lv** [293]	117 [294]	118 [294]

*Lanthanide series	58 **Ce** Cerium 140.116	59 **Pr** Praseodymium 140.90765	60 **Nd** Neodymium 144.24	61 **Pm** Promethium [145]	62 **Sm** Samarium 150.36	63 **Eu** Europium 151.964	64 **Gd** Gadolinium 157.25	65 **Tb** Terbium 158.92534	66 **Dy** Dysprosium 162.50	67 **Ho** Holmium 164.93032	68 **Er** Erbium 167.26	69 **Tm** Thulium 168.93421	70 **Yb** Ytterbium 173.04	71 **Lu** Lutetium 174.967
†Actinide series	90 **Th** Thorium 232.0381	91 **Pa** Protactinium 231.03588	92 **U** Uranium 238.0289	93 **Np** Neptunium 237.048	94 **Pu** Plutonium [244]	95 **Am** Americium [243]	96 **Cm** Curium [247]	97 **Bk** Berkelium [247]	98 **Cf** Californium [251]	99 **Es** Einsteinium [252]	100 **Fm** Fermium [257]	101 **Md** Mendelevium [258]	102 **No** Nobelium [259]	103 **Lr** Lawrencium [262]

Atomic masses in brackets are the masses of the longest-lived or most important isotope of certain radioactive elements.

[a] The labels on top (1, 2, 3 ... 18) are the group numbers recommended by the International Union of Pure and Applied Chemistry.

[b] The labels on the bottom (1A, 2A, ... 8A) are the group numbers commonly used in the United States and the ones we use in this text.

[c] The names and symbols of elements 113, 115, 117, and 118 have not been assigned.

Further information is available at the Web site of WebElements™.

8

OXIDATION AND REDUCTION

Have You Ever Wondered?

1. Why are copper roofs green?
2. How does an electric eel create electricity?
3. Why does a battery go dead?
4. Why are some batteries rechargeable but others are not?
5. Why do we not see more "rust bucket" ships?
6. Does hydrogen have a promising future as a fuel?

Learning Objectives

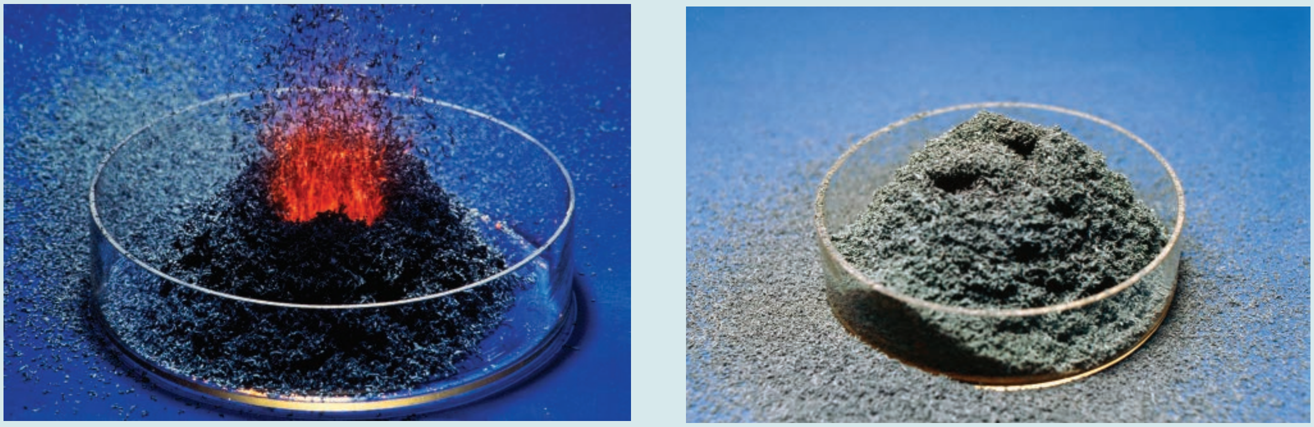
- Classify a particular change within a redox reaction as either oxidation or reduction. (8.1)
- Identify an oxidation–reduction reaction. (8.1)
- Identify the oxidizing agent and the reducing agent in a redox reaction. (8.2)
- Balance redox equations. (8.3)
- Identify and write the half-reactions in an electrochemical cell. (8.3)
- Describe the reactions that occur when iron rusts. (8.4)
- Explain why an explosive reaction is so energetic. (8.4)
- Write equations for reactions in which oxygen is an oxidizing agent. (8.5)
- List some of the common oxidizing agents encountered in daily life. (8.5)
- Identify some common reducing agents. (8.6)
- Write the overall equations for the metabolism of glucose and for photosynthesis. (8.7)
- Use a balanced reaction to calculate the atom economy and E factor of the reaction
- Describe the role of catalysts in minimizing waste in the chemical and allied industries.

BURN AND UNBURN From the conversion of sunlight to food to looking up a recipe on a smart phone to cook the food, to metabolizing the food to gain energy so we can look up the next recipe, to the simple act of breathing oxygen in and carbon dioxide out, we depend on an important group of reactions called *oxidation–reduction reactions*, or *redox reactions* (a shortening of *reduction–oxidation*). These reactions are extremely diverse: charcoal burns, iron rusts, bleach removes stains. Redox reactions are employed in pollution remediation, wastewater treatment, and determination of blood-sugar levels by diabetics. Even the generation of a shock of 600 volts by an electric eel is due to redox processes.

Corrosion is a fundamental process that takes place over time. The cost to the economy of the United States has been estimated to be approximately 3.1% of the gross domestic product, or more than $275 billion each year. The estimated corrosion cost to the Department of Defense is about $20 billion annually. Producing and purifying metals for various applications consumes energy, and corrosion is nature's way of returning these metals to their native energy levels. Metal corrosion nearly always involves redox reactions. Other redox reactions are desirable, or even necessary, to life itself. In this chapter, we will examine the nature of redox reactions, and we will look at some of their applications in life and in modern technology.

Oxidation and reduction always take place together. They represent opposite directions of a single process, a redox reaction. When one substance is oxidized, another is reduced. In other words, you can't have one without the other (Figure 8.1). However, it is sometimes convenient to discuss only a part of the process—the oxidation part or the reduction part.

Reduced forms of matter—foods, coal, and gasoline—are high in energy. *Oxidized* forms—carbon dioxide and water—are low in energy. The energy in foods and fossil fuels is released when these materials are oxidized. In this chapter, we examine the processes of oxidation and reduction in some detail to better understand the chemical reactions that keep us alive and maintain our civilization.



▲ **Figure 8.1** Oxidation and reduction always occur together. Pictured on the left is a reaction called the ammonium dichromate volcano. In the reaction, the ammonium ion (NH_4^+) is oxidized and the dichromate ion ($Cr_2O_7^{2-}$) is reduced. Considerable heat and light are evolved. The equation for the reaction is

$$(NH_4)\,Cr_2O_7 \longrightarrow Cr_2O_3 + N_2 + 4\,H_2O$$

The water is driven off as vapor, and the nitrogen gas escapes, leaving pure Cr_2O_3 as the visible product (right).

8.1 Oxidation and Reduction: Four Views

Learning Objectives › Classify a particular change within a redox reaction as either oxidation or reduction. › Identify an oxidation–reduction reaction.

One of the most important redox reactions is combustion, that is, the burning of a substance in oxygen. The term **oxidation** came from the observation that during combustion, oxygen was added. The opposite process would require the removal of oxygen, and thus, it was called **reduction**.

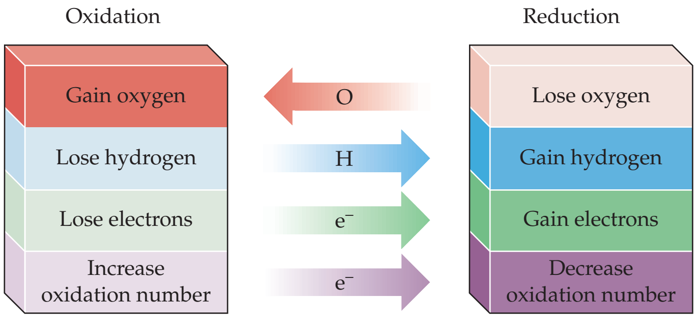
Originally, the term *oxidation* was limited to reactions involving combination with oxygen. As chemists came to realize that combination with chlorine (or bromine or another active nonmetal) was not all that different from combination with oxygen, they broadened the definition of oxidation to include reactions involving these other substances—as we shall shortly see.

Let's take a look at the simplest combustion reaction, the combustion (oxygen present) of hydrogen to form water.

$$2\,H_2 + O_2 \longrightarrow 2\,H_2O$$

In this reaction, oxygen is added to hydrogen, oxidizing it. At the same time, the oxygen is reduced. Whenever oxidation occurs, reduction must also occur in an exactly equivalent amount, and vice versa.

Because oxidation and reduction are chemical opposites and constant companions, their definitions are linked. We can view oxidation and reduction in four different ways (Figure 8.2).



▶ **Figure 8.2** Four different views of oxidation and reduction.

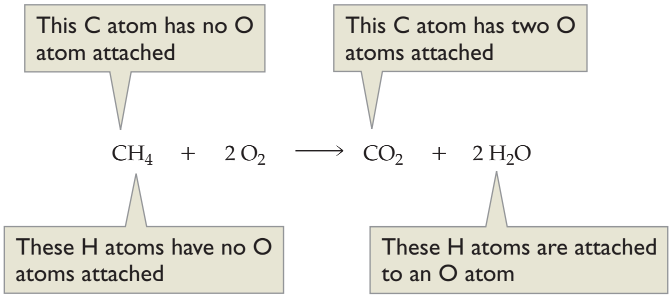
1. *Oxidation* is a gain of oxygen atoms.
   Reduction is a loss of oxygen atoms.

At high temperatures (such as those in automobile engines), nitrogen, which is normally quite unreactive, combines with oxygen to form nitric oxide.

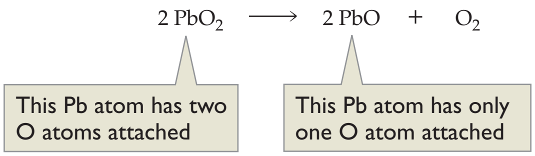
$$N_2 + O_2 \longrightarrow 2\ NO$$

Nitrogen gains oxygen atoms; there are no O atoms in the N_2 molecule and one O atom in each of the NO molecules. Therefore, nitrogen is oxidized.

Now consider what happens when methane is burned to form carbon dioxide and water. Both carbon and hydrogen gain oxygen atoms, and so both elements are oxidized.



When lead dioxide is heated at high temperatures, it decomposes as follows:



The lead dioxide loses oxygen, so it is reduced.

CONCEPTUAL Example 8.1 Redox Processes—Gain or Loss of Oxygen Atoms

In each of the following changes, is the reactant undergoing oxidation or reduction? (These are not complete chemical equations.)

a. $Pb \longrightarrow PbO_2$
b. $SnO_2 \longrightarrow SnO$
c. $KClO_3 \longrightarrow KCl$
d. $Cu_2O \longrightarrow 2\ CuO$

Solution

a. Lead gains oxygen atoms (it has none on the left and two on the right); it is oxidized.

b. Tin loses an oxygen atom (it has two on the left and only one on the right); it is reduced.

c. There are three O atoms on the left and none on the right. The compound loses oxygen; it is reduced.

d. The two copper atoms on the left share a single oxygen atom, that is, half an oxygen atom each. On the right, each Cu atom has an O atom all to itself. Cu has gained oxygen; it is oxidized.

▪ EXERCISE 8.1

In each of the following changes, is the reactant undergoing oxidation or reduction? (These are not complete chemical equations.)

a. $3\ Fe \longrightarrow Fe_3O_4$ **b.** $NO \longrightarrow NO_2$

c. $CrO_3 \longrightarrow Cr_2O_3$ **d.** $C_3H_6O \longrightarrow C_3H_6O_2$

A second view of oxidation and reduction involves hydrogen atoms.

2. *Oxidation* is a loss of hydrogen atoms.
Reduction is a gain of hydrogen atoms.
Look once more at the burning of methane:

$$CH_4 + 2\ O_2 \longrightarrow CO_2 + 2\ H_2O$$

The oxygen gains hydrogen to form water, so the oxygen is reduced. Methane loses hydrogen and is oxidized. (We see that the carbon and hydrogen atoms in CH_4 also gain oxygen, so our two views of oxidation and reduction are consistent with one another.)

Methyl alcohol (CH_3OH), when passed over hot copper gauze, forms formaldehyde and hydrogen gas.

$$CH_3OH \longrightarrow CH_2O + H_2$$

The C and O atoms have four H atoms attached

The C and O atoms have only two H atoms attached

Because the methyl alcohol loses hydrogen, it is oxidized in this reaction.

Methyl alcohol can be made by reaction of carbon monoxide with hydrogen.

$$CO + 2\ H_2 \longrightarrow CH_3OH$$

Because the carbon monoxide gains hydrogen atoms, it is reduced.

Biochemists often find the gain or loss of hydrogen atoms a useful way to look at oxidation–reduction processes. For example, a substance called NAD^+ is changed to NADH in a variety of biochemical redox reactions. The actual molecules are rather complex, but we can write the equation for the oxidation of ethyl alcohol to acetaldehyde, one step in the metabolism of the alcohol, as follows.

$$CH_3CH_2OH + NAD^+ \longrightarrow CH_3CHO + NADH + H^+$$

We can see that ethyl alcohol is oxidized (loses hydrogen) and NAD^+ is reduced (gains hydrogen).

CONCEPTUAL Example 8.2 Redox Processes—Gain or Loss of Hydrogen Atoms

In each of the following changes, is the reactant undergoing oxidation or reduction? (These are not complete chemical equations.)

a. $C_2H_6O \longrightarrow C_2H_4O$ **b.** $C_2H_2 \longrightarrow C_2H_6$

Solution

a. There are six H atoms in the reactant on the left and only four in the product on the right. The reactant loses H atoms; it is oxidized.

b. There are two H atoms in the reactant on the left and six in the product on the right. The reactant gains H atoms; it is reduced.

■ EXERCISE 8.2

In each of the following changes, is the reactant undergoing oxidation or reduction? (These are not complete chemical equations.)

a. $C_3H_6O \longrightarrow C_3H_8O$ **b.** $C_3H_6 \longrightarrow C_3H_4$

A third view of oxidation and reduction involves gain or loss of electrons.

3. *Oxidation* is a loss of electrons.
Reduction is a gain of electrons.
When magnesium metal reacts with chlorine, magnesium ions and chloride ions are formed.

$$Mg + Cl_2 \longrightarrow Mg^{2+} + 2\,Cl^-$$

Because the magnesium atom loses electrons (two), it is oxidized, and because the chlorine atoms gain electrons (one each), they are reduced.

A redox reaction also takes place when zinc is placed in an acidic solution.

$$Zn + 2\,H^+ \longrightarrow Zn^{2+} + H_2$$

In this reaction, it can be seen that zinc loses two electrons, which means it is oxidized. Each of the two hydrogen atoms, on the other hand, gains an electron and is thus reduced.

There are two popular mnemonics for remembering the link between oxidation/reduction and electron loss/gain:

LEO the lion says GER
Loss of
Electrons Is
Oxidation
Gain of
Electrons Is
Reduction

OIL RIG
Oxidation
Is
Loss of Electrons
Reduction
Is
Gain of Electrons

CONCEPTUAL Example 8.3 Redox Processes—Gain or Loss of Electrons

In each of the following changes, is the reactant undergoing oxidation or reduction? (These are not complete chemical equations.)

a. $Zn \longrightarrow Zn^{2+}$ **b.** $Fe^{3+} \longrightarrow Fe^{2+}$

c. $S^{2-} \longrightarrow S$ **d.** $F_2 \longrightarrow 2\,F^-$

Solution

a. In forming a 2+ ion, a Zn atom loses two electrons: $Zn \longrightarrow Zn^{2+} + 2\,e^-$, so zinc is oxidized.

b. To change from a 3+ ion to a 2+ ion, Fe gains an electron: $Fe^{3+} + 1e^- \longrightarrow Fe^{2+}$. This means that Fe ion is reduced.

c. To change from an S^{2-} ion to an atom with no charge, S loses two electrons: $S^{2-} \longrightarrow S + 2e^-$. So, the sulfide ion is oxidized.

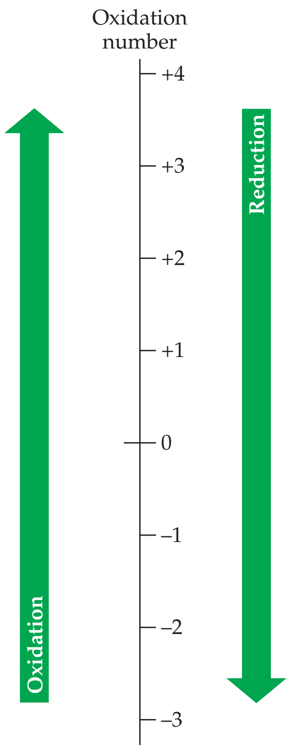
d. Here two F^- ions are formed from neutral diatomic F_2, so an electron is gained by each fluorine atom in F_2: $F_2 + 2e^- \longrightarrow 2\,F^-$. In other words, F is reduced.

■ EXERCISE 8.3

In each of the following changes, is the reactant undergoing oxidation or reduction? (These are not complete chemical equations.)

a. $Cr^{6+} \longrightarrow Cr^{3+}$ **b.** $Sn^{2+} \longrightarrow Sn^{4+}$

c. $2\,H^+ \longrightarrow H_2$ **d.** $Hg^{2+} \longrightarrow Hg$



▲ **Figure 8.3** An increase in oxidation number means a loss of electrons and is therefore oxidation. A decrease in oxidation number means a gain of electrons and is therefore reduction.

At this stage, it would be highly beneficial to introduce the concept of oxidation numbers (or oxidation states) and how it is applied. The fourth view of oxidation and reduction involves an increase or decrease in oxidation number (see Figure 8.3).

4. *Oxidation* increases the oxidation number.
Reduction decreases the oxidation number.

For monoatomic ions, the oxidation number can be defined as the number of unit charges on the atom. For instance, in Fe^{3+} and S^{2-} the oxidation numbers of iron and sulfur atoms are +3 and −2, respectively.

As you already know from Chapter 4, for an atom in a molecule (or a polyatomic ion), the situation is a little more complicated due to the sharing of electrons through bonds. This means that usually the oxidation number for atoms within a molecule is the charge that an atom would have *if the bonding was ionic* and not covalent.

When an oxidation number increases, the actual or perceived charge of an atom becomes more positive or less negative as a result of an electron (or electrons) being lost. The opposite is true for a reduction: The charge of an atom becomes less positive or more negative as a result of an electron (or electrons) being gained.

The following set of rules *generally* yields correct oxidation numbers:

1. An atom in its elemental form has an oxidation number of 0.
2. An atom in a monoatomic ion has an oxidation number equal to the charge of the ion.
3. Hydrogen and oxygen in compounds have oxidation numbers of +1 and −2, respectively. (Exceptions: −1 for oxygen in peroxides, e.g., H_2O_2; −1 for hydrogen in hydrides, e.g., CaH_2)
4. The sum of the oxidation numbers of the atoms in a polyatomic ion (or molecule) equals the charge of the ion (or molecule).

Note the placement of the sign (+ or −):
Fe^{3+} (sign after the number in the charge of an ion)
and: +3 (sign before the number in the oxidation number)

CONCEPTUAL Example 8.4 Determining Oxidation Numbers in Molecules and Polyatomic Ions

What are the oxidation numbers of atoms in the following molecules and ions?

a. SO_2 **b.** HNO_2 **c.** NH_4^+ **d.** $Cr_2O_7^{2-}$

Solution

a.

$\underset{S}{\square} + 2\underset{O_2}{\square}$ Step 1: Place boxes above elements. Multiply each box by the number of atoms of that element in a molecule. Boxes *will* hold oxidation numbers.

$\underset{S}{\square} + 2\underset{O_2}{\square} = 0$ Step 2: Set up an "equation" in which the sum of the oxidation numbers of all atoms equals 0.

$\underset{S}{\square} + 2\underset{O_2}{\boxed{-2}} = 0$ Step 3: Follow oxidation number assignment rules for oxygen (–2).

$\underset{S}{\boxed{+4}} + 2\underset{O_2}{\boxed{-2}} = 0$ Step 4: Determine the oxidation number for sulfur (+4).

b.

$\underset{H}{\square} + \underset{N}{\square} + 2\underset{O_2}{\square}$ Step 1: Place boxes above elements. Multiply each box by the number of atoms of that element in a molecule. Boxes *will* hold oxidation numbers.

$\underset{H}{\square} + \underset{N}{\square} + 2\underset{O_2}{\square} = 0$ Step 2: Set up an "equation" in which the sum of the oxidation numbers of all atoms equals 0.

$\underset{H}{\boxed{+1}} + \underset{N}{\square} + 2\underset{O_2}{\boxed{-2}} = 0$ Step 3: Follow oxidation number assignment rules for oxygen (–2) and hydrogen (+1).

$\underset{H}{\boxed{+1}} + \underset{N}{\boxed{+3}} + 2\underset{O_2}{\boxed{-2}} = 0$ Step 4: Determine the oxidation number for nitrogen (+3).