CHAPTER 17

Reaction Kinetics

Chemists can determine the rates at which chemical reactions occur.

The Thermite Reaction

The Reaction Process

SECTION 1

OBJECTIVES

- Explain the concept of reaction mechanism.
- Use the collision theory to interpret chemical reactions.
- Define *activated complex.*
- Relate activation energy to enthalpy of reaction.

By studying many types of experiments, chemists have found that chemical reactions occur at widely differing rates. For example, in the presence of air, iron rusts very slowly, whereas the methane in natural gas burns rapidly. The speed of a chemical reaction depends on the energy pathway that a reaction follows and the changes that take place on the molecular level when substances interact. In this chapter, you will study the factors that affect how fast chemical reactions take place.

Reaction Mechanisms

If you mix aqueous solutions of HCl and NaOH, an extremely rapid neutralization reaction occurs, as shown in **Figure 1.**

$$H_3O^+(aq) + Cl^-(aq) + Na^+(aq) + OH^-(aq) \longrightarrow 2H_2O(l) + Na^+(aq) + Cl^-(aq)$$

The reaction is practically instantaneous; the rate is limited only by the speed with which the H_3O^+ and OH^- ions can diffuse through the water to meet each other. On the other hand, reactions between ions of the same charge and between molecular substances are not instantaneous. Negative ions repel each other, as do positive ions. The electron clouds of molecules also repel each other strongly at very short distances. Therefore, only ions or molecules with very high kinetic energy can overcome repulsive forces and get close enough to react. In this section, we will limit our discussion to reactions between molecules.

Colorless hydrogen gas consists of pairs of hydrogen atoms bonded together as diatomic molecules, H_2. Violet-colored iodine vapor is also diatomic, consisting of pairs of iodine atoms bonded together as I_2 molecules. A chemical reaction between these two gases at elevated temperatures produces hydrogen iodide, HI, a colorless gas. Hydrogen iodide molecules, in turn, tend to decompose and re-form hydrogen and iodine molecules, producing the violet gas shown in **Figure 2.** The following chemical equations describe these two reactions.

$$H_2(g) + I_2(g) \longrightarrow 2HI(g)$$

$$2HI(g) \longrightarrow H_2(g) + I_2(g)$$

Such equations indicate only which molecular species disappear as a result of the reactions and which species are produced. They do not show the **reaction mechanism,** *the step-by-step sequence of reactions by which the overall chemical change occurs*.

FIGURE 1 As NaOH solution is poured into HCl solution, a very rapid neutralization reaction occurs. Excess NaOH turns the phenolphthalein indicator pink.

FIGURE 2 Colorless hydrogen iodide gas, HI, decomposes into colorless hydrogen gas and violet iodine gas. Some of the hydrogen gas and iodine gas will reform HI.

Although only the net chemical change is directly observable for most chemical reactions, experiments can often be designed that suggest the probable sequence of steps in a reaction mechanism. Each reaction step is usually a simple process. The equation for each step represents the *actual* atoms, ions, or molecules that participate in that step. Even a reaction that appears from its balanced equation to be a simple process may actually be the result of several simple steps.

For many years, the formation of hydrogen iodide, as shown in **Figure 2,** was considered a simple one-step process. It was thought to involve the interaction of two molecules, H_2 and I_2, in the forward reaction and two HI molecules in the reverse reaction. Experiments eventually showed, however, that a direct reaction between H_2 and I_2 does not take place.

Alternative mechanisms for the reaction were proposed based on the experimental results. The steps in each reaction mechanism had to add together to give the overall equation. Note that two of the species in the mechanism steps—I and H_2I—do not appear in the net equation. *Species that appear in some steps but not in the net equation are known as* **intermediates.** (Notice that they cancel each other out in the following mechanisms.) The first possible mechanism has the following two-step pathway.

$$\begin{array}{lr}
\textbf{Step 1:} & I_2 \rightleftharpoons \cancel{2I} \\
\textbf{Step 2:} & \cancel{2I} + H_2 \rightleftharpoons 2HI \\
\cline{2-2}
 & I_2 + H_2 \rightleftharpoons 2HI
\end{array}$$

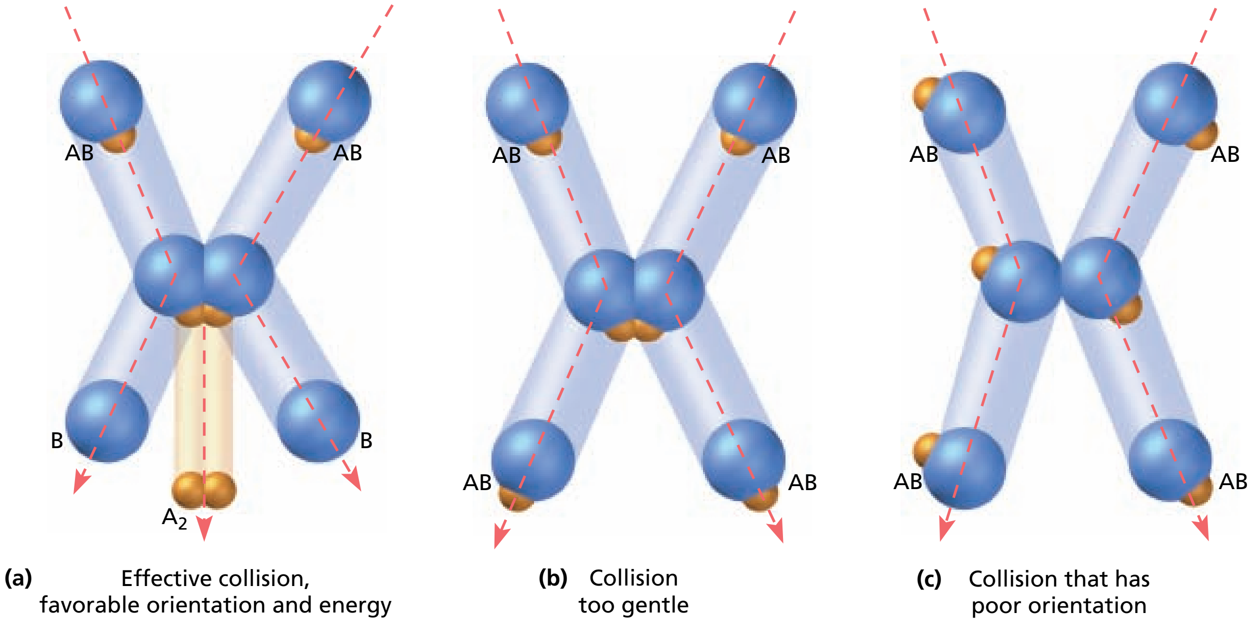
The second possible mechanism has a three-step pathway.

$$\begin{array}{lr}
\textbf{Step 1:} & I_2 \rightleftharpoons \cancel{2I} \\
\textbf{Step 2:} & \cancel{I} + H_2 \rightleftharpoons \cancel{H_2I} \\
\textbf{Step 3:} & \cancel{H_2I} + \cancel{I} \rightleftharpoons 2HI \\
\cline{2-2}
 & I_2 + H_2 \rightleftharpoons 2HI
\end{array}$$

The reaction between hydrogen gas and iodine vapor to produce hydrogen iodide gas is an example of a **homogeneous reaction,** *a reaction whose reactants and products exist in a single phase*—in this case, the gas phase. This reaction system is also an example of a homogeneous chemical system because all reactants and products in all intermediate steps are in the same phase.

Collision Theory

In order for reactions to occur between substances, their particles (molecules, atoms, or ions) must collide. Furthermore, these collisions must result in interactions. *The set of assumptions regarding collisions and reactions is known as* **collision theory.** Chemists use this theory to interpret many of their observations about chemical reactions.



(a) Effective collision, favorable orientation and energy

(b) Collision too gentle

(c) Collision that has poor orientation

FIGURE 3 Three possible collision patterns for AB molecules are shown. Not every collision produces a chemical reaction.

Consider what might happen on a molecular scale in one step of a homogeneous reaction system. We will analyze a proposed first step in a hypothetical decomposition reaction.

$$AB + AB \rightleftharpoons A_2 + 2B$$

According to the collision theory, the two AB molecules must collide in order to react. Furthermore, they must collide with a favorable orientation and with enough energy to merge the valence electrons and disrupt the bonds of the AB molecules. If they do so, a reshuffling of bonds leads to the formation of the products, one A_2 molecule and two B atoms. An effective collision is modeled in **Figure 3a.**

If a collision is too gentle, the two molecules simply rebound from each other unchanged. This effect is illustrated in **Figure 3b.** Similarly, a collision in which the reactant molecules have an unfavorable orientation has little effect. The colliding molecules rebound without reacting. A collision that has poor orientation is shown in **Figure 3c.**

A chemical reaction produces new bonds which are formed between specific atoms in the colliding molecules. Unless the collision brings the correct atoms close together and in the proper orientation, the molecules will not react. For example, if a chlorine molecule collides with the oxygen end of a nitrogen monoxide molecule, the following reaction may occur.

$$NO(g) + Cl_2(g) \longrightarrow NOCl(g) + Cl(g)$$

This reaction will not occur if the chlorine molecule strikes the nitrogen end of the molecule.

Thus, collision theory provides two reasons why a collision between reactant molecules may fail to produce a new chemical species: the collision is not energetic enough to supply the required energy, or the colliding molecules are not oriented in a way that enables them to react with each other.

Activation Energy

Consider the reaction for the formation of water from the diatomic gases oxygen and hydrogen according to the following equation.

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$$

The enthalpy of formation is quite high: $\Delta H_f^0 = -285.8$ kJ/mol at 298.15 K. The free-energy change is also large: $\Delta G^0 = -237.1$ kJ/mol. Why, then, don't oxygen and hydrogen combine spontaneously and immediately to form water when they are mixed at room temperature?

Hydrogen and oxygen gases exist as diatomic molecules. When the molecules approach each other, the electron clouds repel each other, so the molecules might not meet. For a reaction to occur, the colliding molecules must have enough kinetic energy to intermingle the valence electrons. In other words, the bonds of these molecular species must be broken in order for new bonds to be formed between oxygen and hydrogen atoms. Bond breaking is an endothermic process, and bond forming is exothermic. Even though the net process for forming water is exothermic, an initial input of energy is needed to overcome the repulsion forces that occur between reactant molecules when they are brought very close together. This initial energy input activates the reaction.

Once an exothermic reaction is started, the energy released is enough to sustain the reaction by activating other molecules. Thus, the reaction rate keeps increasing. It is limited only by the time required for reactant particles to acquire the energy and make contact. Energy from an outside source may start exothermic reactants along the pathway of reaction. A generalized reaction pathway for an exothermic reaction is shown as the forward reaction in **Figure 4.** The minimum amount of energy needed to activate this reaction is the activation energy represented by E_a. **Activation energy** *is the minimum energy required to transform the reactants into an activated complex.*

The reverse reaction, decomposition of water molecules, is endothermic because the water molecules lie at an energy level lower than that of the hydrogen and oxygen molecules. The water molecules require a larger activation energy before they can decompose to re-form oxygen and hydrogen. The energy needed to activate an endothermic reaction is greater than that required for the original exothermic change and is represented by E_a' in **Figure 4.** The difference between E_a' and E_a is equal to the energy change in the reaction, ΔE. This energy change has the same numerical value for the forward reaction as it has for the reverse reaction but with the opposite sign.

Reaction Pathways for Forward and Reverse Reactions

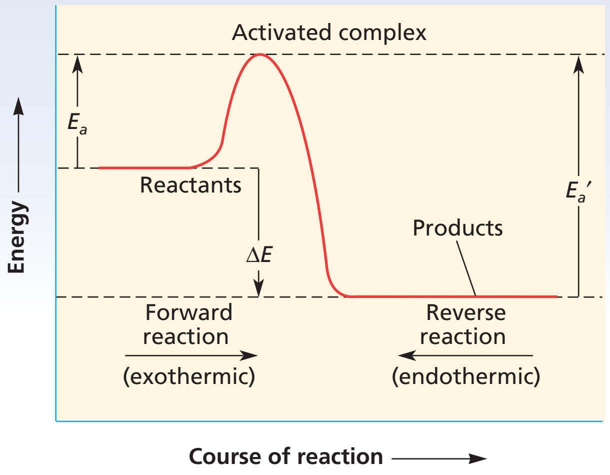


FIGURE 4 The difference between the activation energies for the reverse and forward reactions of a reversible reaction equals the energy change in the reaction, ΔE. The quantity for ΔE is the same for both directions, but is negative for the exothermic direction and positive for the endothermic direction.

The Activated Complex

When molecules collide, some of their high kinetic energy is converted into internal potential energy within the colliding molecules. If enough energy is converted, molecules with suitable orientation become activated. New bonds can then form. In this brief interval of bond breakage and bond formation, the collision complex is in a *transition state.* Some partial bonding exists in this transitional structure. *A transitional structure that results from an effective collision and that persists while old bonds are breaking and new bonds are forming is called an* **activated complex.**

Figure 5 graphically breaks down the reaction pathway of the formation of hydrogen iodide gas into three steps. Beginning with the reactants, H_2 and I_2, a certain amount of activation energy, E_{a1}, is needed to form the activated complex that leads to the formation of the intermediates H_2 and 2I. Then more activation energy, E_{a2}, is needed to form the activated complex leading to the intermediates H_2I and I. In order to arrive at the final product, 2HI, another increase in activation energy is necessary, as seen by the highest peak labeled E_{a3}.

An activated complex is formed when an effective collision raises the internal energies of the reactants to their minimum level for reaction, as in **Figure 4.** Both forward and reverse reactions go through the same activated complex. A bond that is broken in the activated complex for the forward reaction must be re-formed in the activated complex for the reverse reaction. Observe that an activated complex occurs at a high-energy position along the reaction pathway.

The kinetic-molecular theory states that the speeds and therefore the kinetic energies of the molecules increase as the temperature increases. An increase in speed causes more collisions, which can cause an increase in the number of reactions. However, an increase in the reaction rate depends on more than simply the number of collisions, as **Figure 3** illustrates. The collisions between molecules must possess sufficient energy to form an activated complex or a reaction will not take place. Raising the temperature of a reaction provides more molecules that have this activation energy and causes an increase in the reaction rate.

In its brief existence, the activated complex has partial bonding that is characteristic of both reactant and product. It may then re-form the original bonds and separate back into the reactant particles, or it may form new bonds and separate into product particles. The activated complex, unlike the relatively stable intermediate products, is a very short-lived molecular complex in which bonds are in the process of being broken and formed.

Activation Energy Peaks in the Formation of Activated Complexes

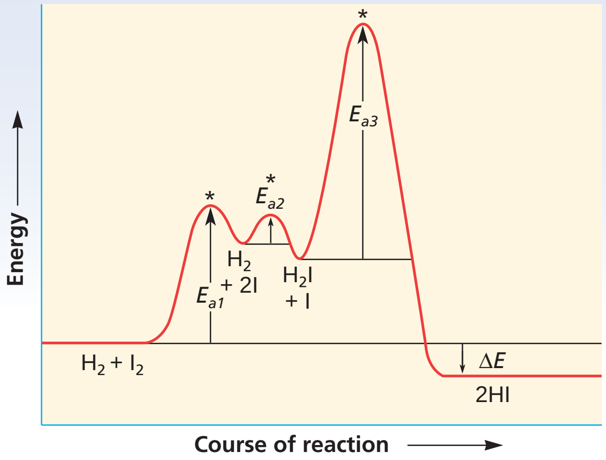
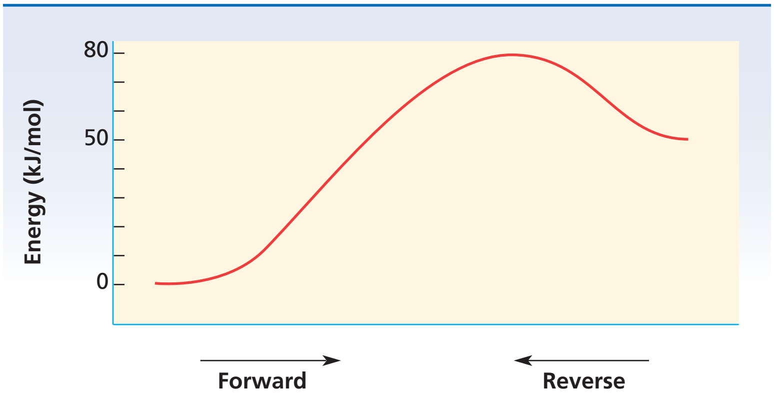


FIGURE 5 This energy profile graphically shows the formation of three activated complexes (*) during the gas-phase reaction $H_2 + I_2 \longrightarrow 2HI$.

SAMPLE PROBLEM A

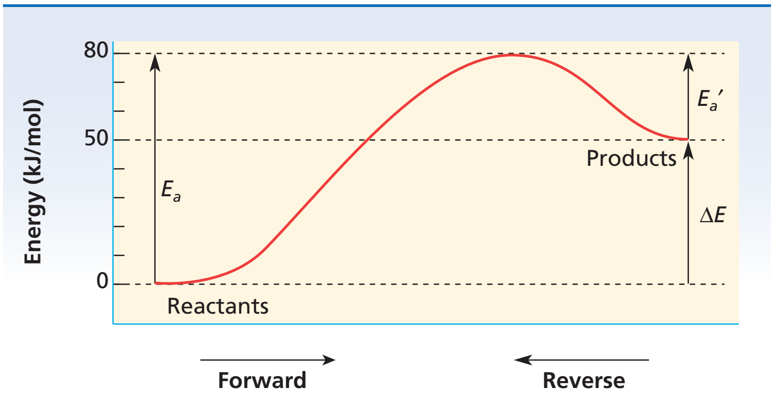
*For more help, go to the **Math Tutor** at the end of this chapter.*

Copy the energy diagram below, and label the reactants, products, ΔE, E_a, *and* E_a'. Determine the value of $\Delta E_{forward}$, $\Delta E_{reverse}$, E_a, and E_a'.



SOLUTION

The energy level of reactants is always at the left-hand end of such a curve, and the energy level of products is always at the right-hand end. The energy change in the reaction, ΔE, is the difference between these two energy levels. The activation energy differs in the forward and reverse directions. It is the minimum energy needed to achieve effective reaction in either direction. As E_a, it is the difference between the reactant energy level and the peak in the curve. As E_a', it is the difference between the product energy level and the peak in the curve.



$\Delta E_{forward}$ = energy of products – energy of reactants
$\Delta E_{forward}$ = 50 kJ/mol – 0 kJ/mol = +50 kJ/mol

$\Delta E_{reverse}$ = energy of reactants – energy of products
$\Delta E_{reverse}$ = 0 kJ/mol – 50 kJ/mol = – 50 kJ/mol

E_a = energy of activated complex – energy of reactants
E_a = 80 kJ/mol – 0 kJ/mol = 80 kJ/mol

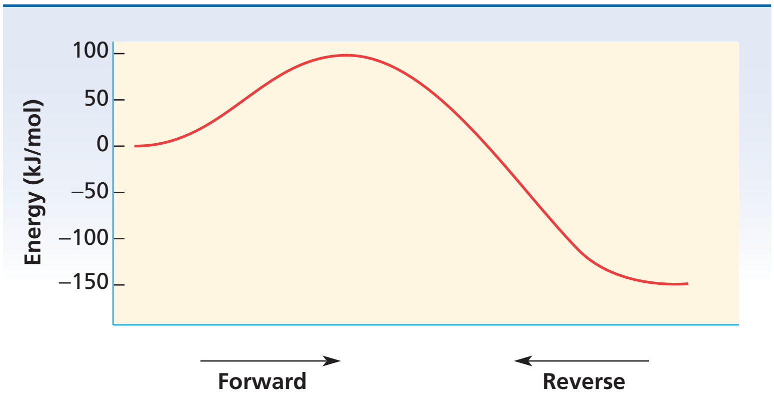
E_a' = energy of activated complex – energy of products
E_a' = 80 kJ/mol – 50 kJ/mol = 30 kJ/mol

PRACTICE

Answers in Appendix E

1. a. Use the method shown in the sample problem to redraw and label the following energy diagram. Determine the value of $\Delta E_{forward}$, $\Delta E_{reverse}$, E_a, and E_a'.

b. Is the forward reaction shown in the diagram exothermic or endothermic? Explain your answer.



2. a. Draw and label an energy diagram similar to the one shown in the sample problem for a reaction in which $E_a = 125$ kJ/mol and $E_a' = 86$ kJ/mol. Place the reactants at energy level zero.

b. Calculate the values of $\Delta E_{forward}$ and $\Delta E_{reverse}$.

c. Is this reaction endothermic or exothermic? Explain your answer.

3. a. Draw and label an energy diagram for a reaction in which $E_a = 154$ kJ/mol and $\Delta E = 136$ kJ/mol.

b. Calculate the activation energy, E_a', for the reverse reaction.

extension

Go to **go.hrw.com** for more practice problems that ask you to determine E_a and ΔE.

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SECTION REVIEW

1. What is meant by reaction mechanism?

2. What factors determine whether a molecular collision produces a reaction?

3. What is activation energy?

4. What is an activated complex?

5. How is activation energy related to the energy of reaction?

6. What is the difference between an activated complex and an intermediate?

7. Explain why, even though a collision may have energy in excess of the activation energy, reaction may not occur.

Critical Thinking

8. ANALYZING INFORMATION Which corresponds to the faster rate: a mechanism with a small activation energy or one with a large activation energy? Explain your answer.

SECTION 2

Reaction Rate

OBJECTIVES

- Define *chemical kinetics*, and explain the two conditions necessary for chemical reactions to occur.
- Discuss the factors that influence reaction rate.
- Define *catalyst*, and discuss two different types.
- Relate the order of a reaction to the rate law for the reaction.
- Explain and write rate laws for chemical reactions.

The change in concentration of reactants per unit time as a reaction proceeds is called the **reaction rate.** The study of reaction rates is concerned with the factors that affect the rate and with the mathematical expressions that reveal the specific dependencies of the rate on concentration. *The area of chemistry that is concerned with reaction rates and reaction mechanisms is called* **chemical kinetics.**

Rate-Influencing Factors

For reactions other than simple decompositions to occur, particles must come into contact in a favorable orientation and with enough energy for activation. Thus, the rate of a reaction depends on the collision frequency of the reactants and on the collision efficiency. Any change in reaction conditions that affects the collision frequency, the collision efficiency, or the collision energy affects the reaction rate. At least five important factors influence the rate of a chemical reaction.

Nature of Reactants

Substances vary greatly in their tendencies to react. For example, hydrogen combines vigorously with chlorine under certain conditions. Under the same conditions, it may react only weakly with nitrogen. Sodium and oxygen combine much more rapidly than iron and oxygen under similar conditions. Bonds are broken and other bonds are formed in reactions. The rate of reaction depends on the particular reactants and bonds involved.

Surface Area

Gaseous mixtures and dissolved particles can mix and collide freely; therefore, reactions involving them can occur rapidly. In heterogeneous reactions, the reaction rate depends on the area of contact of the reaction substances. **Heterogeneous reactions** *involve reactants in two different phases.* These reactions can occur only when the two phases are in contact. Thus, the surface area of a solid reactant is an important factor in determining rate. An increase in surface area increases the rate of heterogeneous reactions.

Solid zinc reacts with aqueous hydrochloric acid to produce zinc chloride and hydrogen gas according to the following equation.

$$Zn(s) + 2HCl(aq) \longrightarrow ZnCl_2(aq) + H_2(g)$$

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This reaction occurs at the surface of the zinc solid. A cube of zinc measuring 1 cm on each edge presents only 6 cm^2 of contact area. The same amount of zinc in the form of a fine powder might provide a contact area thousands of times greater than the original area. Consequently, the reaction rate of the powdered solid is much faster.

A lump of coal burns slowly when kindled in air. The rate of burning can be increased by breaking the lump into smaller pieces, exposing more surface area. If the piece of coal is powdered and then ignited while suspended in air, it burns explosively. This is the cause of some explosions in coal mines.

Temperature

An increase in temperature increases the average kinetic energy of the particles in a substance; this can result in a greater number of effective collisions when the substance is allowed to react with another substance. If the number of effective collisions increases, the reaction rate will increase.

To be effective, the energy of the collisions must be equal to or greater than the activation energy. At higher temperatures, more particles possess enough energy to form the activated complex when collisions occur. Thus, a rise in temperature produces an increase in collision energy as well as in collision frequency.

Decreasing the temperature of a reaction system has the opposite effect. The average kinetic energy of the particles decreases, so they collide less frequently and with less energy, producing fewer effective collisions. Beginning near room temperature, the reaction rates of many common reactions roughly double with each 10 K (10°C) rise in temperature. This rule of thumb should be used with caution, however. The actual rate increase with a given rise in temperature must be determined experimentally.

Concentration

Pure oxygen has five times the concentration of oxygen molecules that air has at the same pressure; consequently, a substance that oxidizes in air oxidizes more vigorously in pure oxygen. For example, in **Figure 6,** the light produced when the lump of charcoal is burned in pure oxygen is much more intense than the light produced when the charcoal lump is heated in air until combustion begins. The oxidation of charcoal is a heterogeneous reaction system in which one reactant is a gas. The reaction rate depends not only on the amount of exposed charcoal surface but also on the concentration of the reacting species, O_2.

In homogeneous reaction systems, reaction rates depend on the concentration of the reactants. Predicting the mathematical relationship between rate and concentration is difficult because most chemical reactions occur in a series of steps, and only one of these steps determines the reaction rate. If the number of effective collisions increases, the rate

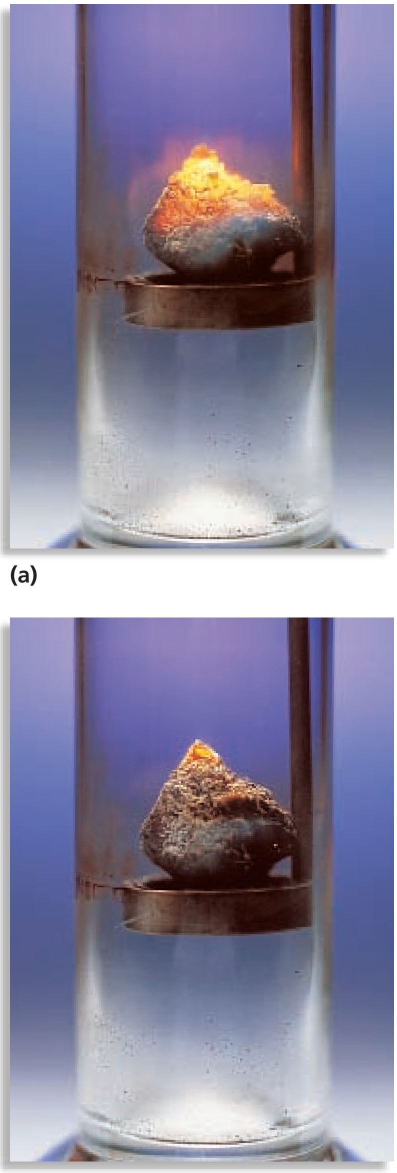


FIGURE 6 Carbon burns faster in pure oxygen (a) than in air (b) because the concentration of the reacting species, O_2, is greater.

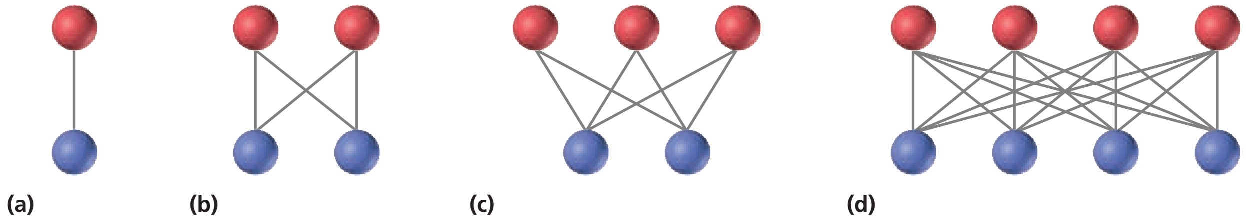


FIGURE 7 The number of molecules of reacting species affects the number of possible collisions and therefore the reaction rate.

increases as well. In general, an increase in rate is expected if the concentration of one or more of the reactants is increased, as depicted by the model in **Figure 7.** In the system with only two molecules, shown in **Figure 7a,** only one collision can possibly occur. When there are four molecules in the system, as in **Figure 7b,** there can be four possible collisions. Under constant conditions, as the number of molecules in the system increases, so does the total number of possible collisions between them. **Figure 7c** and **d** show a five- and eight-molecule system, allowing six and sixteen possible collisions, respectively. Lowering the concentration should have the opposite effect. The actual effect of concentration changes on reaction rate, however, must be determined experimentally.

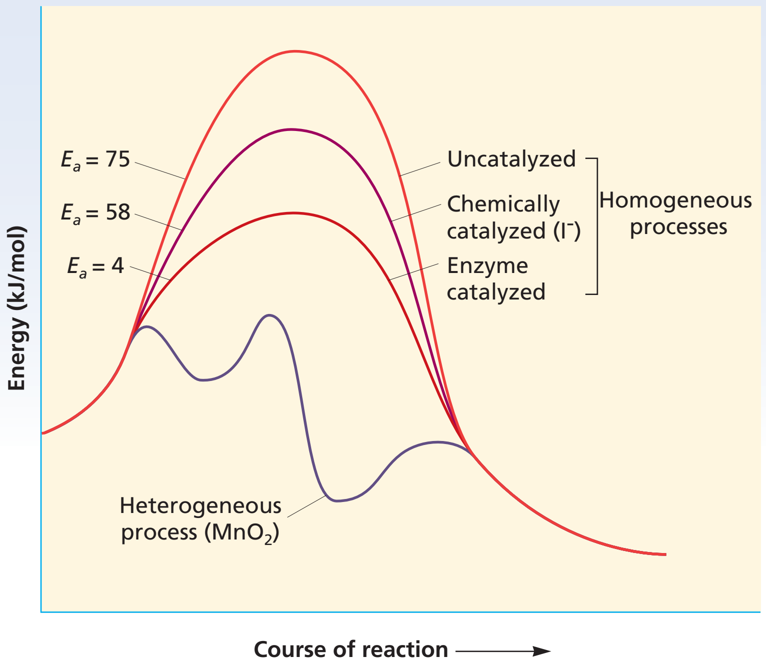
FIGURE 8 The reaction rate of the decomposition of hydrogen peroxide, H_2O_2, can be increased by using a catalyst. The catalyst used here is manganese dioxide, MnO_2, a black solid. A 30% H_2O_2 solution is added dropwise onto the MnO_2 in the beaker and rapidly decomposes to O_2 and H_2O. Both the oxygen and water appear as gases because the energy released by the reaction causes much of the water to vaporize.

Presence of Catalysts

Some chemical reactions proceed quite slowly. Sometimes their reaction rates can be increased dramatically by the presence of a catalyst. *A* **catalyst** *is a substance that changes the rate of a chemical reaction without itself being permanently consumed. The action of a catalyst is called* **catalysis.** The catalysis of the decomposition reaction of hydrogen peroxide by manganese dioxide is shown in **Figure 8.** A catalyst provides an alternative energy pathway or reaction mechanism in which the potential-energy barrier between reactants and products is lowered. The catalyst may be effective in forming an alternative activated complex that requires a lower activation energy—as suggested in the energy profiles of the decomposition of hydrogen peroxide, H_2O_2, shown in **Figure 9**—according to the following equation.

$$2H_2O_2(l) \longrightarrow O_2(g) + 2H_2O(l)$$

Catalysts do not appear among the final products of reactions they accelerate. They may participate in one step along a reaction pathway and be regenerated in a later step. In large-scale and cost-sensitive reaction systems, catalysts are recovered and reused. *A catalyst that is in the same phase as all the reactants and products in a reaction system is called a* **homogeneous catalyst.** *When its phase is different from that of the reactants, it is called a* **heterogeneous catalyst.** Metals are often used as heterogeneous catalysts. The catalysis of many reactions is promoted by adsorption of reactants on the metal surfaces, which has the effect of increasing the concentration of the reactants.



Comparison of Pathways for the Decomposition of H_2O_2 by Various Catalysts

FIGURE 9 The activation energy for a chemical reaction can be reduced by adding an appropriate catalyst.

Rate Laws for Reactions

The relationship between the rate of a reaction and the concentration of one reactant is determined experimentally by first keeping the concentrations of other reactants and the temperature of the system constant. Then the reaction rate is measured for various concentrations of the reactant in question. A series of such experiments reveals how the concentration of each reactant affects the reaction rate.

Hydrogen gas reacts with nitrogen monoxide gas at constant volume and at an elevated constant temperature, according to the following equation.

$$2H_2(g) + 2NO(g) \longrightarrow N_2(g) + 2H_2O(g)$$

Four moles of reactant gases produce three moles of product gases; thus, the pressure of the system diminishes as the reaction proceeds. The rate of the reaction can, therefore, be determined by measuring the change of pressure in the vessel with time.

Suppose a series of experiments is conducted using the same initial concentration of nitrogen monoxide but different initial concentrations of hydrogen. The initial reaction rate is found to vary directly with the hydrogen concentration: doubling the concentration of H_2 doubles the rate, and tripling the concentration of H_2 triples the rate. If R represents the reaction rate and $[H_2]$ is the concentration of hydrogen in moles per

extension

Chemistry in Action

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Keyword: HC6RXKX

liter, the mathematical relationship between rate and concentration can be expressed as follows.

$$R \propto [H_2]$$

The $\propto$ is a symbol that is read "is proportional to."

Now suppose the same initial concentration of hydrogen is used but the initial concentration of nitrogen monoxide is varied. The initial reaction rate is found to increase fourfold when the NO concentration is doubled and ninefold when the concentration of NO is tripled. Thus, the reaction rate varies directly with the square of the nitrogen monoxide concentration, as described by the following proportion.

$$R \propto [NO]^2$$

Because R is proportional to $[H_2]$ and to $[NO]^2$, it is proportional to their product.

$$R \propto [H_2][NO]^2$$

By introduction of an appropriate proportionality constant, k, the expression becomes an equality.

$$R = k[H_2][NO]^2$$

An equation that relates reaction rate and concentrations of reactants is called the **rate law** *for the reaction.* It is applicable for a specific reaction at a given temperature. A rise in temperature increases the reaction rates of most reactions. The value of k usually increases as the temperature increases, but the relationship between reaction rate and concentration almost always remains unchanged.

Chemistry in Action

Explosives

In a tiny fraction of a second, the reactions of explosives such as nitroglycerin, trinitrotoluene (TNT), and dynamite are over. These materials are primarily organic substances containing mostly carbon, hydrogen, oxygen, and nitrogen atoms held together by relatively weak bonds. When "set off," explosive materials experience rapid decomposition. The released elements immediately react to form gaseous N_2, CO, CO_2, and NO_2. The bonds in these small molecules are much stronger than those in the original explosive material, and so an enormous amount of energy is released. In addition, the sudden formation of gaseous material causes a tremendous increase in pressure that provides the force to demolish an unwanted building or break rocks for building roads.

Using the Rate Law

The general form for the rate law is given by the following equation:

$$R = k[A]^n[B]^m$$

The reaction rate is represented by R, k is the specific rate constant, and [A] and [B] represent the molar concentrations of reactants. The respective powers to which the concentrations are raised are represented by n and m. The rate law is applicable for a specific reaction at a given set of conditions and must be determined from experimental data.

The power to which a reactant concentration is raised is called the **order** *in that reactant.* The value of n is said to be the order of the reaction with respect to [A], so the reaction is said to be "n^{th} order in A." Similarly, for the value of m, the reaction is said to be "m^{th} order in B." The orders, or powers, n and m, are usually small integers or zero. An order of *one* for a reactant means that the reaction rate is directly proportional to the concentration of that reactant. An order of *two* means that the reaction rate is directly proportional to the *square* of the reactant. An order of *zero* means that the rate does not depend on the concentration of the reactant, *as long as some of the reactant is present.* The sum of all of the reactant orders is called the *order of the reaction,* or *overall order.* The overall order of the reaction is equal to the sum of the reactant orders, or $n + m$. Some examples of observed rate laws that have been derived experimentally are shown below. Some of these reactions involve nitrogen oxides, which are highly reactive gases that contribute to the formation of smog that can blanket an entire city, as shown in **Figure 10.**

$3NO(g) \longrightarrow N_2O(g) + NO_2(g)$	$R = k[NO]^2$ second order in NO, second order overall
$NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$	$R = k[NO_2]^2$ second order in NO_2, zero order in CO, second order overall
$2NO_2(g) \longrightarrow 2NO(g) + O_2(g)$	$R = k[NO_2]^2$ second order in NO_2, second order overall
$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$	$R = k[H_2O_2]$ first order in H_2O_2, first order overall

It is important to understand that the orders in the rate law *may* or *may not* match the coefficients in the balanced equation. These orders must be determined from experimental data.

Specific Rate Constant

The *specific rate constant* (k) is the proportionality constant relating the rate of the reaction to the concentrations of reactants. It is important to remember the following about the value of k:

1. Once the reaction orders (powers) are known, the value of k must be determined from experimental data.
2. The value of k is for a *specific reaction;* k has a different value for other reactions, even at the same conditions.
3. The units of k depend on the *overall order of the reaction.*
4. The value of k *does not change* for different concentrations of reactants or products. So, the value of k for a reaction remains the same throughout the reaction and does not change with time.
5. The value of k is for the reaction *at a specific temperature*; if we increase the temperature of the reaction, the value of k increases.
6. The value of k changes (becomes larger) if a *catalyst* is present.

FIGURE 10 A cloud of polluted air, commonly known as smog, settles over a city. Smog is common in industrialized areas, where highly reactive gases and particulate matter are released into the air.

SAMPLE PROBLEM B

For more help, go to the ***Math Tutor*** *at the end of this chapter.*

Three experiments that have identical conditions were performed to measure the initial rate of the reaction

$$2HI(g) \longrightarrow H_2(g) + I_2(g)$$

The results for the three experiments in which only the HI concentration was varied are as follows:

Experiment	[HI] (M)	Rate (M/s)
1	0.015	1.1×10^{-3}
2	0.030	4.4×10^{-3}
3	0.045	9.9×10^{-3}

Write the rate law for the reaction. Find the value and units of the specific rate constant.

SOLUTION

1 ***ANALYZE*** The general rate law for this reaction has the form $R = k[HI]^n$. We need to deduce the value of the power n.

2 ***PLAN*** Find the ratio of the reactant concentrations between two experiments, such as 1 and 2, $\frac{[HI]_2}{[HI]_1}$. Then, see how the ratio of concentration affects the ratio of rates, $\frac{R_2}{R_1}$.

3 ***COMPUTE*** Concentration ratio: $\frac{[HI]_2}{[HI]_1} = \frac{0.030\ M}{0.015\ M} = 2.0$; rate ratio: $\frac{R_2}{R_1} = \frac{4.4 \times 10^{-3}\ M/s}{1.1 \times 10^{-3}\ M/s} = 4.0$

Thus, when the concentration changes by a factor of 2, the rate changes by a factor of 4, or 2^2, so the rate law is $R = k[HI]^2$.

To find the value of k, we can rearrange the rate law and substitute known values for any one experiment. Do the following for Experiment 1:

$$k = \frac{R}{[HI]^2} = \frac{1.1 \times 10^{-3}\ M/s}{(0.015\ M)^2} = 4.9\ M^{-1}s^{-1}$$

4 ***EVALUATE*** By comparing items 1 and 3 in the table, we see that when [HI] is tripled, the rate changes by a factor of 9, or 3^2. This rate change confirms that the order is 2. The same value of k can be calculated from any other experiment. Thus, the rate law and k are correct.

PRACTICE

Answers in Appendix E

1. For the reaction $3A \longrightarrow C$, the initial concentration of A was 0.2 M and the reaction rate was 1.0 M/s. When [A] was doubled, the reaction rate increased to 4.0 M/s. Determine the rate law for the reaction.
2. The rate law for a reaction is found to be rate = $k[X]^3$. By what factor does the rate increase if [X] is tripled?

extension

Go to **go.hrw.com** for more practice problems that ask you to determine rate law and rate constant.

Keyword: HC6RXKX

SAMPLE PROBLEM C *For more help, go to the* ***Math Tutor*** *at the end of this chapter.*

Three experiments were performed to measure the initial rate of the reaction

$$\mathrm{A + B \longrightarrow C}$$

Conditions were identical in the three experiments, except that the concentrations of reactants varied. The results are as follows:

Experiment	[A] (M)	[B] (M)	Rate (M/s)
1	1.2	2.4	8.0×10^{-8}
2	1.2	1.2	4.0×10^{-8}
3	3.6	2.4	7.2×10^{-7}

Write the rate law for the reaction. Find the value and units of the specific rate constant.

SOLUTION

1 ***ANALYZE*** The general rate law for this reaction has the form $R = k[\mathrm{A}]^n[\mathrm{B}]^m$. We need to calculate the values of the powers n and m.

2 ***PLAN*** Find the ratio of the reactant concentrations between two experiments that have the same [A] but different [B]. Then, see how this ratio affects the ratio of rates, $\frac{R_2}{R_1}$; this ratio of rates lets us find the value of m. A similar approach of comparing two experiments that have the same [B] but a different [A] lets us find the value of n.

3 ***COMPUTE*** First compare Experiments 1 and 2, which have the same [A], to find m:

$$\text{Concentration ratio: } \frac{[\mathrm{B}]_1}{[\mathrm{B}]_2} = \frac{2.4\ \mathrm{M}}{1.2\ \mathrm{M}} = 2.0; \quad \text{rate ratio: } \frac{R_1}{R_2} = \frac{8.0 \times 10^{-8}\ \mathrm{M/s}}{4.0 \times 10^{-8}\ \mathrm{M/s}} = 2.0$$

Thus, when the concentration of B changes by a factor of 2, the rate changes by a factor of 2, or 2^1. So, m is 1, and the reaction is first order in B.

Then, compare Experiments 1 and 3, which have the same [B], to find n:

$$\text{Concentration ratio: } \frac{[\mathrm{A}]_3}{[\mathrm{A}]_1} = \frac{3.6\ \mathrm{M}}{1.2\ \mathrm{M}} = 3.0; \quad \text{rate ratio: } \frac{R_3}{R_1} = \frac{7.2 \times 10^{-7}\ \mathrm{M/s}}{8.0 \times 10^{-8}\ \mathrm{M/s}} = 9.0$$

Thus, when the concentration of A changes by a factor of 3, the rate changes by a factor of 9, or 3^2. So, n is 2, and the reaction is second order in A.

The rate law is $R = k[\mathrm{A}]^2[\mathrm{B}]$.

To find the value of k, we can rearrange the rate law and substitute known values for any one experiment. Do the following for Experiment 1:

$$k = \frac{R}{[\mathrm{A}]^2[\mathrm{B}]} = \frac{8.0 \times 10^{-8}\mathrm{M/s}}{(1.2\ \mathrm{M})^2(2.4\ \mathrm{M})} = 2.3 \times 10^{-8}\ \mathrm{M^{-2}s^{-1}}$$

4 ***EVALUATE*** The same value of k can be calculated from the data for any other experiment. So, the rate law and the calculation of k are correct.

Rate Laws and Reaction Pathway

The form of the rate law depends on the reaction mechanism. For a reaction that occurs in a *single step,* the reaction rate of that step is proportional to the product of the reactant concentrations, each of which is raised to its stoichiometric coefficient. For example, suppose one molecule of gas A collides with one molecule of gas B to form two molecules of substance C, according to the following equation.

$$\mathrm{A} + \mathrm{B} \longrightarrow 2\mathrm{C}$$

One particle of each reactant is involved in each collision. Thus, doubling the concentration of either reactant will double the collision frequency. It will also double the reaction rate *for this step.* Therefore, the rate for this step is directly proportional to the concentration of A and B. The rate law for this one-step forward reaction follows.

$$R_{forward} = k_{forward}[\mathrm{A}][\mathrm{B}]$$

Now suppose the reaction is reversible. In the reverse step, two molecules of C must decompose to form one molecule of A and one of B or $2\mathrm{C} \longrightarrow \mathrm{A} + \mathrm{B}$.

Thus, the reaction rate for this reverse step is directly proportional to $[\mathrm{C}] \times [\mathrm{C}]$. The rate law for the reverse step is $R_{reverse} = k_{reverse}[\mathrm{C}]^2$.

The power to which the molar concentration of each reactant is raised in the rate laws above corresponds to the coefficient for the reactant in the balanced chemical equation. Such a relationship holds *only* if the reaction follows a simple one-step path, that is, if the reaction occurs at the molecular level exactly as written in the chemical equation.

If a chemical reaction proceeds in a sequence of steps, the rate law is determined from the slowest step because it has the lowest rate. *This slowest-rate step is called the* **rate-determining step** *for the chemical reaction.*

Consider the reaction of nitrogen dioxide and carbon monoxide.

$$NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$$

The reaction is believed to be a two-step process represented by the following mechanism.

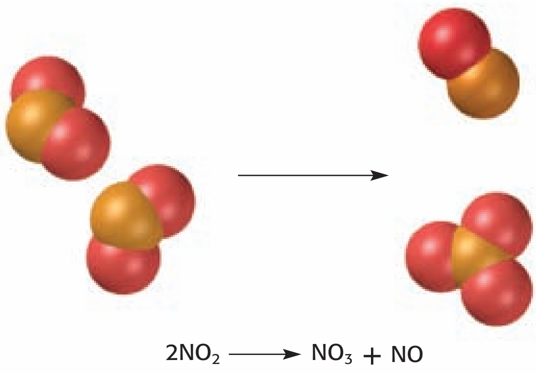
Step 1: $NO_2 + NO_2 \longrightarrow NO_3 + NO$ slow
Step 2: $NO_3 + CO \longrightarrow NO_2 + CO_2$ fast

In the first step, shown in **Figure 11,** two molecules of NO_2 collide, forming the intermediate species NO_3. This molecule then collides with one molecule of CO and reacts quickly to produce one molecule each of NO_2 and CO_2. The first step is the slower of the two and is therefore the rate-determining step. We can write the rate law from this rate-determining step, which has two molecules of NO_2 as the reactants.

$$R = k[NO_2]^2$$

The rate law does not include [CO] because CO reacts after the rate-determining step and does not affect the rate.

FIGURE 11 This diagram is a representation of Step 1 in the reaction of nitrogen dioxide and carbon monoxide. Notice the formation of the intermediate species NO_3 after two molecules of NO_2 collide.


$2NO_2 \longrightarrow NO_3 + NO$

SAMPLE PROBLEM D

For more help, go to the Math Tutor at the end of this chapter.

Nitrogen dioxide and fluorine react in the gas phase according to the following equation.

$$2NO_2(g) + F_2(g) \longrightarrow 2NO_2F(g)$$

A proposed mechanism for this reaction follows.

Step 1: $NO_2 + F_2 \longrightarrow NO_2F + F$ **(slow)**
Step 2: $F + NO_2 \longrightarrow NO_2F$ **(fast)**

Identify the rate-determining step, and write an acceptable rate law.

SOLUTION If we combine these two steps, the intermediate, F, cancels out and we are left with the original equation. The first step is the slower step, and is considered the rate-determining step. We can write the rate law from this rate-determining step.

$$R = k\,[NO_2][F_2]$$

SAMPLE PROBLEM E

A reaction involving reactants X and Y was found to occur by a one-step mechanism: $X + 2Y \longrightarrow XY_2$. Write the rate law for this reaction, and then determine the effect of each of the following on the reaction rate:

a. doubling the concentration of X
b. doubling the concentration of Y
c. using one-third the concentration of Y

SOLUTION Because the equation represents a single-step mechanism, the rate law can be written from the equation (otherwise, it could not be). The rate will vary directly with the concentration of X, which has an implied coefficient of 1 in the equation. And the rate will vary directly with the square of the concentration of Y, which has the coefficient of 2: $R = k[X][Y]^2$.

a. Doubling the concentration of X will double the rate ($R = k[2X][Y]^2$).
b. Doubling the concentration of Y will increase the rate fourfold ($R = k[X][2Y]^2$).
c. Using one-third the concentration of Y will reduce the rate to one-ninth of its original value ($R = k[X][\frac{1}{3}Y]^2$).

PRACTICE

Answers in Appendix E

1. The rate of a hypothetical reaction involving L and M is found to double when the concentration of L is doubled and to increase fourfold when the concentration of M is doubled. Write the rate law for this reaction.

2. At temperatures below 498 K, the following reaction takes place.

$$NO_2(g) + CO(g) \longrightarrow CO_2(g) + NO(g)$$

Doubling the concentration of NO_2 quadruples the rate of CO_2 formed if the CO concentration is held constant. However, doubling the concentration of CO has no effect on the rate of CO_2 formation. Write a rate-law expression for this reaction.

extension

Go to **go.hrw.com** for more practice problems that ask you to determine rate laws and effects on reaction rates.

Keyword: HC6RXKX

QuickLAB Wear safety goggles and an apron.

Factors Influencing Reaction Rate

Question

How do the type of reactants, surface area of reactants, concentration of reactants, and catalysts affect the rates of chemical reactions?

Procedure

Remove all combustible material from the work area. Wear safety goggles and an apron. Record all your results in a data table.

1. Add 10 mL of vinegar to each of three test tubes. To one test tube, add a 3 cm piece of magnesium ribbon; to a second, add a 3 cm zinc strip; and to a third, add a 3 cm copper strip. (All metals should be the same width.) If necessary, polish the metals with sandpaper until they are shiny.
2. Using tongs, hold a paper clip in the hottest part of the burner flame for 30 s. Repeat with a ball of steel wool 2 cm in diameter.
3. To one test tube, add 10 mL of vinegar; to a second, add 5 mL of vinegar plus 5 mL of water; and to a third, add 2.5 mL of vinegar plus 7.5 mL of water. To each of the three test tubes, add a 3 cm piece of magnesium ribbon.
4. Using tongs, hold a sugar cube and try to ignite it with a match. Then try to ignite it in a burner flame. Rub paper ash on a second cube, and try to ignite it with a match.

Discussion

1. What are the rate-influencing factors in each step of the procedure?
2. What were the results from each step of the procedure? How do you interpret each result?

Materials

- Bunsen burner
- paper ash
- copper foil strip
- graduated cylinder, 10 mL
- magnesium ribbon
- matches
- paper clip
- sandpaper
- steel wool
- 2 sugar cubes
- white vinegar
- zinc strip
- 6 test tubes, 16 × 150 mm
- tongs

SECTION REVIEW

1. What is studied in the branch of chemistry that is known as chemical kinetics?
2. List five important factors that influence the rate of chemical reactions.
3. What is a catalyst? Explain the effect of a catalyst on the rate of chemical reactions. How does a catalyst influence the activation energy required by a particular reaction?
4. What is meant by a rate law for a chemical reaction? Explain the conditions under which a rate law can be written from a chemical equation. When can a rate law not be written from a single step?

Critical Thinking

5. **RELATING IDEAS** Using the ideas of reaction kinetics, explain the purpose of food refrigeration.

Chemistry in Action

Catalytic Converters

To see an important example of *heterogeneous catalysis*, you do not need to look any farther than the streets near your home. The *catalytic converter,* an important part of a vehicle's exhaust system, uses metal catalysts to reduce harmful gaseous pollutants.

In an automobile engine, hydrocarbon molecules in gasoline or diesel fuel undergo a combustion reaction with oxygen from air to make carbon dioxide, CO_2, and water. The correct stoichiometric ratio of fuel to oxygen is required for the fuel to be completely burned in the reaction. Additional reaction products are formed when not enough oxygen or excess oxygen is present. These products include carbon monoxide, CO, and NO_x compounds, such as nitric oxide, NO, and nitrogen dioxide, NO_2. There is also leftover unburned fuel, which is called a volatile organic compound (VOC).

The Clean Air Act, enacted in 1990, regulates automobile emissions of CO, NO_x, and VOCs. Without a catalytic converter, a car would release all of the byproducts of incomplete combustion into the atmosphere. In addition to being harmful themselves, NO_x compounds, CO, and VOCs react with sunlight to make ozone, O_3. In the lower atmosphere, ozone is a major part of photochemical smog. NO_x gases can also mix with rainwater to produce acid rain.

Catalytic converters use precious metal catalysts to change the gases coming from the engine into less harmful gases. A combination of rhodium and platinum, and sometimes palladium, is used to convert nitrogen compounds back into N_2 and O_2. This combination also converts CO into CO_2 and converts VOCs into CO_2 and water. The catalysts need O_2 from the air and temperatures above approximately 500°F to work properly. The temperatures are achieved from the normal operation of the car engine. However, until the car engine reaches the temperatures needed for the catalysts to work, CO, NO_x, and VOCs will be released into the air by the automobile.

The interior structure of a catalytic converter is usually made of a ceramic honeycomb with a surface coating of metal catalyst particles. The honeycomb has many holes for the gases to pass through and provides a large surface area for the metal to be deposited on. A large surface area is needed to maximize the reactions that occur during heterogeneous catalysis because the transformation of the gas molecules occurs at the surface of the metal.

Up to 90% of CO, NO_x, and VOCs are typically eliminated from automobile exhaust by a catalytic converter. Although catalytic converters are beneficial to our environment, they could still be improved.

▲ *The ceramic honeycomb inside a catalytic converter is coated with a metal catalyst.*

Catalysts that work at lower temperatures would reduce an automobile's emission during the first few minutes of operation. Other gases that are emitted by cars may also pose problems for the environment. Nitrous oxide, N_2O, can be formed from the incomplete reduction of NO_x in catalytic converters. Unlike the NO_x gases, N_2O can travel to the upper atmosphere, where it can destroy ozone. As a greenhouse gas, N_2O is more that 300 times more potent than CO_2.

Questions

1. Why do you think a heterogeneous catalyst is used instead of homogeneous catalyst in a catalytic converter?
2. Nitrous oxide, N_2O, actually has beneficial uses, despite its role as a greenhouse gas. Can you name a beneficial use of N_2O?

CHAPTER HIGHLIGHTS

The Reaction Process

Vocabulary

reaction mechanism
intermediate
homogenous reaction
collision theory
activation energy
activated complex

- The step-by-step process by which an overall chemical reaction occurs is called the *reaction mechanism.*
- In order for chemical reactions to occur, the particles of the reactants must collide.
- Activation energy is needed to merge valence electrons and to loosen bonds sufficiently for molecules to react.
- An activated complex is formed when an effective collision between molecules of reactants raises the internal energy to the minimum level necessary for a reaction to occur.

Reaction Rate

Vocabulary

reaction rate
chemical kinetics
heterogeneous reactions
catalyst
catalysis
homogeneous catalyst
heterogeneous catalyst
rate law
order
rate-determining step

- The rate of reaction is influenced by the following factors: nature of reactants, surface area, temperature, concentration of reactants, and the presence of catalysts.
- The rates at which chemical reactions occur can sometimes be experimentally measured and expressed in terms of mathematical equations called *rate laws.*
- Rate laws are determined by studying how reaction rate depends on concentration.

CHAPTER REVIEW

The Reaction Process

SECTION 1 REVIEW

1. a. What is the collision theory?
   b. According to this theory, what two conditions must be met for a collision between reactant molecules to be effective in producing new chemical species?

2. a. What condition must be met for an activated complex to result from the collision of reactant particles?
   b. Where, in terms of energy, does the activated complex occur along a typical reaction pathway?

3. In a reversible reaction, how does the activation energy required for the exothermic change compare with the activation energy required for the endothermic change?

4. Would you expect the following equation to represent the mechanism by which propane, C_3H_8, burns? Why or why not?

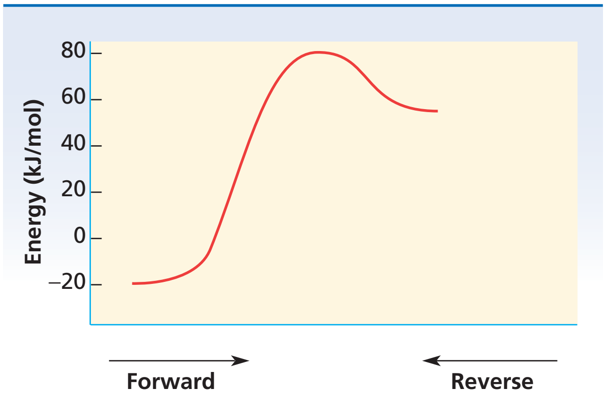
$$C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(g)$$

5. The decomposition of nitrogen dioxide $2NO_2 \longrightarrow 2NO + O_2$ occurs in a two-step sequence at elevated temperatures. The first step is $NO_2 \longrightarrow NO + O$. Predict a possible second step that, when combined with the first step, gives the complete reaction.

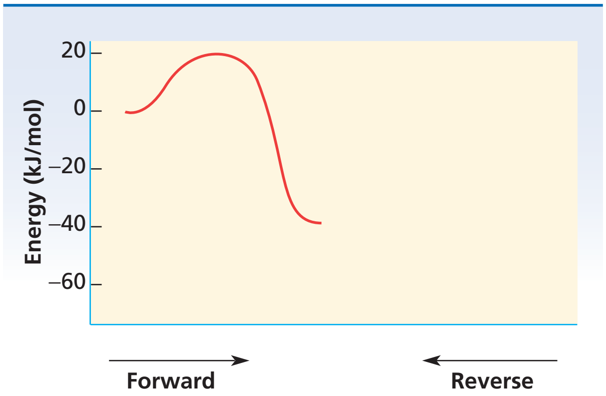
PRACTICE PROBLEMS

6. For each of the energy diagrams provided below, label the reactants, products, ΔE, E_a, and E_a'. Also determine the values of ΔE for the forward and reverse reactions, and determine the values of E_a and E_a'. (Hint: See Sample Problem A.)

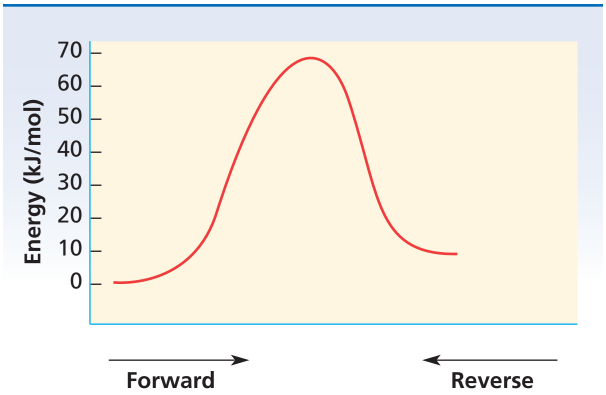
a.



b.



c.



7. Draw and label energy diagrams that depict the following reactions, and determine all remaining values. Place the reactants at energy level zero.

a. $\Delta E_{forward} = -10$ kJ/mol $E_a' = 40$ kJ/mol
b. $\Delta E_{forward} = -95$ kJ/mol $E_a = 20$ kJ/mol
c. $\Delta E_{reverse} = -40$ kJ/mol $E_a' = 30$ kJ/mol

Reaction Rate

SECTION 2 REVIEW

8. Define the rate-determining step for a chemical reaction.

9. Write the general equation for the rate law, and label the various factors.

PRACTICE PROBLEMS

10. a. Determine the overall balanced equation for a reaction that has the following proposed mechanism, and write an acceptable rate law. (Hint: See Sample Problem C.)

Step 1: $B_2 + B_2 \longrightarrow E_3 + D$ slow
Step 2: $E_3 + A \longrightarrow B_2 + C_2$ fast

b. Give the order of the reaction with respect to each reactant.

c. What is the overall order of the reaction?

11. A reaction that involves reactants A and B is found to occur in the one-step mechanism: $2A + B \longrightarrow A_2B$. Write the rate law for this reaction, and predict the effect of doubling the concentration of either reactant on the overall reaction rate. (Hint: See Sample Problem C.)

12. A chemical reaction is expressed by the balanced chemical equation $A + 2B \longrightarrow C$. Three reaction-rate experiments yield the following data.

Experiment number	Initial [A]	Initial [B]	Initial rate of formation of C
1	0.20 M	0.20 M	2.0×10^{-4} M/min
2	0.20 M	0.40 M	8.0×10^{-4} M/min
3	0.40 M	0.40 M	1.6×10^{-3} M/min

a. Determine the rate law for the reaction.

b. Calculate the value of the specific rate constant.

c. If the initial concentrations of both A and B are 0.30 M, at what initial rate is C formed?

d. What is the order of the reaction with respect to A?

e. What is the order of the reaction with respect to B?

MIXED REVIEW

13. Draw and label energy diagrams that depict the following reactions, and determine all remaining values. Place the reactants at energy level zero.

a. $\Delta E = +30$ kJ/mol $E_a' = 20$ kJ/mol
b. $\Delta E = -30$ kJ/mol $E_a = 20$ kJ/mol

14. A particular reaction is found to have the following rate law.

$$R = k[A][B]^2$$

How is the rate affected by each of the following changes?

a. The initial concentration of A is cut in half.

b. The initial concentration of B is tripled.

c. The concentration of A is doubled, but the concentration of B is cut in half.

d. A catalyst is added.

15. For each of the following pairs, choose the substance or process that you would expect to react more rapidly.

a. granulated sugar or powdered sugar

b. zinc in HCl at 298.15 K or zinc in HCl at 320 K

c. 5 g of thick platinum wire or 5 g of thin platinum wire

16. The following data relate to the reaction $A + B \longrightarrow C$. Find the order with respect to each reactant.

[A] (M)	[B] (M)	Rate (M/s)
0.08	0.06	0.012
0.08	0.03	0.006
0.04	0.06	0.003

CRITICAL THINKING

17. **Predicting Outcomes** The balanced equation for a rapid homogeneous reaction between two gases is as follows: $4A + B \longrightarrow 2C + 2D$. Because the simultaneous collision of four molecules of one reactant with one molecule of the other reactant is extremely improbable, what would you predict about the nature of the reaction mechanism for this reaction system?

18. **Evaluating Ideas**
   a. How can you justify calling the reaction pathway that is shown in **Figure 4** the minimum-energy pathway for reaction?
   b. What significance is associated with the maximum-energy region of this minimum-energy pathway?

19. **Applying Models** Explain why there is a danger of explosion in places such as coal mines, sawmills, and grain elevators, where large amounts of dry, powdered combustible materials are present.

20. **Evaluating Methods** What property would you measure to determine the reaction rate for the following reaction? Justify your choice.

$$2NO_2(g) \longrightarrow N_2O_4(g)$$

RESEARCH & WRITING

21. Look for situations around your house in which processes are speeded up by an increase in temperature or slowed down by a decrease in temperature. Make a list, and discuss the different processes.

ALTERNATIVE ASSESSMENT

22. Boilers are sometimes used to heat large buildings. Deposits of $CaCO_3$, $MgCO_3$, and $FeCO_3$ can hinder the boiler operation. Aqueous solutions of hydrochloric acid are commonly used to remove these deposits. The general equation for the reaction is written below.

$$MCO_3(s) + 2H_3O^+(aq) \longrightarrow M^{2+}(aq) + 3H_2O(l) + CO_2(g)$$

In the equation, M stands for Ca, Mg, or Fe. Design an experiment to determine the effect of various HCl concentrations on the rates of this reaction. Present your design to the class.

extension

Graphing Calculator
Reaction Orders

Go to **go.hrw.com** for a graphing calculator exercise that asks you to calculate the order of a reaction from the reaction rates and concentrations.

Keyword: HC6RXKX

Math Tutor WRITING RATE LAWS

Factors such as surface area and temperature affect the rate of reactions because they affect the frequency and energy of collisions between particles. The concentrations of reactants can also affect the frequency of collisions. If other factors are kept constant, the rates of most chemical reactions will be determined by the concentrations of reactants. Thus, it is possible to write an equation called a *rate law* that relates the rate of a reaction to the concentrations of reactants.

SAMPLE

Fluorine gas reacts with chlorine dioxide according to the following equation.

$$F_2(g) + 2ClO_2(g) \longrightarrow 2FClO_2(g)$$

Use the following experimental data to write a rate law for this reaction.

Trial	Concentration of F_2	Concentration of ClO_2	Rate (mol/L•s)
1	0.10 *M*	0.10 *M*	1.1×10^{-3}
2	0.20 *M*	0.10 *M*	2.2×10^{-3}
3	0.10 *M*	0.20 *M*	2.2×10^{-3}
4	0.20 *M*	0.20 *M*	4.4×10^{-3}

To write the rate law, first examine the data to see how the rate of reaction changes as the concentrations of the reactants change.

- When $[F_2]$ doubles and $[ClO_2]$ remains constant, the rate of reaction doubles from 1.1×10^{-3} mol/L•s to 2.2×10^{-3} mol/L•s. So, the rate is directly proportional to $[F_2]$, or $R \alpha [F_2]$.
- When $[ClO_2]$ doubles and $[F_2]$ remains constant, the rate of reaction also doubles from 1.1×10^{-3} mol/L•s to 2.2×10^{-3} mol/L•s. So, the rate is directly proportional to $[ClO_2]$, or $R \alpha [ClO_2]$.
- Because rate is proportional to both $[F_2]$ and $[ClO_2]$, you can write the rate law $R = k[F_2][ClO_2]$. The data from Trial 4 help confirm the rate law because when both $[F_2]$ and $[ClO_2]$ double, the rate increases by a factor of four, from 1.1×10^{-3} mol/L•s to 4.4×10^{-3} mol/L•s.

PRACTICE PROBLEMS

1. Nitrogen monoxide and oxygen react to produce nitrogen dioxide according to the following equation:
$$O_2(g) + 2NO(g) \longrightarrow 2NO_2(g)$$
Use the data in the following table to write a rate law for this reaction.

2. Hydrogen reacts with ethyne, C_2H_2, to produce ethane, C_2H_6, as shown below:
$$2H_2(g) + C_2H_2(g) \longrightarrow C_2H_6(g)$$
Use the data in the following table to write a rate law for this reaction.

Trial	$[O_2]$	[NO]	Reaction Rate (mol/L•s)
1	1.20×10^{-2} *M*	1.40×10^{-2} *M*	3.30×10^{-3}
2	2.40×10^{-2} *M*	1.40×10^{-2} *M*	6.60×10^{-3}
3	1.20×10^{-2} *M*	2.80×10^{-2} *M*	1.32×10^{-2}

Trial	$[H_2]$	$[C_2H_2]$	Reaction Rate (mol/L•min)
1	0.20 *M*	0.20 *M*	1.5×10^{-4}
2	0.40 *M*	0.20 *M*	3.0×10^{-4}
3	0.20 *M*	0.40 *M*	1.5×10^{-4}

Standardized Test Prep

Answer the following items on a separate piece of paper.

MULTIPLE CHOICE

1. The sequence of steps that occurs in a reaction process is called the
A. order of the reaction.
B. rate law.
C. overall reaction.
D. reaction mechanism.

2. To be effective, a collision requires
A. enough energy only.
B. favorable orientation only.
C. enough energy and a favorable orientation.
D. a reaction mechanism.

3. How does the energy of the activated complex compare with the energies of the reactants and products?
A. It is lower than both the energy of the reactants and the energy of the products.
B. It is lower than the energy of the reactants but higher than the energy of the products.
C. It is higher than the energy of the reactants but lower than the energy of the products.
D. It is higher than both the energy of the reactants and the energy of the products.

4. If a collision between molecules is very gentle, the molecules are
A. more likely to be oriented favorably.
B. less likely to be oriented favorably.
C. likely to react.
D. likely to rebound without reacting.

5. A species that changes the rate of a reaction but is neither consumed nor changed is
A. a catalyst.
B. an activated complex.
C. an intermediate.
D. a reactant.

6. A rate law relates
A. reaction rate and temperature.
B. reaction rate and concentration.
C. temperature and concentration.
D. energy and concentration.

7. In a graph of how energy changes with reaction progress, the activated complex appears at the
A. left end of the curve.
B. right end of the curve.
C. bottom of the curve.
D. peak of the curve.

8. The slowest step in a mechanism is called
A. the rate-determining step.
B. the uncatalyzed reaction.
C. the activation step.
D. None of the above

9. A certain reaction is zero order in reactant A and second order in reactant B. What happens to the reaction rate when the concentrations of both reactants are doubled?
A. The reaction rate remains the same.
B. The reaction increases by a factor of two.
C. The reaction rate increases by a factor of four.
D. The reaction rate increases by a factor of eight.

SHORT ANSWER

10. Two molecules collide but bounce apart unchanged. What two reasons could account for their failure to react?

11. Sketch a diagram that shows how the energy changes with the progress of an endothermic reaction. Label the curve "Reactants," "Products," and "Activated complex." On the same diagram, sketch a second curve to show the change caused by a catalyst.

EXTENDED RESPONSE

12. Suggest ways of measuring the concentration of a reactant or product in a reaction mixture.

13. Why are reaction orders not always equal to the coefficients in a balanced chemical equation?

Test TIP Sometimes, only one part of a graph or table is needed to answer a question. In such cases, focus on only the information that is required to answer the question.

CHAPTER LAB

MICRO-LAB

Rate of a Chemical Reaction

OBJECTIVES

- ***Prepare* and *observe* several different reaction mixtures.**
- ***Demonstrate* proficiency in measuring reaction rates.**
- ***Relate* experimental results to a rate law that can be used to predict the results of various combinations of reactants.**

MATERIALS

- **8-well microscale reaction strips, 2**
- **distilled or deionized water**
- **fine-tipped dropper bulbs or small microtip pipets, 3**
- **solution A**
- **solution B**
- **stopwatch or clock with second hand**

BACKGROUND

In this experiment, you will determine the rate of the reaction whose net equation is written as follows:

$$3Na_2S_2O_5(aq) + 2KIO_3(aq) + 3H_2O(l) \xrightarrow{H^+} 2KI(aq) + 6NaHSO_4(aq)$$

One way to study the rate of this reaction is to observe how fast $Na_2S_2O_5$ is used up. After all the $Na_2S_2O_5$ solution has reacted, the concentration of iodine, I_2, an intermediate in the reaction, increases. A starch indicator solution, added to the reaction mixture, will change from clear to a blue-black color in the presence of I_2.

In the procedure, the concentrations of the reactants are given in terms of drops of solution A and drops of solution B. Solution A contains $Na_2S_2O_5$, the starch indicator solution, and dilute sulfuric acid to supply the hydrogen ions needed to catalyze the reaction. Solution B contains KIO_3. You will run the reaction with several different concentrations of the reactants and record the time it takes for the blue-black color to appear.

SAFETY

For review of safety, please see the **Safety in the Chemistry Laboratory** in the front of your book.

PREPARATION

1. Prepare a data table with six rows and six columns. Label the boxes in the first row of the second through sixth columns “Well 1,” “Well 2,” “Well 3,” “Well 4,” and “Well 5.” In the first column, label the boxes in the second through sixth rows “Time reaction began,” “Time reaction stopped,” “Drops of solution A,” “Drops of solution B,” and “Drops of H_2O.”

2. Obtain three dropper bulbs or small microtip pipets, and label them "A," "B," and "H_2O."

3. Fill the bulb or pipet A with solution A, the bulb or pipet B with solution B, and the bulb or pipet for H_2O with distilled water.

PROCEDURE

1. Using the first 8-well strip, place five drops of solution A into each of the first five wells. Record the number of drops in the appropriate places in your data table. **For the best results, try to make all drops about the same size.**

2. In the second 8-well reaction strip, place one drop of solution B in the first well, two drops in the second well, three drops in the third well, four drops in the fourth well, and five drops in the fifth well. Record the number of drops in your data table.

3. In the second 8-well strip that contains drops of solution B, add four drops of water to the first well, three drops to the second well, two drops to the third well, and one drop to the fourth well. Do not add any water to the fifth well.

4. Carefully invert the second strip. The surface tension should keep the solutions from falling out of the wells. Place the strip well-to-well on top of the first strip, as shown in Figure A.

5. Hold the strips tightly together as shown in Figure A, and record the exact time, or set the stopwatch, as you shake the strips once. This procedure should mix the upper solutions with each of the corresponding lower ones.

FIGURE A

6. Observe the lower wells. Note the sequence in which the solutions react, and record the number of seconds it takes for each solution to turn a blue-black color.

CLEANUP AND DISPOSAL

7. Dispose of the solutions in the container designated by your teacher. Wash your hands thoroughly after cleaning up the area and equipment.

ANALYSIS AND INTERPRETATION

1. **Organizing Data:** Calculate the time elapsed for the complete reaction of each combination of solutions A and B.

2. **Evaluating Data:** Make a graph of your results. Label the *x*-axis "Number of drops of solution B." Label the *y*-axis "Time elapsed." Make a similar graph for drops of solution B versus rate (1/time elapsed).

3. **Analyzing Information:** Which mixture reacted the fastest? Which mixture reacted the slowest?

4. **Evaluating Methods:** Why was it important to add the drops of water to the wells that contained fewer than five drops of solution B? (Hint: Figure out the total number of drops in each of the reaction wells.)

CONCLUSIONS

1. **Evaluating Conclusions:** Which of the following variables that can affect the rate of a reaction is tested in this experiment: temperature, catalyst, concentration, surface area, or nature of reactants? Explain your answer.

2. **Applying Ideas:** Use your data and graphs to determine the relationship between the concentration of solution B and the rate of the reaction. Describe this relationship in terms of a rate law.

EXTENSIONS

1. **Predicting Outcomes:** What combination of drops of solutions A and B would you use if you wanted the reaction to last exactly 2.5 min?

CHAPTER 18

Chemical Equilibrium

The creation of stalactites and stalagmites is the result of a reversible chemical reaction.

Carlsbad Caverns, New Mexico

SECTION 1

The Nature of Chemical Equilibrium

Objectives

- Define *chemical equilibrium.*
- Explain the nature of the equilibrium constant.
- Write chemical equilibrium expressions and carry out calculations involving them.

In systems that are in equilibrium, opposing processes occur at the same time and at the same rate. For example, when an excess of sugar is placed in water, some sugar molecules go into solution, and others remain undissolved. At equilibrium, molecules of sugar are crystallizing at the same rate that molecules from the crystal are dissolving. The rate of evaporation of a liquid in a closed vessel can eventually be equaled by the rate of condensation of its vapor. The resulting equilibrium vapor pressure is a characteristic of the liquid at the prevailing temperature. The preceding examples are physical equilibria. In this chapter, we will expand on the concept of equilibrium to include chemical reactions. You will learn how a system at equilibrium responds when equilibrium conditions are altered by changing concentration, pressure, and temperature.

Reversible Reactions

Theoretically, every reaction can proceed in two directions, forward and reverse. Thus, essentially all chemical reactions are considered to be reversible under suitable conditions. *A chemical reaction in which the products can react to re-form the reactants is called a* **reversible reaction.**

Mercury(II) oxide decomposes when heated.

$$2HgO(s) \xrightarrow{\Delta} 2Hg(l) + O_2(g)$$

Mercury and oxygen combine to form mercury(II) oxide when heated gently.

$$2Hg(l) + O_2(g) \xrightarrow{\Delta} 2HgO(s)$$

Figure 1 shows both of these reactions taking place. Suppose mercury(II) oxide is heated in a closed container from which neither the mercury nor the oxygen can escape. Once decomposition has begun, the mercury and oxygen released can recombine to form mercury(II) oxide again. Thus, both reactions can proceed at the same time. Under these conditions, the rate of the synthesis reaction will eventually equal that of the decomposition reaction. At equilibrium, mercury and oxygen will

FIGURE 1 When heated, mercury(II) oxide decomposes into its elements, mercury and oxygen. Liquid mercury reacts with oxygen to re-form mercury(II) oxide. Together these reactions represent a reversible chemical process.

combine to form mercury(II) oxide at the same rate that mercury(II) oxide decomposes into mercury and oxygen. The amounts of mercury(II) oxide, mercury, and oxygen can then be expected to remain constant as long as these conditions persist. At this point, a state of dynamic equilibrium has been reached between the two chemical reactions. Both reactions continue, but there is no net change in the composition of the system. *A reversible chemical reaction is in* **chemical equilibrium** *when the rate of its forward reaction equals the rate of its reverse reaction and the concentrations of its products and reactants remain unchanged.* The chemical equation for the reaction at equilibrium is written using double arrows to indicate the overall reversibility of the reaction.

$$2HgO(s) \rightleftarrows 2Hg(l) + O_2(g)$$

Equilibrium, a Dynamic State

Many chemical reactions are reversible under ordinary conditions of temperature and concentration. They will reach a state of equilibrium unless at least one of the substances involved escapes or is removed from the reaction system. In some cases, however, the forward reaction is so predominant that essentially all reactants will react to form products. Here, the products of the forward reaction are favored, meaning that at equilibrium there is a much higher concentration of products than of reactants. Hence, we can say that the equilibrium "lies to the right," because products predominate, and products conventionally are written on the right-hand side of a chemical equation. An example of such a system is the formation of sulfur trioxide from sulfur dioxide and oxygen.

$$2SO_2(g) + O_2(g) \overset{\longrightarrow}{\leftarrow} 2SO_3(g)$$

Notice that the equation is written showing an inequality of the two arrow lengths. The forward reaction is represented by the longer arrow to imply that the product is favored in this reaction.

In other cases, the forward reaction is barely under way when the rate of the reverse reaction becomes equal to that of the forward reaction, and equilibrium is established. In these cases, the amounts of reactants remain high and the amounts of products are low. Here we say that the equilibrium "lies to the left," because the reactants are the predominant species. An example of such a system is the acid-base reaction between carbonic acid and water.

$$H_2CO_3(aq) + H_2O(l) \overset{\rightarrow}{\longleftarrow} H_3O^+(aq) + HCO_3^-(aq)$$

In still other cases, both forward and reverse reactions occur to nearly the same extent before chemical equilibrium is established. Neither reaction is favored, and considerable concentrations of both reactants and products are present at equilibrium. An example is the dissociation of sulfurous acid in water.

$$H_2SO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HSO_3^-(aq)$$

Chemical reactions ordinarily are used to convert available reactants into more desirable products. Chemists try to convert as much of these reactants as possible into products. The extent to which reactants are converted to products is indicated by the numerical value of the equilibrium constant.

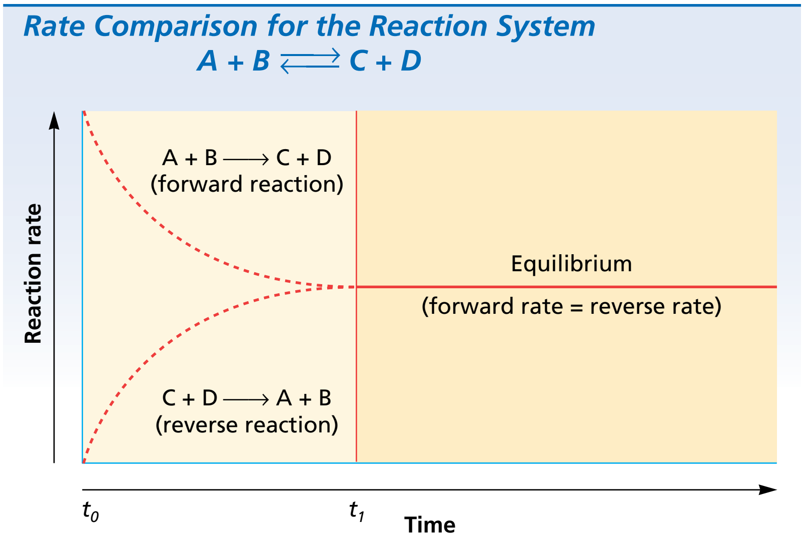
The Equilibrium Expression

Suppose two substances, A and B, react to form products C and D. In turn, C and D react to produce A and B. Under appropriate conditions, equilibrium occurs for this reversible reaction. This hypothetical equilibrium reaction is described by the following general equation.

$$nA + mB \rightleftharpoons xC + yD$$

Initially, the concentrations of C and D are zero and those of A and B are maximum. **Figure 2** shows that over time the rate of the forward reaction decreases as A and B are used up. Meanwhile, the rate of the reverse reaction increases as C and D are formed. When these two reaction rates become equal, equilibrium is established. The individual concentrations of A, B, C, and D undergo no further change if conditions remain the same.

After equilibrium is attained, the concentrations of products and reactants remain constant, so a ratio of their concentrations should also



Rate Comparison for the Reaction System
$A + B \rightleftharpoons C + D$

FIGURE 2 Shown are reaction rates for the hypothetical equilibrium reaction system $A + B \rightleftharpoons C + D$. From the time A and B are mixed together at t_0, the rate of the forward reaction declines and the rate of the reverse reaction increases until both forward and reverse reaction rates are equal at t_1, when the equilibrium condition begins.

remain constant. The ratio of the mathematical product $[C]^x \times [D]^y$ to the mathematical product $[A]^n \times [B]^m$ for this reaction has a definite value at a given temperature. It is the equilibrium constant of the reaction and is designated by the letter K. The following equation describes the equilibrium constant for the hypothetical equilibrium system. The brackets ([ ]) indicate the concentration of each substance as expressed in mol/L. The superscripts are the coefficients of each substance in the balanced chemical equation.

$$K = \frac{[C]^x[D]^y}{[A]^n[B]^m}$$

The concentrations of substances on the right side of the chemical equation appear in the numerator of the ratio, with each concentration raised to a power equal to the coefficient of that substance in the balanced chemical equation. These substances are the products of the forward reaction. The concentrations of substances on the left side of the chemical equation are in the denominator of the ratio, with each concentration raised to a power equal to the coefficient of that substance in the balanced chemical equation. These substances are the reactants of the forward reaction. The constant K is independent of the initial concentrations. It is, however, dependent on the temperature of the system.

The Equilibrium Constant

The numerical value of K for a particular equilibrium system is obtained experimentally. The chemist must analyze the equilibrium mixture and determine the concentrations of all substances. The value of K for a given equilibrium reaction at a given temperature shows the extent to which the reactants are converted into the products of the reaction. If the value of K is small, the forward reaction occurs only very slightly before equilibrium is established, and the reactants are favored. A large value of K indicates an equilibrium in which the original reactants are largely converted to products. Only the concentrations of substances that can actually change are included in K. This means that *pure* solids and liquids are omitted because their concentrations cannot change.

In general, then, *the* **equilibrium constant,** *K, is the ratio of the mathematical product of the concentrations of substances formed at equilibrium to the mathematical product of the concentrations of reacting substances. Each concentration is raised to a power equal to the coefficient of that substance in the chemical equation. The equation for K is sometimes referred to as the* **chemical equilibrium expression.**

The H_2, I_2, HI Equilibrium System

Consider the reaction between H_2 and I_2 vapor in a sealed flask at an elevated temperature. The rate of reaction can be followed by observing the rate at which the violet color of the iodine vapor diminishes, as shown in **Figure 3.** If colorless H_2 gas is present in excess, we might expect that the reaction would continue until all of the I_2 is used up. The violet color of the tube would decrease in intensity until all of the iodine reacts. At that time, the tube would be colorless, because both HI and the excess H_2 are colorless gases.

In actuality, the color fades to a constant intensity but does not disappear completely because the reaction is reversible. Hydrogen iodide decomposes to re-form hydrogen and iodine. The rate of this reverse reaction increases as the concentration of hydrogen iodide increases. The rate of the forward reaction decreases accordingly. The concentrations of hydrogen and iodine decrease as they react. As the rates of the opposing reactions become equal, equilibrium is established. The constant color achieved indicates that equilibrium exists among hydrogen, iodine, and hydrogen iodide. The net chemical equation for the reaction system at equilibrium follows.

$$H_2(g) + I_2(g) \rightleftarrows 2HI(g)$$

From this chemical equation, the following chemical equilibrium expression can be written. The concentration of HI is raised to the power of 2 because the coefficient of HI in the balanced chemical equation is 2.

$$K = \frac{[HI]^2}{[H_2][I_2]}$$

Chemists have carefully measured the concentrations of H_2, I_2, and HI in equilibrium mixtures at various temperatures. In some experiments, the flasks were filled with hydrogen iodide at known pressure. The flasks were held at fixed temperatures until equilibrium was established. In other experiments, hydrogen and iodine were the original substances. Experimental data, together with the calculated values for *K*, are listed in **Table 1.** Experiments 1 and 2 began with hydrogen iodide. Experiments 3 and 4 began with hydrogen and iodine. Note the close agreement obtained for the numerical values of the equilibrium constant in all cases.

At 425°C, the equilibrium constant for this equilibrium reaction system has the average value of 54.34. This value for *K* is constant for any system of H_2, I_2, and HI at equilibrium at this temperature. If the

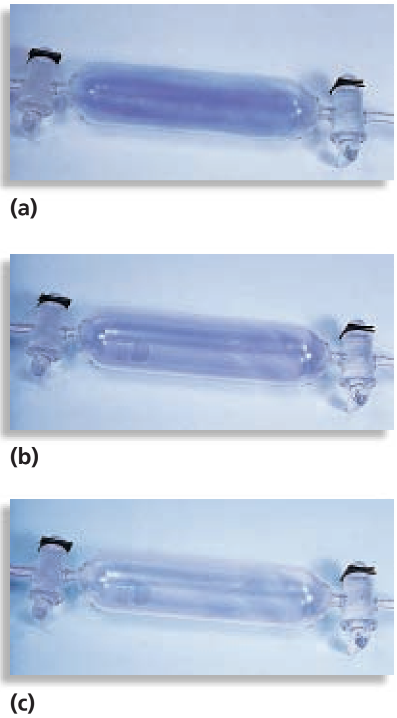


FIGURE 3 Hydrogen iodide gas is produced from gaseous hydrogen and iodine. The violet color of iodine gas (a) becomes fainter as the reaction consumes the iodine (b). The violet does not disappear but reaches a constant intensity when the reaction reaches equilibrium (c).

TABLE 1 ***Typical Equilibrium Concentrations of H_2, I_2, and HI in mol/L at 425°C***

Experiment	$[H_2]$	$[I_2]$	$[HI]$	$K = \frac{[HI]^2}{[H_2][I_2]}$
1	0.4953×10^{-3}	0.4953×10^{-3}	3.655×10^{-3}	54.46
2	1.141×10^{-3}	1.141×10^{-3}	8.410×10^{-3}	54.33
3	3.560×10^{-3}	1.250×10^{-3}	15.59×10^{-3}	54.62
4	2.252×10^{-3}	2.336×10^{-3}	16.85×10^{-3}	53.97

calculation for K yields a different result, there must be a reason. Either the H_2, I_2, and HI system has not reached equilibrium or the system is not at 425°C.

The balanced chemical equation for an equilibrium system is necessary to write the expression for the equilibrium constant. The data in **Table 1** show that the validity of this expression is confirmed when the actual values of the equilibrium concentrations of reactants and products are determined experimentally. The values of K are calculated from these concentrations. No information concerning the kinetics of the reacting systems is required.

Once the value of the equilibrium constant is known, the equilibrium-constant expression can be used to calculate concentrations of reactants or products at equilibrium. Suppose an equilibrium system at 425°C is found to contain 0.015 mol/L each of H_2 and I_2. To find the concentration of HI in this system, rearrange the chemical equilibrium expression as shown in the two equations that follow.

$$K = \frac{[\mathrm{HI}]^2}{[\mathrm{H_2}][\mathrm{I_2}]}$$

$$[\mathrm{HI}] = \sqrt{K[\mathrm{H_2}][\mathrm{I_2}]}$$

Using the known K value and the given concentrations for H_2 and I_2, solve the equation for [HI].

$$[\mathrm{HI}] = \sqrt{0.015 \times 0.015 \times 54.34}$$
$$[\mathrm{HI}] = 0.11 \text{ mol/L}$$

SAMPLE PROBLEM A

For more help, go to the *Math Tutor* at the end of this chapter.

An equilibrium mixture of N_2, O_2, and NO gases at 1500 K is determined to consist of 6.4×10^{-3} mol/L of N_2, 1.7×10^{-3} mol/L of O_2, and 1.1×10^{-5} mol/L of NO. What is the equilibrium constant for the system at this temperature?

SOLUTION

1 ANALYZE

Given: $[\mathrm{N_2}] = 6.4 \times 10^{-3}$ mol/L
$[\mathrm{O_2}] = 1.7 \times 10^{-3}$ mol/L
$[\mathrm{NO}] = 1.1 \times 10^{-5}$ mol/L

Unknown: K

2 PLAN

The balanced chemical equation is $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$.

The chemical equilibrium expression is $K = \frac{[\mathrm{NO}]^2}{[\mathrm{N_2}][\mathrm{O_2}]}$.

3 COMPUTE

Substitute the given values for the concentrations into the equilibrium expression.

$$K = \frac{(1.1 \times 10^{-5} \text{ mol/L})^2}{(6.4 \times 10^{-3} \text{ mol/L})(1.7 \times 10^{-3} \text{ mol/L})} = 1.1 \times 10^{-5}$$

4 ***EVALUATE*** The value of K is small, which is consistent with more N_2 and O_2 being present at equilibrium than NO. The answer has the correct number of significant figures and is close to an estimated value of

$$8 \times 10^{-6}\text{, calculated as } \frac{(1 \times 10^{-5})^2}{(6 \times 10^{-3})(2 \times 10^{-3})}.$$

PRACTICE

Answers in Appendix E

1. At equilibrium a mixture of N_2, H_2, and NH_3 gas at 500°C is determined to consist of 0.602 mol/L of N_2, 0.420 mol/L of H_2, and 0.113 mol/L of NH_3. What is the equilibrium constant for the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ at this temperature?

2. The reaction $AB_2C(g) \rightleftharpoons B_2(g) + AC(g)$ reached equilibrium at 900 K in a 5.00 L vessel. At equilibrium 0.084 mol of AB_2C, 0.035 mol of B_2, and 0.059 mol of AC were detected. What is the equilibrium constant at this temperature for this system? (Don't forget to convert amounts to concentrations.)

3. A reaction between gaseous sulfur dioxide and oxygen gas to produce gaseous sulfur trioxide takes place at 600°C. At that temperature, the concentration of SO_2 is found to be 1.50 mol/L, the concentration of O_2 is 1.25 mol/L, and the concentration of SO_3 is 3.50 mol/L. Using the balanced chemical equation, calculate the equilibrium constant for this system.

extension

Go to **go.hrw.com** for more practice problems that ask you to calculate equilibrium constants.

Keyword: HC6EQUX

SECTION REVIEW

1. What is meant by *chemical equilibrium*?
2. What is an equilibrium constant?
3. How does the value of an equilibrium constant relate to the relative quantities of reactants and products at equilibrium?
4. What is meant by a *chemical equilibrium expression*?
5. Hydrochloric acid, HCl, is a strong acid that dissociates completely in water to form H_3O^+ and Cl^-. Would you expect the value of K for the reaction $HCl(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Cl^-(aq)$ to be 1×10^{-2}, 1×10^{-5}, or "very large"? Justify your answer.
6. Write the chemical equilibrium expression for the reaction $4HCl(g) + O_2(g) \rightleftharpoons 2Cl_2(g) + 2H_2O(g)$.
7. At equilibrium at 2500 K, $[HCl] = 0.0625$ mol/L and $[H_2] = [Cl_2] = 0.00450$ mol/L for the reaction $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$. Find the value of K.
8. An equilibrium mixture at 425°C is found to consist of 1.83×10^{-3} mol/L of H_2, 3.13×10^{-3} mol/L of I_2, and 1.77×10^{-2} mol/L of HI. Calculate the equilibrium constant, K, for the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$.
9. For the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ at 425°C, calculate [HI], given $[H_2] = [I_2] = 4.79 \times 10^{-4}$ mol/L and $K = 54.3$.

Critical Thinking

10. **INFERRING RELATIONSHIPS** Use the data from Experiment 1 in **Table 1** to calculate the value of K for the reaction $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$. Do you see a relationship between the value you obtained and the value in the table?

HISTORICAL CHEMISTRY

Fixing the Nitrogen Problem

Historical Perspective

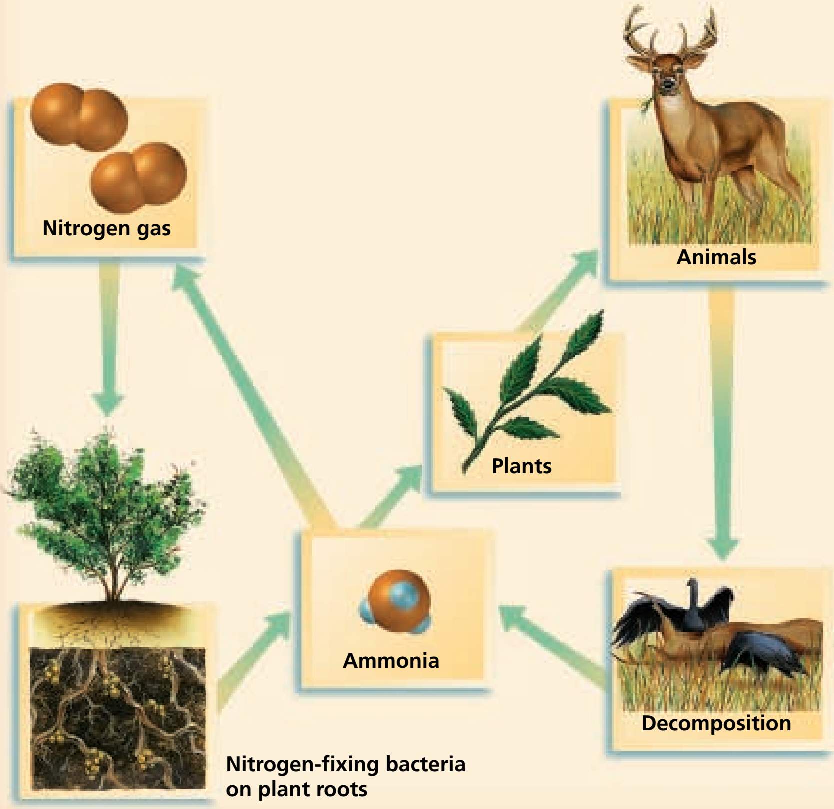
Each year, the chemical industry synthesizes tons of nitrogenous fertilizers, increasing agricultural production around the globe. But prior to 1915, humans had to rely solely on natural resources for fertilizer, and the dwindling supply of these materials caused widespread fear of world starvation. A crisis was averted, however, through the discovery of an answer to the "nitrogen problem," a term used at the time to describe the shortage of useful nitrogen despite its abundance in the atmosphere.

The Malthusian Threat

In 1798, Thomas Malthus published his famous "Essay on Population," a report predicting that the world's food supplies could not keep up with the growing human population and that famine, death, and misery were inevitable. Malthus's warning seemed to be echoed in the 1840s by the great Irish potato famine. In fact, the rest of Europe likely would have suffered serious food shortages as well had crop yields per acre not been increased through the use of fertilizers containing nitrogen.

Few living things can utilize the gas that forms 78% of the atmosphere; they need nitrogen that has been combined with other elements, or "fixed," to survive.

But soil often lacks sufficient amounts of the organisms that fix nitrogen for plants, so fertilizers containing usable nitrogen compounds are added. In 1898, two-thirds of the world's supply of these compounds came from Chile, where beds of sodium nitrate, or Chile saltpeter, were abundant. But, as the chemist William Crookes emphasized in his speech to the British Association that year, these reserves



◀*Nitrogen is released when living things die and also from animal wastes and plant material. Some bacteria are able to break the bond holding the nitrogen molecule together, freeing the nitrogen atoms to combine with hydrogen to form ammonia. Plants can absorb the nitrogen in this form from the soil. Animals then benefit from the nitrogen by eating the plants.*

were limited; it was up to his colleagues to discover alternatives and prevent Malthus's dire forecast from coming true.

The Haber-Nernst Controversy

As early as the 1890s, chemists had shown that ammonia, a practical source of fixed nitrogen, could be synthesized at high temperatures and at atmospheric pressure from elemental hydrogen and nitrogen. The problem was that the end product was present in such minute amounts that the process was not industrially practical.

In 1904, the German chemist Fritz Haber seemed to confirm this assessment. He tried reacting hydrogen and nitrogen at temperatures of up to 1020°C using pure iron as well as other metals as a catalyst. He found that the amount of ammonia was a mere 0.005% to 0.012% at equilibrium.

Haber had apparently closed the door on the synthesis of ammonia from its elements. But in 1906, Walther Nernst, using his new heat theorem, calculated the reaction's theoretical ammonia concentration at equilibria corresponding to several pressures. He found that his value at atmospheric pressure disagreed significantly with Haber's, and he publicly challenged Haber's values.

Haber was convinced that he was right. He ran the reaction at increased pressure to attain an amount of ammonia that could be measured more accurately.

Haber and his assistants confirmed their original findings, and Nernst later conceded a mathematical error. But more important, the new round of experiments indicated that a reasonable amount of ammonia might be attained at pressures of 200 atm (20,000 kPa) using a uranium or osmium catalyst.

Scaling Up

Large-scale equipment that could withstand such high pressures was unheard of at the time, and osmium and uranium were far too scarce to be cost-effective for industry. Nevertheless, in 1909, the German firm BASF bought the rights to Haber's findings and put its gifted chemical engineer Karl Bosch in charge of creating an industrial-scale system that would make the process profitable.

After nearly five years, Bosch and the company's chief chemist, Alwin Mittasch, succeeded in developing a suitable reactor that could handle the reaction's high pressures. They also discovered that a catalyst of iron containing small amounts of impurities was an effective replacement for the rare metals used by Haber.

▲*Today, ammonia is produced on an industrial scale in plants like this one.*

An Eerie Epilogue

By September 1913, BASF was producing 20 metric tons of ammonia a day using the Haber-Bosch process. Eventually, enough ammonia was produced by the chemical industry to free Germany and the world of dependence on Chile saltpeter for fertilizer. Chemists had thwarted the Malthusian threat. Yet, the victory proved bittersweet; the new ammonia synthesis also became the basis of the production of nitric acid, used to make many of the explosives employed in the wars that rocked Europe and the rest of the globe in the first half of the twentieth century.

Questions

1. What is the major use for ammonia?
2. What did Haber find when he tried to synthesize ammonia at increased pressure?

SCLINKS.
www.scilinks.org
Topic: Nitrogen
Code: HC61035

SECTION 2

Shifting Equilibrium

OBJECTIVES

- Discuss the factors that disturb equilibrium.
- Discuss conditions under which reactions go to completion.
- Describe the common-ion effect.

In systems that have attained chemical equilibrium, the relative amounts of reactants and products stay the same. But changes in pressure, concentration, or temperature can alter the equilibrium position and thereby change the relative amounts of reactants and products. By shifting an equilibrium in the desired direction, chemists can often improve the yield of the product they are seeking.

Predicting the Direction of Shift

In 1888, the French chemist Henri Louis Le Châtelier developed a principle that provides a means of predicting the influence of stress factors on equilibrium systems. Le Châtelier's principle states that *if a system at equilibrium is subjected to a stress, the equilibrium is shifted in the direction that tends to relieve the stress.* This principle is true for all dynamic equilibria, chemical as well as physical. Changes in pressure, concentration, and temperature illustrate Le Châtelier's principle.

Changes in Pressure

A change in pressure affects only equilibrium systems in which gases are involved. For changes in pressure to affect the system, the *total* number of moles of gas on the left side of the equation must be different from the *total* number of moles of gas on the right side of the equation.

Let us consider the Haber process for the synthesis of ammonia. Note that there is a total of four molecules of gas on the reactant side of the equation and two molecules of gas on the product side of the equation.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

First, consider an increase in pressure as the applied stress. Can the system shift in a way that reduces the stress? Yes. An increase in pressure causes increases in the concentrations of all species. The system can reduce the number of molecules, and hence the total pressure, by shifting the equilibrium to the right. For each four molecules of reactants, nitrogen and hydrogen, there are two molecules of product, ammonia. By producing more NH_3, and using up N_2 and H_2, the system can reduce the total number of molecules. This leads to a decrease in pressure. Although the new equilibrium pressure is still higher than before, it is not as high as the pressure caused by the initial stress.

An increase in pressure on confined gases causes an increase in the concentrations of these gases. Even though changes in pressure may

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shift the equilibrium position, they do not affect the value of the equilibrium constant.

Ammonia produced in the Haber process is continuously removed by condensing it to liquid ammonia. This condensation removes most of the product from the gas phase in which the reaction occurs. The resulting decrease in the partial pressure of NH_3 gas in the reaction vessel is a stress and is the same as a decrease in product concentration, which shifts the equilibrium to the right.

The introduction of an inert gas, such as helium, into the reaction vessel for the synthesis of ammonia increases the total pressure in the vessel. But it does not change the partial pressures of the reaction gases present. Therefore, increasing pressure by adding a gas that is not a reactant or a product *cannot* affect the equilibrium position of the reaction system.

Changes in Concentration

An increase in the concentration of a reactant is a stress on the equilibrium system. Consider the following hypothetical reaction.

$$A + B \rightleftharpoons C + D$$

An increase in the concentration of A creates a stress. To relieve the stress, some of the added A reacts with B to form products C and D. The equilibrium is reestablished with a higher concentration of A than before the addition but a lower concentration of B. **Figure 4** illustrates the effect on a system in equilibrium produced by increasing the concentration of a reactant. Similarly, an increase in the concentration of B drives the reaction to the right. An increase in the concentration of either C or D shifts the equilibrium to the left. A decrease in the concentration of C or D has the same effect on the position of the equilibrium as does an increase in the concentration of A or B; the equilibrium shifts to the right.

Changes in concentration have no effect on the value of the equilibrium constant. Although concentrations of both reactants and products do change, the new concentrations give the same value of the equilibrium constant when equilibrium is reestablished.

Many chemical processes involve heterogeneous reactions in which reactants or products are in different phases. The concentrations of pure solids and liquids do not change, and by convention are not written in the equilibrium expression. Also, when a solvent such as water, in a system involving acids and bases, is in an equilibrium equation, it is not included in the equilibrium expression. In Chapter 15, the expression for K_w used this convention and the concentration of water is not included in the expression. The reaction representing the self-ionization of water is

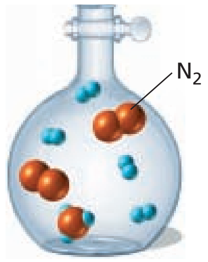
$$2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

and the equation for K_w is $K_w = [H_3O^+][OH^-]$.

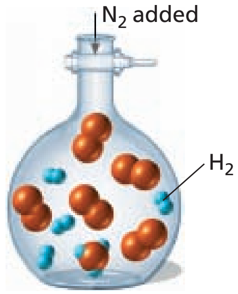
The following equation describes the equilibrium system established by the decomposition of solid calcium carbonate.

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

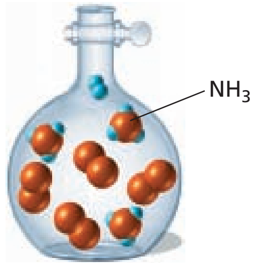
(a) at equilibrium



(b) stressed (not at equilibrium)



(c) at new equilibrium



$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

FIGURE 4 (a) N_2, H_2, and NH_3 are in equilibrium within a closed system. (b) Addition of more N_2 causes a stress on the initial equilibrium. (c) The new equilibrium position for this system has a higher concentration of N_2, a lower concentration of H_2, and a higher concentration of NH_3 than initially.

The products are a solid and a gas. Because both $CaCO_3$ and CaO are solids, they are not in the equilibrium constant expression. This leads to the following expression for the equilibrium constant.

$$K = [CO_2]$$

Carbon dioxide is the only substance in the system that appears in the equilibrium expression. Because the total number of moles of gas on the left side of the equation is different from the total number of moles on the right side of the equation, pressure changes will affect the equilibrium. High pressure favors the reverse reaction, which causes CO_2 molecules to react with the solid CaO to form solid $CaCO_3$. Low pressure favors the formation of CO_2 from the decomposition of $CaCO_3$. Because both CaO and $CaCO_3$ are solids, changing their amounts will not change the equilibrium concentration of CO_2.

Changes in Temperature

Reversible reactions are exothermic in one direction and endothermic in the other. Remember, equilibrium constants are for a given temperature because changing the temperature changes the relative amounts of reactants and products.

Increasing the temperature is, in effect, the addition of enery in the form of heat. According to Le Châtelier's principle, the stress of the added heat will be lessened by shifting the equilibrium in the direction that removes heat (lowers the temperature). This means that energy must be absorbed so the reaction that is endothermic occurs until a new equilibrium is established. Likewise, the removal of energy as a result of lowering the temperature causes the exothermic reaction to take place.

The synthesis of ammonia by the Haber process is exothermic, as indicated by the energy as heat shown on the product side of the equation.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + 92\ \text{kJ}$$

A high temperature favors the decomposition of ammonia, the endothermic reaction. But at low temperatures, the forward reaction is too slow to be commercially useful. The temperature used represents a compromise between kinetic and equilibrium requirements. It is high enough that equilibrium is established rapidly but low enough that the equilibrium concentration of ammonia is significant. Moderate temperature (about 500°C) and very high pressure (700–1000 atm) produce a satisfactory yield of ammonia.

The production of colorless dinitrogen tetroxide gas, N_2O_4, from dark red-brown NO_2 gas is also an exothermic reaction. **Figure 5** shows how temperature affects the equilibrium of this system. **Figure 5b** shows the NO_2/N_2O_4 equilibrium mixture at 25°C. When the temperature of the system is lowered to 0°C, the system experiences a stress (removal of energy as heat). To counteract this stress, the system shifts to the right, or in the direction of the exothermic reaction. This shift increases the amount of colorless N_2O_4 gas and decreases the amount of brown NO_2 gas, as shown in **Figure 5a.** Because more N_2O_4 is present, K is increased. When the system is heated to 100°C, the added energy is the stress, and the equi-

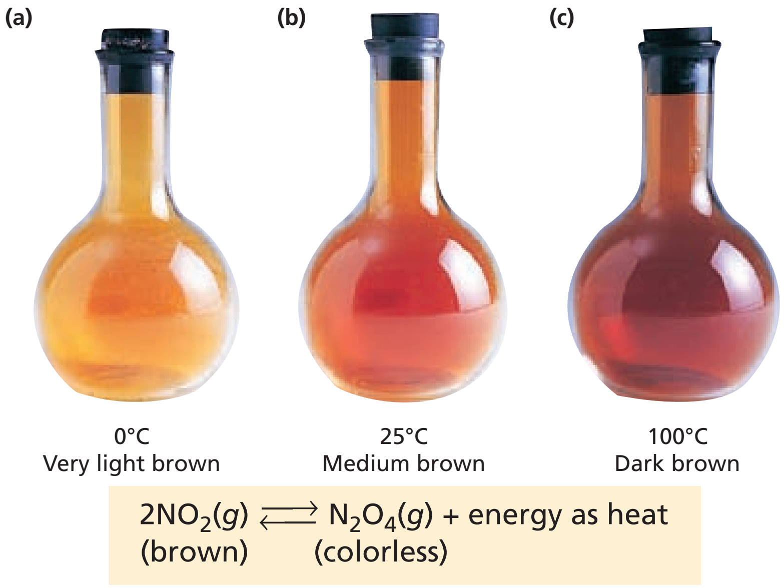


FIGURE 5 Different temperatures can cause an equilibrium system to shift and seek a new equilibrium position.

librium shifts to the left, or in the direction of the endothermic reaction. This shift decreases the amount of colorless N_2O_4 gas and increases the amount of brown NO_2 gas, as shown in **Figure 5c.** Because less N_2O_4 gas is present, K is decreased. The change in temperature changes the value of K. For any system in which the forward reaction is an exothermic reaction, increasing the temperature decreases the value of K.

For an endothermic reaction, such as the decomposition of calcium carbonate, energy as heat shows up on the reactant side of the equation.

$$556 \text{ kJ} + CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

An increase in temperature caused by adding energy to the system causes the value of K to increase and the equilibrium to shift to the right.

Catalysts speed up the rate of reactions. So what happens to equilibrium concentrations if a catalyst is present? Nothing! When a catalyst is added to an equilibrium system, it speeds up both the forward and reverse reactions. The equilibrium concentrations are achieved faster, but the concentrations and K remain the same.

Reactions That Go to Completion

Some reactions involving compounds formed by the chemical interaction of ions in solutions appear to go to completion in the sense that the ions are almost completely removed from solution. The extent to which reacting ions are removed from solution depends on the solubility of the compound formed and, if the compound is soluble, on the degree of ionization. Thus, a product that escapes as a gas, precipitates as a solid, or is only slightly ionized effectively removes from solution the bulk of the reacting ions that compose it. Consider some specific examples of situations in which such ionic reactions go to completion.

Formation of a Gas

Reactions that form a gas as a product are one example of reactions that go to completion. When a strong acid is added to an aqueous solution of baking soda, or sodium bicarbonate, carbon dioxide is formed. The net ionic equation shows that ions are removed.

$$H_3O^+ + HCO_3^- \longrightarrow 2H_2O(l) + CO_2(g)$$

This reaction goes practically to completion because one of the products, CO_2, escapes as a gas if the container is open to the air.

Formation of a Precipitate

When solutions of sodium chloride and silver nitrate are mixed, a white precipitate of silver chloride immediately forms, as shown in **Figure 6.** The overall ionic equation for this reaction follows.

$$Na^+(aq) + Cl^-(aq) + Ag^+(aq) + NO_3^-(aq) \longrightarrow Na^+(aq) + NO_3^-(aq) + AgCl(s)$$

If chemically equivalent amounts of the two solutes are mixed, only Na^+ ions and NO_3^- ions remain in solution in appreciable quantities. Almost all of the Ag^+ ions and Cl^- ions combine and separate from the solution as a precipitate of AgCl. The reason is that AgCl is only very slightly soluble in water. The solution is now a saturated solution of AgCl. The reaction thus effectively goes to completion because an essentially insoluble product is formed.

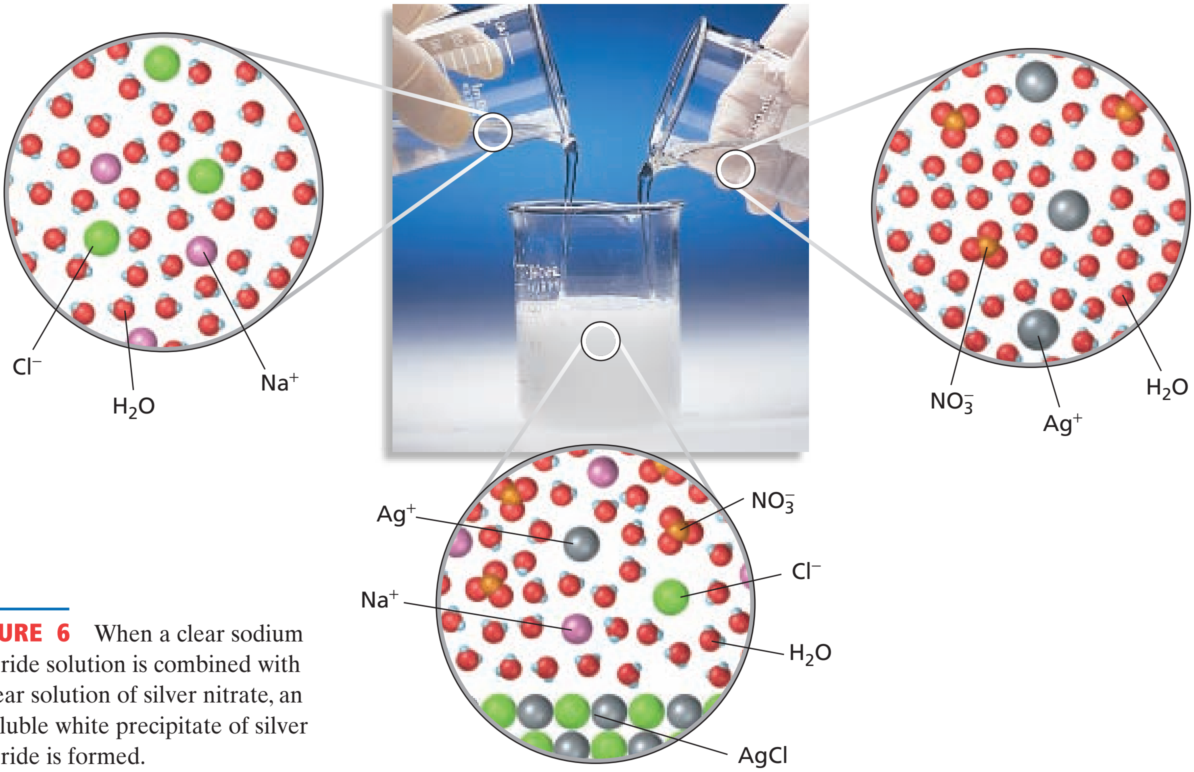


FIGURE 6 When a clear sodium chloride solution is combined with a clear solution of silver nitrate, an insoluble white precipitate of silver chloride is formed.

Formation of a Slightly Ionized Product

Neutralization reactions between H_3O^+ ions from aqueous acids and OH^- ions from aqueous bases result in the formation of water molecules, which are only slightly ionized. A reaction between HCl and NaOH illustrates this process. Aqueous HCl supplies H_3O^+ ions and Cl^- ions to the solution, and aqueous NaOH supplies Na^+ ions and OH^- ions, as shown in the following overall ionic equation.

$$H_3O^+(aq) + Cl^-(aq) + Na^+(aq) + OH^-(aq) \longrightarrow Na^+(aq) + Cl^-(aq) + 2H_2O(l)$$

Neglecting the spectator ions, the net ionic equation is as follows.

$$H_3O^+(aq) + OH^-(aq) \longrightarrow 2H_2O(l)$$

Because it is only slightly ionized, the water exists almost entirely as molecules. Thus, hydronium ions and hydroxide ions are almost entirely removed from the solution. The reaction effectively goes to completion because the product is only slightly ionized.

extension

CROSS-DISCIPLINARY

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Keyword: HC6EQUX

Common-Ion Effect

An equilibrium reaction may be driven in the desired direction by applying Le Châtelier's principle. Suppose hydrogen chloride gas is bubbled into a saturated solution of sodium chloride. Hydrogen chloride is extremely soluble in water, and it is completely ionized.

$$HCl(g) + H_2O(l) \longrightarrow H_3O^+(aq) + Cl^-(aq)$$

The equilibrium for a saturated solution of sodium chloride is described by the following equation.

$$NaCl(s) \rightleftarrows Na^+(aq) + Cl^-(aq)$$

As the hydrogen chloride dissolves in sufficient quantity, it increases the concentration of Cl^- ions in the solution, which is a stress on the equilibrium system. The system can compensate, according to Le Châtelier's principle, by combining some of the added Cl^- ions with an equivalent amount of Na^+ ions. This causes some solid NaCl to precipitate out, relieving the stress of added chloride. The new equilibrium has a greater concentration of Cl^- ions but a decreased concentration of Na^+ ions. However, the product of $[Na^+]$ and $[Cl^-]$ still has the same value as before. *This phenomenon, in which the addition of an ion common to two solutes brings about precipitation or reduced ionization, is an example of the* **common-ion effect.**

The common-ion effect is also observed when one ion species of a weak electrolyte is added in excess to a solution. Acetic acid, CH_3COOH, is such an electrolyte. A 0.1 M CH_3COOH solution is only about 1.3% ionized as hydronium ions and acetate ions, CH_3COO^-. The ionic equilibrium is shown by the following equation.

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$

Addition of sodium acetate, $NaCH_3COO$ (an ionic salt that is soluble in water), to a solution containing acetic acid increases the acetate ion concentration. The equilibrium then shifts in the direction that uses up some of the added acetate ions in accordance with Le Châtelier's principle. More molecules of acetic acid are formed, and the concentration of hydronium ions is reduced. In general, the addition of a salt with an ion in common with the weak electrolyte reduces the ionization of the electrolyte. **Figure 7** shows a 0.25 M CH_3COOH solution on the left that has a pH of about 2.7. Mixing that with the 0.10 M $NaCH_3COO$ solution in the center produces the solution on the right, which has a pH of about 4.5, indicating lower $[H_3O^+]$ and thus lowered acetic acid ionization.

FIGURE 7 The solution of CH_3COOH on the left is combined with the solution of $NaCH_3COO$ in the center. Both contain the common ion, CH_3COO^-. They produce the solution on the right, which is only slightly acidic due to the decreased ionization of the acid. The colors of the solutions are due to the addition of an acid-base indicator.

SECTION REVIEW

1. Name three ways the chemical equilibrium can be disturbed.
2. Describe three situations in which ionic reactions go to completion.
3. Describe the common-ion effect.
4. Identify the common ion in each of the following situations.
   - **a.** 5 g of NaCl is added to a 2.0 M solution of HCl
   - **b.** 50 mL of 1.0 M $NaCH_3COO$ is added to 1.0 M CH_3COOH
   - **c.** 1 g of NH_4Cl is added to 100 mL of aqueous NH_3
5. Predict the effect that decreasing pressure would have on each of the following reaction systems at equilibrium.
   - **a.** $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$
   - **b.** $NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$
   - **c.** $2H_2O_2(aq) \rightleftharpoons 2H_2O(l) + O_2(g)$
   - **d.** $3O_2(g) \rightleftharpoons 2O_3(g)$

Critical Thinking

6. **PREDICTING OUTCOMES** Carbon dioxide and water react to form bicarbonate ion and hydronium ion. Hyperventilation (rapid breathing) causes more carbon dioxide to be exhaled than normal. How will hyperventilation affect the pH of blood? Explain.

Equilibria of Acids, Bases, and Salts

SECTION 3

Objectives

- Explain the concept of acid ionization constants, and write acid ionization equilibrium expressions.
- Review the ionization constant of water.
- Explain buffering.
- Compare cation and anion hydrolysis.

Ionization Constant of a Weak Acid

About 1.3% of the solute molecules in a 0.1 M acetic acid solution are ionized at room temperature. The remaining 98.7% of the acetic acid molecules, CH_3COOH, remain nonionized. Thus, the solution contains three species of particles in equilibrium: CH_3COOH molecules, H_3O^+ ions, and acetate ions, CH_3COO^-. From the equilibrium equation for the ionization of acetic acid, the equilibrium constant equation can be written.

$$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$$

$$K = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH][H_2O]}$$

Notice that the concentration of water is not included in the equilibrium expression. The reason is that water is the solvent, and water molecules greatly exceed the number of acetic acid molecules. Without introducing a measurable error, one can assume that the molar concentration of H_2O molecules remains constant in such a solution. Thus, because both K and $[H_2O]$ are constant, the product $K[H_2O]$ is constant.

$$K[H_2O] = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$

The left side of the equation can be simplified by setting $K[H_2O] = K_a$.

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$

The term K_a is called the **acid ionization constant.** The acid ionization constant, K_a, like the equilibrium constant, K, is constant for a specified temperature but has a new value for each new temperature.

The acid ionization constant for a weak acid represents a small value. To determine the numerical value of the ionization constant for acetic acid at a specific temperature, the equilibrium concentrations of H_3O^+ ions, CH_3COO^- ions, and CH_3COOH molecules must be known. The ionization of a molecule of CH_3COOH in water yields one H_3O^+ ion and one CH_3COO^- ion. These concentrations can, therefore, be found experimentally by measuring the pH of the solution.

TABLE 2 Ionization of Acetic Acid

Molarity	% ionized	$[H_3O^+]$	$[CH_3COOH]$	K_a
0.100	1.33	0.00133	0.0987	1.79×10^{-5}
0.0500	1.89	0.000945	0.0491	1.82×10^{-5}
0.0100	4.17	0.000417	0.00958	1.81×10^{-5}
0.00500	5.86	0.000293	0.00471	1.82×10^{-5}
0.00100	12.6	0.000126	0.000874	1.82×10^{-5}

Ionization data and constants for some dilute acetic acid solutions at 25°C are given in **Table 2.** Notice that the numerical value of K_a is almost identical for each solution molarity shown. The numerical value of K_a for CH_3COOH at 25°C can be determined by substituting numerical values for concentration into the equilibrium equation.

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$

At constant temperature, an increase in the concentration of CH_3COO^- ions through the addition of sodium acetate, $NaCH_3COO$, disturbs the equilibrium, as predicted by Le Châtelier's principle. This disturbance causes a decrease in $[H_3O^+]$ and an increase in $[CH_3COOH]$. Eventually, the equilibrium is reestablished with the *same* value of K_a. But there is a higher concentration of nonionized acetic acid molecules and a lower concentration of H_3O^+ ions than before the extra CH_3COO^- was added. Changes in the hydronium ion concentration affect pH. In this example, the reduction in $[H_3O^+]$ means an increase in the pH of the solution.

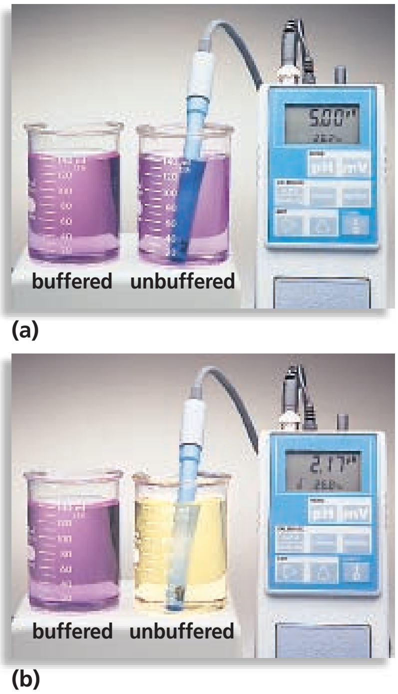

FIGURE 8 (a) The beaker on the left contains a buffered solution and an indicator with a pH of about 5. The beaker on the right contains mostly water with a trace amount of acid and an indicator. The pH meter shows a pH of 5.00 for this solution. (b) After 5 mL of 0.10 M HCl is added to both beakers, the beaker on the left does not change color, indicating no substantial change in its pH. However, the beaker on the right undergoes a definite color change, and the pH meter shows a pH of 2.17.

Buffers

The solution just described contains both a weak acid, CH_3COOH, and a salt of the weak acid, $NaCH_3COO$. The solution can react with either an acid or a base. When small amounts of acids or bases are added, the pH of the solution remains nearly constant. The weak acid and the common ion, CH_3COO^-, act as a "buffer" against significant changes in the pH of the solution. *Because it can resist changes in pH, this solution is a* **buffered solution. Figure 8** shows how a buffered and a nonbuffered solution react to the addition of an acid.

Suppose a small amount of acid is added to the acetic acid–sodium acetate solution. Acetate ions react with most of the added hydronium ions to form nonionized acetic acid molecules.

$$CH_3COO^-(aq) + H_3O^+(aq) \longrightarrow CH_3COOH(aq) + H_2O(l)$$

The hydronium ion concentration and the pH of the solution remain practically unchanged.

Suppose a small amount of a base is added to the original solution. The OH^- ions of the base react with and remove hydronium ions to form nonionized water molecules. Acetic acid molecules then ionize and mostly replace the hydronium ions neutralized by the added OH^- ions.

$$CH_3COOH(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + CH_3COO^-(aq)$$

The pH of the solution again remains practically unchanged.

A solution of a weak base containing a salt of the base behaves in a similar manner. The hydroxide ion concentration and the pH of the solution remain essentially constant with small additions of acids or bases. Suppose a base is added to an aqueous solution of ammonia that also contains ammonium chloride. Ammonium ions donate a proton to the added hydroxide ions to form nonionized water molecules.

$$NH_4^+(aq) + OH^-(aq) \longrightarrow NH_3(aq) + H_2O(l)$$

If a small amount of an acid is added to the solution instead, hydroxide ions from the solution accept protons from the added hydronium ions to form nonionized water molecules. Ammonia molecules in the solution then ionize and mostly replace the hydroxide ions neutralized by added H_3O^+.

$$NH_3(aq) + H_2O(l) \longrightarrow NH_4^+(aq) + OH^-(aq)$$

Buffer action has many important applications in chemistry and physiology. Human blood is naturally buffered to maintain a pH of between 7.3 and 7.5. This is essential because large changes in pH would lead to serious disturbances of normal body functions. **Figure 9** shows an example of one of the many medicines buffered to prevent large and potentially damaging changes in pH.

FIGURE 9 Many consumer products are buffered to protect the body from potentially harmful pH changes.

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Ionization Constant of Water

Recall from Chapter 15 that the self-ionization of water is an equilibrium reaction.

$$H_2O(l) + H_2O(l) \rightleftarrows H_3O^+(aq) + OH^-(aq)$$

Equilibrium is established with a very low concentration of H_3O^+ and OH^- ions. The expression for the equilibrium constant, $K_w = [H_3O^+][OH^-]$, is derived from the balanced chemical equation. The numerical value of K_w, obtained experimentally, is 1.0×10^{-14} at 25°C.

Hydrolysis of Salts

Salts are formed during neutralization reactions between acids and bases. When a salt dissolves in water, it produces positive ions (cations) of the base from which it was formed and negative ions (anions) of the acid from which it was formed. Therefore, the solution might be expected to be neutral. The aqueous solutions of some salts, such as NaCl and KNO_3, are neutral, having a pH of 7. However, when sodium carbonate dissolves in water, the resulting solution turns red litmus paper blue, indicating a pH greater than 7. Ammonium chloride produces an aqueous solution that turns blue litmus paper red, indicating a pH less than 7. Salts formed from the combination of strong or weak acids and bases are shown in **Figure 10.**

The variation in pH values can be accounted for by examining the ions formed when each of these salts dissociates. If the ions formed are from weak acids or bases, they react chemically with the water molecules, and the pH of the solution will have a value other than 7. *A reaction between water molecules and ions of a dissolved salt is* **hydrolysis.** If the anions react with water, the process is anion hydrolysis and results in a more basic solution. If the cations react with water molecules, the process is cation hydrolysis and results in a more acidic solution.

Anion Hydrolysis

In the Brønsted sense, the anion of the salt is the conjugate base of the acid from which it was formed. It is also a proton acceptor. If the acid is weak, its conjugate base (the anion) will be strong enough to remove pro-

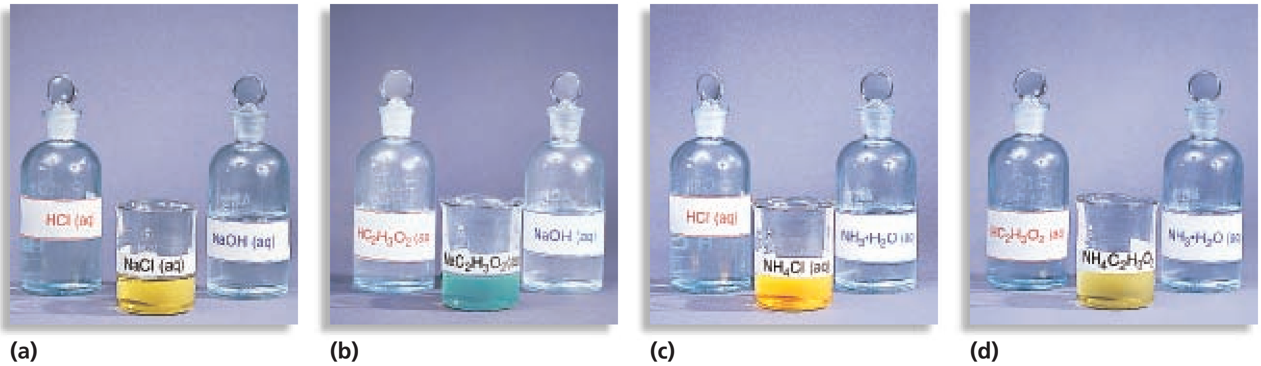


FIGURE 10 The universal indicator shows that the pH of salt solutions varies, depending on the strength of the acid and the base that formed the salt. (a) NaCl is formed from a strong acid and a strong base; the color of the indicator shows the pH is neutral. (b) The indicator shows the pH of the sodium acetate solution is basic. This was formed from a strong base and a weak acid. (c) The strong acid and weak base combination in ammonium chloride produces an acidic solution, as shown by the reddish tint of the indicator. (d) The weak acid and weak base that form ammonium acetate are of comparable strength. A solution of ammonium acetate is essentially neutral.

tons from some water molecules, proton donors, to form OH^- ions. An equilibrium is established in which the net effect of the anion hydrolysis is an increase in the hydroxide ion concentration, $[OH^-]$, of the solution.

The equilibrium equation for a typical weak acid in water, HA, forming hydronium ion and an anion, A^-, is as follows.

$$HA(aq) + H_2O(l) \rightleftarrows H_3O^+(aq) + A^-(aq)$$

From this equation, the generalized expression for K_a can be written. Note that as before, water does not appear in the general equilibrium equation.

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

The hydrolysis reaction between water and the anion, A^-, that is produced by the ionization of the weak acid, HA, is represented by the general equilibrium equation that follows.

$$A^-(aq) + H_2O(l) \rightleftarrows HA(aq) + OH^-(aq)$$

Neutral water has equal concentrations of H_3O^+ and OH^-. Since HA is a weak acid, the anion A^- has a strong attraction for protons. Adding A^- to water in effect attracts (removes) H_3O^+ in water to form HA. This causes OH^- to increase relative to H_3O^+ as represented in the equation above. The lower the value of K_a, the stronger the attraction A^- will have for protons and the larger the concentration of OH^-. In other words, the weaker the acid, HA, the stronger its conjugate base, A^-.

Aqueous solutions of sodium carbonate are strongly basic. The sodium ions, Na^+, in sodium carbonate do not undergo hydrolysis in aqueous solution, but the carbonate ions, CO_3^{2-}, react as a Brønsted base. A CO_3^{2-} anion acquires a proton from a water molecule to form the weak Brønsted acid, HCO_3^-, and the OH^- ion.

$$CO_3^{2-}(aq) + H_2O(l) \rightleftarrows HCO_3^-(aq) + OH^-(aq)$$

The OH^- ion concentration increases until equilibrium is established. Consequently, the H_3O^+ ion concentration decreases so that the product $[H_3O^+][OH^-]$ remains equal to the ionization constant, K_w, of water at the temperature of the solution. Thus, the pH is *higher* than 7, and the solution is basic.

Cation Hydrolysis

In the Brønsted sense, the cation of the salt is the conjugate acid of the base from which it was formed. It is also a proton donor. If the base is weak, the cation is an acid strong enough to donate a proton to a water molecule, a proton acceptor, to form H_3O^+ ions. An equilibrium is established in which the net effect of the cation hydrolysis is an increase in the hydronium ion concentration, $[H_3O^+]$, of the solution.

CROSS-DISCIPLINARY

Blood Buffers

Blood normally has a pH of 7.4. If the pH of blood in a human rises above 7.8 or falls below 7.0, this change in pH is usually fatal. The primary buffer in blood is the carbonic acid–bicarbonate ion system, $CO_2(g) + H_2O(l) \rightleftarrows H_2CO_3(aq) + HCO_3^-(aq)$. A condition called *respiratory acidosis* causes the pH to drop. It is the result of *hypoventilation,* or slowed breathing, the opposite of hyperventilation. Hypoventilation can be caused by congestive heart failure, pneumonia, or narcotics. Because breathing is slowed, carbon dioxide accumulates and its concentration rises. This change causes a shift in the equilibrium to the right due to Le Châtelier's principle, and the blood becomes more acidic because of the higher concentration of carbonic acid.

The following equilibrium equation for a typical weak base, B, is used to derive the generalized expression for K_b, the base dissociation constant.

$$B(aq) + H_2O(l) \rightleftharpoons BH^+(aq) + OH^-(aq)$$

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

The hydrolysis reaction between water and the cation, BH^+, produced by the dissociation of the weak base, B, is represented by the general equilibrium equation that follows.

$$BH^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + B(aq)$$

In the forward reaction, the cation BH^+ donates a proton to the water molecule to form the hydronium ion. Because H_3O^+ ions are formed, the solution must become more acidic, as shown in the equation above. The extent of H_3O^+ ion formation depends on the relative strength of the base B. The weaker the base, the greater the concentration of H_3O^+ ions will be. Therefore, the weaker the base, the stronger its conjugate acid.

Ammonium chloride, NH_4Cl, dissociates in water to produce NH_4^+ ions and Cl^- ions. Chloride ions are the conjugate base of the strong acid HCl, so they do not hydrolyze in water. Ammonium ions, however, are the conjugate acid of a weak base, NH_3. Ammonium ions donate protons to water molecules. Equilibrium is established with an increased $[H_3O^+]$, so the pH is *lower* than 7.

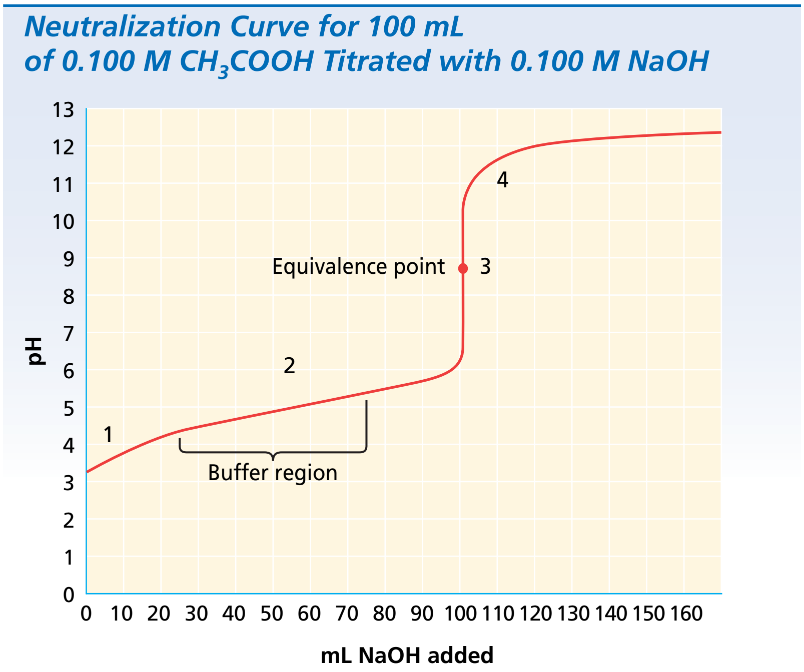

Neutralization Curve for 100 mL of 0.100 M CH_3COOH Titrated with 0.100 M NaOH

FIGURE 11 At point *1* on the titration curve, only acetic acid is present. The pH depends on the weak acid alone. At *2* there is a mixture of CH_3COOH and CH_3COO^-. Adding NaOH changes the pH slowly. At point *3* all acid has been converted to CH_3COO^-. This hydrolyzes to produce a slightly basic solution. At *4* the pH is due to the excess OH^- that has been added.

Hydrolysis in Acid-Base Reactions

Hydrolysis can help explain why the end point of a neutralization reaction can occur at a pH other than 7. The hydrolysis properties of salts are determined by the relative strengths of the acids and bases from which the salts were formed. Salts can be placed in four general categories, depending on their hydrolysis properties: strong acid–strong base, strong acid–weak base, weak acid–strong base, and weak acid–weak base.

Salts of strong acids and strong bases produce neutral solutions because neither the cation of a strong base nor the anion of a strong acid hydrolyzes appreciably in aqueous solutions. HCl(*aq*) is a strong acid, and NaOH(*aq*) is a strong base. Neither the Na^+ cation of the strong base nor the Cl^- anion of the strong acid undergoes hydrolysis in water solutions. Therefore, aqueous solutions of NaCl are neutral. Similarly, KNO_3 is the salt of the strong acid HNO_3 and the strong base KOH. Measurements show that the pH of an aqueous KNO_3 solution is always very close to 7.

The aqueous solutions of salts formed from reactions between weak acids and strong bases are basic at the equivalence point, as shown in **Figure 11.** Anions of the dissolved salt are hydrolyzed by the water molecules, and the pH of the solution is raised, indicating that the hydroxide-ion concentration has increased. Aqueous solutions of sodium acetate, $NaCH_3COO$, are basic. The acetate ions, CH_3COO^-, undergo hydrolysis because they are the anions of the weak acid acetic acid. The cations of the salt are from a strong base, NaOH, and do not hydrolyze, because NaOH is 100% dissociated.

Figure 12 shows that salts of strong acids and weak bases are acidic at the equivalence point. Cations of the dissolved salt are hydrolyzed in

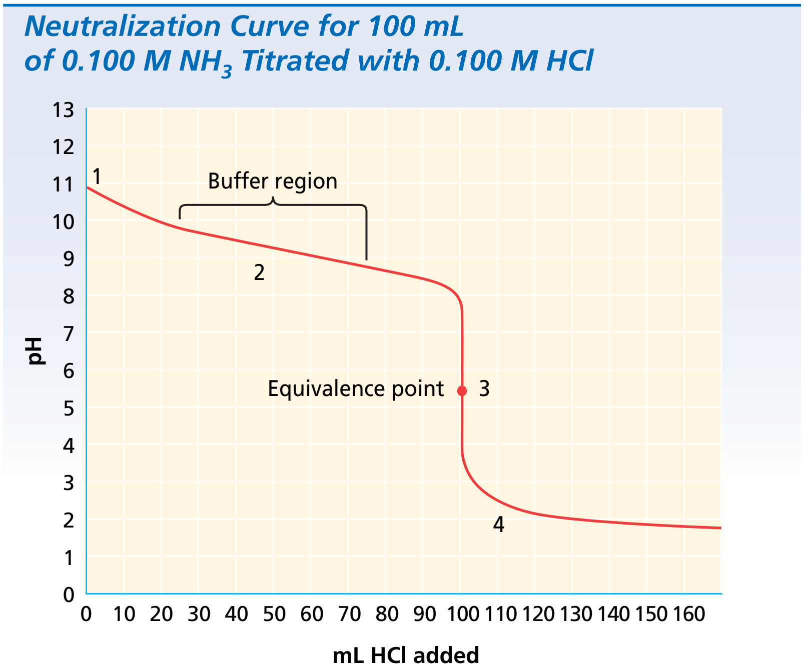


FIGURE 12 At point *1* on the titration curve, only aqueous ammonia is present. The pH is determined by the base alone. At *2* there is a mixture of NH_3 and NH_4^+. Adding HCl changes the pH slowly. At point *3* all aqueous ammonia has been converted to NH_4^+. At *4* the pH is determined by the excess H_3O^+ that is being added.

the water solvent, and the pH of the solution is lowered, indicating that the hydronium ion concentration has increased. In this case, the cations of the salt undergo hydrolysis because they are the positive ions from a weak base. The anions of the salt are the negative ions from a strong acid and do not hydrolyze appreciably. Ammonium chloride, NH_4Cl, is a salt that produces an acidic solution.

Salts of weak acids and weak bases can produce either acidic, neutral, or basic aqueous solutions, depending on the salt dissolved. This is because both ions of the dissolved salt are hydrolyzed extensively. If both ions are hydrolyzed equally, the solution remains neutral. The ions in ammonium acetate, NH_4CH_3COO, hydrolyze equally, producing a neutral solution, as shown in **Figure 10d** on page 608.

In salts formed from a weak acid and weak base, the cation and anion both undergo hydrolysis. For example, when aluminum sulfide is placed in water, Al^{3+} reacts with OH^- forming $Al(OH)_3$, and S^{2-} reacts with H^+ forming H_2S. The reaction is symbolized by the following chemical equation.

$$Al_2S_3(s) + 6H_2O(l) \longrightarrow 2Al(OH)_3(s) + 3H_2S(g)$$

Since $Al(OH)_3$ is a precipitate and H_2S is a gas, both are removed from solution.

SECTION REVIEW

1. What is meant by an *acid ionization constant*?
2. How is an acid ionization equilibrium expression written?
3. What is meant by the term *buffered solution*?
4. Which of the following combinations of solutions would form buffers when they are mixed?
   a. 50 mL of 1.0 M HCl and 50 mL of 1.0 M NaCl
   b. 25 mL of 0.5 M HNO_2 and 50 mL of 1.0 M $NaNO_2$
   c. 25 mL of 1.0 M HNO_2 and 25 mL of 1.0 M NaCl
5. What is meant by the *ion product constant* for water? What is the value of this constant?
6. For each of the following reactions, identify each conjugate acid-base pair.
   a. $H_2CO_3 + H_2O \rightleftharpoons HCO_3^- + H_3O^+$
   b. $H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$
   c. $H_2S + NH_3 \rightleftharpoons HS^- + NH_4^+$
   d. $H_2PO_4^- + H_2O \rightleftharpoons H_3PO_4 + OH^-$
7. What is hydrolysis? Compare cation and anion hydrolysis.
8. Which of the following ions hydrolyze in aqueous solution?
   a. NO_3^-
   b. F^-
   c. NH_4^+
   d. K^+
   e. CH_3COO^-
   f. SO_4^{2-}
   g. CO_3^{2-}
   h. PO_4^{3-}
9. Identify the following solutions as acidic, basic, or neutral.
   a. 0.5 M KI
   b. 0.10 M $Ba(OH)_2$
   c. 0.25 M NH_4NO_3
   d. 0.05 M K_2CO_3
10. Identify the acid and base from which each of the following salts was formed.
   a. K_2CrO_4
   b. $Ca(CH_3COO)_2$
   c. CaF_2
   d. $(NH_4)_2SO_4$

Critical Thinking

11. **RELATING IDEAS** Describe how to make a buffer solution using a strong base and one other reagent.

Solubility Equilibrium

SECTION 4

OBJECTIVES

- Explain what is meant by *solubility product constants,* and calculate their values.
- Calculate solubilities using solubility product constants.
- Carry out calculations to predict whether precipitates will form when solutions are combined.

Ionic solids dissolve in water until they are in equilibrium with their ions. An equilibrium expression can be written from the balanced chemical equation of the solid's dissociation. Concentrations of the ions can be determined from the balanced chemical equation and solubility data. The ion concentrations can then be used to determine the value of the equilibrium constant. The numerical value for the equilibrium constant can be used to predict whether precipitation occurs when solutions of various concentrations are combined.

Solubility Product

A saturated solution contains the maximum amount of solute possible at a given temperature in equilibrium with an undissolved excess of the substance. A saturated solution is not necessarily a concentrated solution. The concentration may be high or low, depending on the solubility of the solute.

A general rule is often used to express solubilities qualitatively. By this rule, a substance is said to be *soluble* if the solubility is *greater than* 1 g per 100 g of water and slightly soluble if less than that. Even substances we have previously referred to as "insoluble" are slightly soluble. We will describe the degree of solubility with an equilibrium constant.

The equilibrium principles developed in this chapter apply to all saturated solutions of slightly soluble salts. Silver chloride is an example of a slightly soluble salt. Its solution reaches saturation when the Ag^+ and Cl^- concentrations are 1.3×10^{-5} M, or about 2×10^{-4} g of AgCl in 100 mL. When mixed, all Ag^+ and Cl^- ions in excess of this concentration eventually precipitate as AgCl.

Consider the equilibrium system in a saturated solution of silver chloride containing an excess of the solid AgCl. This system is represented by the following equilibrium equation and equilibrium-constant expression.

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

The equation represents a heterogeneous reaction, as described on page 599. Once again, we follow the convention of writing the equilibrium expression without including the solid species. Therefore, [AgCl] does not appear in the final expression. The resulting equilibrium expression gives the solubility product constant K_{sp}. *The* **solubility product constant** *of a substance is the product of the molar concentra-*

tions of its ions in a saturated solution, each raised to the power that is the coefficient of that ion in the balanced chemical equation.

$$K_{sp} = [\mathrm{Ag}^+][\mathrm{Cl}^-]$$

This equation is the solubility equilibrium expression for the reaction. It expresses the fact that the solubility product constant, K_{sp}, of AgCl is the product of the molar concentrations of its ions in a saturated solution.

Calcium fluoride is another slightly soluble salt. The equilibrium in a saturated $\mathrm{CaF_2}$ solution is described by the following equation.

$$\mathrm{CaF_2}(s) \rightleftharpoons \mathrm{Ca}^{2+}(aq) + 2\mathrm{F}^-(aq)$$

The solubility product constant has the following form.

$$K_{sp} = [\mathrm{Ca}^{2+}][\mathrm{F}^-]^2$$

Notice that K_{sp} is the product of the molar concentration of Ca^{2+} ions and the molar concentration of F^- ions squared, as required by the balanced chemical equilibrium expression.

The numerical value of K_{sp} can be determined from solubility data. These data indicate that a maximum of 1.9×10^{-4} g of AgCl can dissolve in 100. g of water at 25°C. One mole of AgCl has a mass of 143.32 g. The solubility of AgCl can therefore be expressed in moles per liter of water, which is very nearly equal to moles per liter of solution.

$$\frac{1.9 \times 10^{-4}\ \cancel{\mathrm{g\ AgCl}}}{100.\ \cancel{\mathrm{g\ H_2O}}} \times \frac{1\ \cancel{\mathrm{g\ H_2O}}}{1\ \cancel{\mathrm{mL\ H_2O}}} \times \frac{1000\ \cancel{\mathrm{mL}}}{1\ \mathrm{L}} \times \frac{1\ \mathrm{mol\ AgCl}}{143.32\ \cancel{\mathrm{g\ AgCl}}}$$
$$= 1.3 \times 10^{-5}\ \mathrm{mol/L}$$

Silver chloride dissociates in solution, contributing equal numbers of Ag^+ and Cl^- ions. The ion concentrations in the saturated solution are therefore 1.3×10^{-5} mol/L.

$$[\mathrm{Ag}^+] = 1.3 \times 10^{-5}$$
$$[\mathrm{Cl}^-] = 1.3 \times 10^{-5}$$

and

$$K_{sp} = [\mathrm{Ag}^+][\mathrm{Cl}^-]$$
$$K_{sp} = (1.3 \times 10^{-5})(1.3 \times 10^{-5})$$
$$K_{sp} = (1.3 \times 10^{-5})^2$$
$$K_{sp} = 1.7 \times 10^{-10}$$

This result is the solubility product constant of AgCl at 25°C.

The solubility of $\mathrm{CaF_2}$ is 8.6×10^{-3} g/100 g of water at 25°C. Expressed in moles per liter, as before, this concentration becomes 1.1×10^{-3} mol/L. $\mathrm{CaF_2}$ dissociates in solution to yield twice as many F^- ions as

Ca^{2+} ions. The ion concentrations in the saturated solution are 1.1×10^{-3} for the calcium ion and $2(1.1 \times 10^{-3})$, or 2.2×10^{-3}, for the fluoride ion. Note that at equilibrium at 25°C, $[Ca^{2+}]$ equals the solubility of 1.1×10^{-3} mol/L but $[F^-]$ equals twice the solubility, or 2.2×10^{-3} mol/L. The number of moles of positive and negative ions per mole of compound must always be accounted for when using K_{sp} and solubilities.

$$K_{sp} = [Ca^{2+}][F^-]^2$$

$$K_{sp} = (1.1 \times 10^{-3})(2.2 \times 10^{-3})^2$$

$$K_{sp} = 5.3 \times 10^{-9}$$

Thus, the solubility product constant of CaF_2 is 5.3×10^{-9} at 25°C.

It is difficult to measure very small concentrations of a solute with precision. For this reason, solubility data from different sources may report different values of K_{sp} for a substance. Thus, calculations of K_{sp} ordinarily should be limited to two significant figures. Representative values of K_{sp} at 25°C for some slightly soluble compounds are listed in **Table 3.** Assume that all data used in K_{sp} calculations have been taken at 25°C unless otherwise specified.

At this point, you should note the difference between the solubility of a given solid and its solubility product constant. Remember that the *solubility product constant* is an equilibrium constant representing the product of the molar concentrations of its ions in a saturated solution. It

TABLE 3 *Solubility Product Constants, K_{sp}, at 25°C*

Salt	Ion product	K_{sp}	Salt	Ion product	K_{sp}
$AgCH_3COO$	$[Ag^+][CH_3COO^-]$	1.9×10^{-3}	$CuCl$	$[Cu^+][Cl^-]$	1.2×10^{-6}
$AgBr$	$[Ag^+][Br^-]$	5.0×10^{-13}	CuS	$[Cu^{2+}][S^{2-}]$	6.3×10^{-36}
Ag_2CO_3	$[Ag^+]^2[CO_3^{2-}]$	8.1×10^{-12}	FeS	$[Fe^{2+}][S^{2-}]$	6.3×10^{-18}
$AgCl$	$[Ag^+][Cl^-]$	1.8×10^{-10}	$Fe(OH)_2$	$[Fe^{2+}][OH^-]^2$	8.0×10^{-16}
AgI	$[Ag^+][I^-]$	8.3×10^{-17}	$Fe(OH)_3$	$[Fe^{3+}][OH^-]^3$	4×10^{-38}
Ag_2S	$[Ag^+]^2[S^{2-}]$	6.3×10^{-50}	HgS	$[Hg^{2+}][S^{2-}]$	1.6×10^{-52}
$Al(OH)_3$	$[Al^{3+}][OH^-]^3$	1.3×10^{-33}	$MgCO_3$	$[Mg^{2+}][CO_3^{2-}]$	3.5×10^{-8}
$BaCO_3$	$[Ba^{2+}][CO_3^{2-}]$	5.1×10^{-9}	$Mg(OH)_2$	$[Mg^{2+}][OH^-]^2$	1.8×10^{-11}
$BaSO_4$	$[Ba^{2+}][SO_4^{2-}]$	1.1×10^{-10}	MnS	$[Mn^{2+}][S^{2-}]$	2.5×10^{-13}
CdS	$[Cd^{2+}][S^{2-}]$	8.0×10^{-27}	$PbCl_2$	$[Pb^{2+}][Cl^-]^2$	1.6×10^{-5}
$CaCO_3$	$[Ca^{2+}][CO_3^{2-}]$	2.8×10^{-9}	$PbCrO_4$	$[Pb^{2+}][CrO_4^{2-}]$	2.8×10^{-13}
CaF_2	$[Ca^{2+}][F^-]^2$	5.3×10^{-9}	$PbSO_4$	$[Pb^{2+}][SO_4^{2-}]$	1.6×10^{-8}
$Ca(OH)_2$	$[Ca^{2+}][OH^-]^2$	5.5×10^{-6}	PbS	$[Pb^{2+}][S^{2-}]$	8.0×10^{-28}
$CaSO_4$	$[Ca^{2+}][SO_4^{2-}]$	9.1×10^{-6}	SnS	$[Sn^{2+}][S^{2-}]$	1.0×10^{-25}
$CoCO_3$	$[Co^{2+}][CO_3^{2-}]$	1.4×10^{-13}	$SrSO_4$	$[Sr^{2+}][SO_4^{2-}]$	3.2×10^{-7}
CoS	$[Co^{2+}][S^{2-}]$	4.0×10^{-21}	ZnS	$[Zn^{2+}][S^{2-}]$	1.6×10^{-24}

has only one value for a given solid at a given temperature. The *solubility* of a solid is an equilibrium position that represents the amount of the solid required to form a saturated solution with a specific amount of solvent. It has an infinite number of possible values at a given temperature and is dependent on other conditions, such as the presence of a common ion.

SAMPLE PROBLEM B

Calculate the solubility product constant, K_{sp}, for copper(I) chloride, CuCl, given that the solubility of this compound at 25°C is 1.08×10^{-2} g/100. g H_2O.

SOLUTION

1 ANALYZE

Given: solubility of CuCl = 1.08×10^{-2} g CuCl/100. g H_2O

Unknown: K_{sp}

2 PLAN

Start by converting the solubility of CuCl in g/100. g H_2O to mol/L. You will need the molar mass of CuCl to get moles CuCl from grams CuCl. Then use the solubility of the $[Cu^+]$ and $[Cl^-]$ ions in the K_{sp} expression and solve for K_{sp}.

$$\frac{\text{g CuCl}}{100.\ \text{g H}_2\text{O}} \times \frac{1\ \text{g H}_2\text{O}}{1\ \text{mL H}_2\text{O}} \times \frac{1000\ \text{mL}}{1\ \text{L}} \times \frac{1\ \text{mol CuCl}}{\text{g CuCl}} = \text{solubility in mol/L}$$

$$\text{CuCl}(s) \rightleftharpoons \text{Cu}^+(aq) + \text{Cl}^-(aq)$$

$$K_{sp} = [\text{Cu}^+][\text{Cl}^-]$$

$$[\text{Cu}^+] = [\text{Cl}^-] = \text{solubility in mol/L}$$

3 COMPUTE

The molar mass of CuCl is 99.0 g/mol.

$$\text{solubility} = \frac{1.08 \times 10^{-2}\ \cancel{\text{g CuCl}}}{100.\ \cancel{\text{g H}_2\text{O}}} \times \frac{1\ \cancel{\text{g H}_2\text{O}}}{1\ \cancel{\text{mL}}} \times \frac{1000\ \cancel{\text{mL}}}{1\text{L}} \times \frac{1\ \text{mol CuCl}}{99.0\ \cancel{\text{g CuCl}}} =$$

$$1.09 \times 10^{-3}\ \text{mol/L CuCl}$$

$$[\text{Cu}^+] = [\text{Cl}^-] = 1.09 \times 10^{-3}\ \text{mol/L}$$

$$K_{sp} = (1.09 \times 10^{-3})(1.09 \times 10^{-3}) = 1.19 \times 10^{-6}$$

4 EVALUATE

The answer contains the proper number of significant figures and is close to the K_{sp} value given in **Table 3.**

PRACTICE

Answers in Appendix E

1. Calculate the solubility product constant, K_{sp}, of lead(II) chloride, $PbCl_2$, which has a solubility of 1.0 g/100. g H_2O at 20°C.
2. A 5.0 gram sample of Ag_2SO_4 will dissolve in 1.0 L of water. Calculate the solubility product constant for this salt.

extension

Go to **go.hrw.com** for more practice problems that ask you to calculate solubility product constants.

Keyword: HC6EQUX

Calculating Solubilities

Once known, the solubility product constant can be used to determine the solubility of a slightly soluble salt. Suppose you wish to know how many moles of barium carbonate, $BaCO_3$, can be dissolved in 1 L of water at 25°C. From **Table 3,** K_{sp} for $BaCO_3$ has the numerical value 5.1×10^{-9}. The equilibrium equation is written as follows.

$$BaCO_3(s) \rightleftarrows Ba^{2+}(aq) + CO_3^{2-}(aq)$$

Given the value for K_{sp}, we can write the solubility equilibrium expression as follows.

$$K_{sp} = [Ba^{2+}][CO_3^{2-}] = 5.1 \times 10^{-9}$$

Therefore, $BaCO_3$ dissolves until the product of the molar concentrations of Ba^{2+} ions and CO_3^{2-} ions equals 5.1×10^{-9}. The solubility equilibrium equation shows that Ba^{2+} ions and CO_3^{2-} ions enter the solution in equal numbers as the salt dissolves. Thus, they have the same concentration. Let $[Ba^{2+}] = x$. Then $[CO_3^{2-}] = x$ also.

$$[Ba^{2+}][CO_3^{2-}] = K_{sp} = 5.1 \times 10^{-9}$$

$$(x)(x) = x^2 = 5.1 \times 10^{-9}$$

$$x = \sqrt{5.1 \times 10^{-9}}$$

The molar solubility of $BaCO_3$ is 7.1×10^{-5} mol/L.

Thus, the solution concentration is 7.1×10^{-5} M for Ba^{2+} ions and 7.1×10^{-5} M for CO_3^{2-} ions.

SAMPLE PROBLEM C

Calculate the solubility of silver bromide, AgBr, in mol/L, using the K_{sp} value for this compound listed in Table 3.

SOLUTION

1 ANALYZE

Given: $K_{sp} = 5.0 \times 10^{-13}$

Unknown: solubility of AgBr

2 PLAN

$$AgBr \rightleftarrows Ag^+(aq) + Br^-(aq)$$

$$K_{sp} = [Ag^+][Br^-]$$

$[Ag^+] = [Br^-]$, so let $[Ag^+] = x$ and $[Br^-] = x$

3 COMPUTE

$$K_{sp} = [Ag^+][Br^-]$$

$$K_{sp} = x^2$$

$$x^2 = 5.0 \times 10^{-13}$$

$$x = \sqrt{5.0 \times 10^{-13}}$$

Solubility of AgBr $= \sqrt{5.0 \times 10^{-13}} = 7.1 \times 10^{-7}$ mol/L

4 EVALUATE The answer has the proper number of significant figures and is close to an estimated value of 7.0×10^{-7} calculated as $\sqrt{49 \times 10^{-14}}$.

PRACTICE *Answers in Appendix E*

1. Calculate the solubility of cadmium sulfide, CdS, in mol/L, given the K_{sp} value listed in **Table 3.**
2. Determine the concentration of strontium ions in a saturated solution of strontium sulfate, $SrSO_4$, if the K_{sp} for $SrSO_4$ is 3.2×10^{-7}.

extension

Go to **go.hrw.com** for more practice problems that ask you to calculate solubilities.

Keyword: HC6EQUX

Precipitation Calculations

In an earlier example, $BaCO_3$ served as the source of both Ba^{2+} and CO_3^{2-} ions. Because each mole of $BaCO_3$ yields one mole of Ba^{2+} ions and one mole of CO_3^{2-} ions, the concentrations of the two ions were equal. However, the equilibrium condition does not require that the two ion concentrations be equal. Equilibrium will still be established so that the ion product $[Ba^{2+}][CO_3^{2-}]$ does not exceed the value of K_{sp} for the system.

Similarly, if the ion product $[Ca^{2+}][F^-]^2$ is less than the value of K_{sp} at a particular temperature, the solution is unsaturated. If the ion product is greater than the value for K_{sp}, CaF_2 precipitates. This precipitation reduces the concentrations of Ca^{2+} and F^- ions until equilibrium is established.

Suppose that unequal quantities of $BaCl_2$ and Na_2CO_3 are dissolved in water and that the solutions are mixed. If the ion product $[Ba^{2+}][CO_3^{2-}]$ exceeds the K_{sp} of $BaCO_3$, a precipitate of $BaCO_3$ forms. After precipitation, the ion concentrations are such that $[Ba^{2+}][CO_3^{2-}]$ equals the K_{sp}.

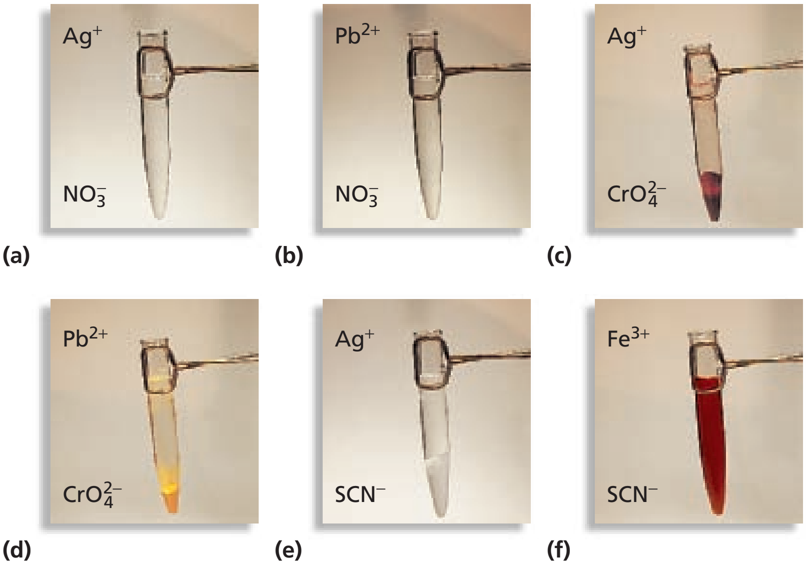


FIGURE 13 Nitrate salts of Ag^+ (a) and Pb^{2+} (b) are soluble. When chromate ions, CrO_4^{2-}, combine with Ag^+ (c) or Pb^{2+} (d), a slightly soluble salt forms. Thiocyanate ions, SCN^-, can form a slightly soluble salt with Ag^+ (e) or a soluble salt with Fe^{3+} (f).

Substances differ greatly in their tendencies to form precipitates when mixed in moderate concentrations. The photos in **Figure 13** show the behavior of some anions in the presence of certain cations. Note that some of the combinations have produced precipitates and some have not. The solubility product can be used to predict whether a precipitate forms when two solutions are mixed.

SAMPLE PROBLEM D

Will a precipitate form if 20.0 mL of 0.010 M $BaCl_2$ is mixed with 20.0 mL of 0.0050 M Na_2SO_4?

SOLUTION

1 ***ANALYZE***

Given: concentration of $BaCl_2 = 0.010$ M
volume of $BaCl_2 = 20.0$ mL
concentration of $Na_2SO_4 = 0.0050$ M
volume of $Na_2SO_4 = 20.0$ mL

Unknown: whether a precipitate forms

2 ***PLAN***

The two possible new pairings of ions are NaCl and $BaSO_4$. Of these, only $BaSO_4$ is a slightly soluble salt. It will precipitate if the ion product $[Ba^{2+}][SO_4^{2-}]$ in the mixed solution exceeds K_{sp} for $BaSO_4$. From the list of solubility products in **Table 3,** the K_{sp} is found to be 1.1×10^{-10}. The solubility equilibrium equation follows.

$$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$$

The solubility equilibrium expression is written as follows.

$$K_{sp} = [Ba^{2+}][SO_4^{2-}] = 1.1 \times 10^{-10}$$

First $[Ba^{2+}]$ and $[SO_4^{2-}]$ in the above solution must be found. Then the ion product is calculated and compared with the K_{sp}.

3 ***COMPUTE***

Calculate the mole quantities of Ba^{2+} and SO_4^{2-} ions.

$$0.020\ \cancel{L} \times \frac{0.010\text{ mol }Ba^{2+}}{1\ \cancel{L}} = 0.000\ 20\text{ mol }Ba^{2+}$$

$$0.020\ \cancel{L} \times \frac{0.0050\text{ mol }SO_4^{2-}}{1\ \cancel{L}} = 0.000\ 10\text{ mol }SO_4^{2-}$$

Calculate the total volume of solution containing Ba^{2+} and SO_4^{2-} ions.

$$0.020\text{ L} + 0.020\text{ L} = 0.040\text{ L}$$

Calculate the Ba^{2+} and SO_4^{2-} ion concentrations in the combined solution.

$$\frac{0.000\ 20\text{ mol }Ba^{2+}}{0.040\text{ L}} = 5.0 \times 10^{-3}\text{ mol/L }Ba^{2+}$$

$$\frac{0.000\ 10\text{ mol }SO_4^{2-}}{0.040\text{ L}} = 2.5 \times 10^{-3}\text{ mol/L }SO_4^{2-}$$

Calculate the ion product.

$$[Ba^{2+}][SO_4^{2-}] = (5.0 \times 10^{-3})(2.5 \times 10^{-3})$$
$$= 1.2 \times 10^{-5}$$

The ion product, 1.2×10^{-5}, is greater than the value of K_{sp}, 1.1×10^{-10}, so precipitation occurs.

4 ***EVALUATE*** The answer contains the appropriate number of significant figures and is close to an estimated value of 1×10^{-5}, calculated as $(5 \times 10^{-3})(2 \times 10^{-3})$; because $10^{-5} > 10^{-10}$, precipitation should occur.

PRACTICE

Answers in Appendix E

1. Does a precipitate form when 100. mL of 0.0025 M $AgNO_3$ and 150. mL of 0.0020 M NaBr solutions are mixed?
2. Does a precipitate form when 20. mL of 0.038 M $Pb(NO_3)_2$ and 30. mL of 0.018 M KCl solutions are mixed?

extension

Go to **go.hrw.com** for more practice problems that ask you to perform precipitation calculations.

Keyword: HC6EQUX

Limitations on the Use of K_{sp}

The solubility product principle can be very useful when applied to solutions of slightly soluble substances. It *cannot* be applied to solutions of soluble substances. This is because the positive and negative ions attract each other, and this attraction becomes appreciable when the ions are close together. Sometimes it is necessary to consider two equilibria simultaneously. For example, if either ion hydrolyzes, the salt will be more soluble than predicted when only the solubility product constant is used. The solubility product is also sensitive to changes in solution temperature to the extent that the solubility of the dissolved substance is affected by such changes. All of these factors limit the conditions under which the solubility product principle can be applied.

SECTION REVIEW

1. What is a solubility product constant? How are such constants determined?
2. How are solubility product constants used to calculate solubilities?
3. What is an ion product?
4. How are calculations to predict possible precipitation carried out?
5. What is the value of K_{sp} for Ag_2SO_4 if 5.40 g is soluble in 1.00 L of water?
6. Determine whether a precipitate will form if 20.0 mL of 1.00×10^{-7} M $AgNO_3$ is mixed with 20.0 mL of 2.00×10^{-9} M NaCl at 25°C.

Critical Thinking

7. **ANALYZING DATA** A solution is 0.20 M in each of the following: $Ca(NO_3)_2$, $Cr(NO_3)_3$, and $La(NO_3)_3$. Solid NaF is added to the solution until the $[F^-]$ of the solution is 1.0×10^{-4} M. Given the values of K_{sp} below, describe what will happen.
$CaF_2 = 3.9 \times 10^{-11}$; $CrF_3 = 6.6 \times 10^{-11}$; and
$LaF_3 = 4.0 \times 10^{-17}$

CHAPTER HIGHLIGHTS

The Nature of Chemical Equilibrium

Vocabulary
reversible reaction
chemical equilibrium
equilibrium constant
chemical equilibrium expression

- A reaction system in which the forward and reverse reactions occur simultaneously and at the same rate is said to be at *equilibrium.* Both reactions continue, but there is no net change in the composition of the system.
- At equilibrium, the ratio of the product of the molar concentrations of substances formed to the product of the molar concentrations of reactants, each raised to the appropriate power, has a definite numerical value, K, which is the equilibrium constant at a given temperature.

Shifting Equilibrium

Vocabulary
common-ion effect

- According to Le Châtelier's principle, when a stress (a change in concentration, pressure, or temperature) is applied to a system at equilibrium, the equilibrium is shifted in the direction that relieves the stress.
- The common-ion effect is recognized when a solution containing ions such as those of a reactant or a product in an equilibrium system is added to the system. Le Châtelier's principle explains the response of the system to the stress.

Equilibria of Acids, Bases, and Salts

Vocabulary
acid ionization constant
buffered solution
hydrolysis

- The equilibrium expression for the ionization constant of the weak acid HA follows.

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

- Salts formed from strong bases and weak acids produce aqueous solutions that are basic because of *anion hydrolysis.*
- Salts formed from strong acids and weak bases produce aqueous solutions that are acidic because of *cation hydrolysis.*
- Salts formed from strong acids and strong bases do not hydrolyze in water, and their solutions are neutral.
- Salts formed from weak acids and weak bases may produce neutral, acidic, or basic solutions, depending on the relative amounts of cation and anion hydrolysis.

Solubility Equilibrium

Vocabulary
solubility product constant

- Ions of salts that are slightly soluble form saturated aqueous solutions at low concentrations. The solubility equilibrium expression for such salts yields a constant—the solubility product constant, K_{sp}.

CHAPTER REVIEW

For more practice, go to the Problem Bank in Appendix D.

The Nature of Chemical Equilibrium

SECTION 1 REVIEW

1. Describe and explain how the concentrations of A, B, C, and D change from the time when A and B are first combined to the point at which equilibrium is established for the reaction $A + B \rightleftharpoons C + D$.

2. a. Write the general expression for an equilibrium constant based on the equation $nA + mB + \ldots \rightleftharpoons xC + yD + \ldots$

b. What information is provided by the value of K for a given equilibrium system at a specified temperature?

3. In general, which reaction is favored (forward or reverse) if the value of K at a specified temperature is

a. very small?

b. very large?

PRACTICE PROBLEMS

4. Determine the value of the equilibrium constant for each reaction given, assuming that the equilibrium concentrations are found to be those specified. (Concentrations are in mol/L.) (Hint: See Sample Problem A.)

a. $A + B \rightleftharpoons C$; [A] = 2.0; [B] = 3.0; [C] = 4.0

b. $D + 2E \rightleftharpoons F + 3G$; [D] = 1.5; [E] = 2.0; [F] = 1.8; [G] = 1.2

c. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$; $[N_2] = 0.45$; $[H_2] = 0.14$; $[NH_3] = 0.62$

5. An equilibrium mixture at a specific temperature is found to consist of 1.2×10^{-3} mol/L HCl, 3.8×10^{-4} mol/L O_2, 5.8×10^{-2} mol/L H_2O, and 5.8×10^{-2} mol/L Cl_2 according to the following:

$$4HCl(g) + O_2(g) \rightleftharpoons 2H_2O(g) + 2Cl_2(g).$$

Determine the value of the equilibrium constant for this system.

6. At 450°C, the value of the equilibrium constant for the following system is 6.59×10^{-3}. If $[NH_3] = 1.23 \times 10^{-4}$ M and $[H_2] = 2.75 \times 10^{-2}$ M at equilibrium, determine the concentration of N_2 at that point.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

7. The value of the equilibrium constant for the reaction below is 40.0 at a specified temperature. What would be the value of that constant for the reverse reaction under the same conditions?

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

Shifting Equilibrium

SECTION 2 REVIEW

8. Predict whether each of the following pressure changes would favor the forward or reverse reaction.

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

a. increased pressure

b. decreased pressure

9. In heterogeneous reaction systems, what types of substances do not appear in the equilibrium constant expression? Why?

10. Explain the effect of a catalyst on an equilibrium system.

11. Predict the effect of each of the following on the indicated equilibrium system in terms of the direction of equilibrium shift (forward, reverse, or neither).

$$H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g) + 184\text{ kJ}$$

a. addition of Cl_2

b. removal of HCl

c. increased pressure

d. decreased temperature

e. removal of H_2

f. decreased pressure

g. addition of a catalyst

h. increased temperature

i. decreased system volume

12. How would the changes in (a) through (i) of item 11 affect the new equilibrium concentration of HCl and the value of K at the new equilibrium?

13. Explain why changes in the concentrations of the reactants and products at equilibrium have no impact on the value of the equilibrium constant.

14. What relative pressure (high or low) would result in the production of the maximum level of CO_2 according to the following equation? Why?

$$2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g)$$

15. What relative conditions (reactant concentrations, pressure, and temperature) would favor a high equilibrium concentration of the underlined substance in each of the following equilibrium systems?

a. $2CO(g) + O_2(g) \rightleftharpoons \underline{2CO_2(g)} + 167 \text{ kJ}$

b. $Cu^{2+}(aq) + 4NH_3(aq) \rightleftharpoons \underline{Cu(NH_3)_4^{2+}(aq)} + 42 \text{ kJ}$

c. $2HI(g) + 12.6 \text{ kJ} \rightleftharpoons H_2(g) + \underline{I_2(g)}$

d. $4HCl(g) + O_2(g) \rightleftharpoons 2H_2O(g) + \underline{2Cl_2(g)} + 113 \text{ kJ}$

e. $PCl_5(g) + 88 \text{ kJ} \rightleftharpoons PCl_3(g) + \underline{Cl_2(g)}$

16. The reaction between hemoglobin, Hb, and oxygen, O_2, in red blood cells is responsible for transporting O_2 to body tissues. This process can be represented by the following equilibrium reaction:

$$Hb(aq) + O_2(g) \rightleftharpoons HbO_2(aq)$$

What will happen to the concentration of oxygenated hemoglobin, HbO_2, at high altitude, where the pressure of oxygen is 0.1 atm instead of 0.2 atm, as it is at sea level?

17. What two factors determine the extent to which reacting ions are removed from solution?

18. Identify the three conditions under which ionic reactions can run to completion, and write an equation for each.

Equilibria of Acids, Bases, and Salts

SECTION 3 REVIEW

19. a. Write the ion product constant expression for water.

b. What is the value of this constant at 25°C?

20. List and distinguish between the four general categories of salts, based on their hydrolysis properties, and give an example of each.

21. Explain why the pH of a solution containing both acetic acid and sodium acetate is higher than that of a solution containing the same concentration of acetic acid alone.

22. The ionization constant, K_a, for acetic acid is 1.8×10^{-5} at 25°C. Explain the significance of this value.

23. a. From the development of K_a described in Section 3, show how you would express an ionization constant, K_b, for the weak base NH_3.

b. In this case, $K_b = 1.8 \times 10^{-5}$. What is the significance of this numerical value to equilibrium?

Solubility Equilibrium

SECTION 4 REVIEW

24. Explain why a saturated solution is not necessarily a concentrated solution.

25. What rule of thumb is used to distinguish between soluble and slightly soluble substances?

26. What is the relative ion concentration of an ionic substance typically involved in solubility equilibrium systems?

27. What is the relationship between K_{sp} and the product of the ion concentrations in terms of determining whether a solution of those ions is saturated?

PRACTICE PROBLEMS

28. The ionic substance EJ dissociates to form E^{2+} and J^{2-} ions. The solubility of EJ is 8.45×10^{-6} mol/L. What is the value of the solubility product constant? (Hint: See Sample Problem B.)

29. Calculate the solubility product constant K_{sp} for each of the following, based on the solubility information provided:

a. $BaSO_4 = 2.4 \times 10^{-4}$ g/100. g H_2O at 20°C

b. $Ca(OH)_2 = 0.173$ g/100. g H_2O at 20°C

30. Calculate the molar solubility of a substance MN that ionizes to form M^{2+} and N^{2-} ions, given that $K_{sp} = 8.1 \times 10^{-6}$. (Hint: See Sample Problem C.)

31. Use the K_{sp} values given in **Table 3** to evaluate the solubility of each of the following in moles per liter.
   a. AgBr
   b. CoS

32. Complete each of the following relative to the reaction that occurs when 25.0 mL of 0.0500 M $Pb(NO_3)_2$ is combined with 25.0 mL of 0.0400 M Na_2SO_4 if equilibrium is reached at 25°C.
   a. Write the solubility equilibrium equation at 25°C.
   b. Write the solubility equilibrium expression for the net reaction.

33. The ionic substance T_3U_2 ionizes to form T^{2+} and U^{3-} ions. The solubility of T_3U_2 is 3.8×10^{-10} mol/L. What is the value of the solubility product constant?

34. A solution of AgI contains 2.7×10^{-10} mol/L Ag^+. What is the maximum I^- concentration that can exist in this solution?

35. Calculate whether a precipitate will form if 0.35 L of 0.0044 M $Ca(NO_3)_2$ and 0.17 L of 0.000 39 M NaOH are mixed at 25°C. (See **Table 3** for K_{sp} values.) (Hint: See Sample Problem D.)

36. Determine whether a precipitate will form if 1.70 g of solid $AgNO_3$ and 14.5 g of solid NaCl are dissolved in 200. mL of water to form a solution at 25°C.

37. If 2.50×10^{-2} g of solid $Fe(NO_3)_3$ is added to 100. mL of a 1.0×10^{-4} M NaOH solution, will a precipitate form?

MIXED REVIEW

38. Calcium carbonate is only slightly soluble in water.
   a. Write the equilibrium equation for calcium carbonate in solution.
   b. Write the solubility product constant expression, K_{sp}, for the equilibrium in a saturated solution of $CaCO_3$.

39. Calculate the concentration of Hg^{2+} ions in a saturated solution of HgS(*s*). How many Hg^{2+} ions are in 1000 L of the solution?

40. Calculate the equilibrium constant, *K*, for the following reaction at 900°C.

$$H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$$

The components were analyzed, and it was found that $[H_2] = 0.061$ mol/L, $[CO_2] = 0.16$ mol/L, $[H_2O] = 0.11$ mol/L, and $[CO] = 0.14$ mol/L.

41. A solution in equilibrium with solid barium phosphate is found to have a barium ion concentration of 5.0×10^{-4} M and a K_{sp} of 3.4×10^{-23}. Calculate the concentration of phosphate ion.

42. At 25°C, the value of *K* is 1.7×10^{-13} for the following reaction.

$$2N_2O(g) + O_2(g) \rightleftharpoons 4NO(g)$$

It is determined that $[N_2O] = 0.0035$ mol/L and $[O_2] = 0.0027$ mol/L. Using this information, what is the concentration of NO(*g*) at equilibrium?

43. Tooth enamel is composed of the mineral hydroxyapatite, $Ca_5(PO_4)_3OH$, which has a K_{sp} of 6.8×10^{-37}. The molar solubility of hydroxyapatite is 2.7×10^{-5} mol/L. When hydroxyapatite is reacted with fluoride, the OH^- is replaced with the F^- ion on the mineral, forming fluorapatite, $Ca_5(PO_4)_3F$. (The latter is harder and less susceptible to cavities.) The K_{sp} of fluorapatite is 1×10^{-60}. Calculate the molar solubility of fluorapatite in water. Given your calculations, can you support the fluoridation of drinking water?

44. Determine if a precipitate will form when 0.96 g Na_2CO_3 is combined with 0.20 g $BaBr_2$ in a 10. L solution ($K_{sp} = 2.8 \times 10^{-9}$).

45. For the formation of ammonia, the equilibrium constant is calculated to be 5.2×10^{-5} at 25°C. After analysis, it is determined that $[N_2] = 2.00$ M and $[H_2] = 0.80$ M. How many grams of ammonia are in the 10. L reaction vessel at equilibrium? Use the following equilibrium equation.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

CRITICAL THINKING

46. **Relating Ideas** Let *s* equal the solubility, in mol/L, of AB_2. In terms of *s*, what is the molar concentration of A? of B? What is the K_{sp} of AB_2?

47. **Predicting Outcomes** When gasoline burns in an automobile engine, nitric oxide is formed from oxygen and nitrogen. Nitric oxide is a major air pollutant. High temperatures such as those found in a combustion engine are needed for the following reaction:

$$N_2(g) + O_2(g) \rightleftarrows 2NO(g)$$

K for the reaction is 0.01 at 2000°C. If 4.0 mol of N_2, 0.1 mol of O_2, and 0.08 mol of NO are placed in a 1.0 L vessel at 2000°C, predict which reaction will be favored.

USING THE HANDBOOK

48. An equilibrium system helps maintain the pH of the blood. Review the material on the carbon dioxide–bicarbonate ion equilibrium system in Group 14 of the *Elements Handbook,* and answer the following.

a. Write the equation for the equilibrium system that responds to changes in H_3O^+ concentration.

b. Use Le Châtelier's principle to explain how hyperventilation affects this system.

c. How does this system maintain pH when acid is added?

49. The reactions used to confirm the presence of transition metal ions often involve the formation of precipitates. Review the analytical tests for the transition metals in the *Elements Handbook.* Use that information and **Table 3** to determine the minimum concentration of Zn^{2+} needed to produce a precipitate that confirms the presence of Zn. Assume enough sulfide ion reagent is added to the unknown solution in the test tube to produce a sulfide ion concentration of 1.4×10^{-20} M.

RESEARCH & WRITING

50. Find photos of several examples of stalagmites and stalactites in various caves. Investigate the equilibrium processes involved in the formation of stalagmites and stalactites.

51. Carry out library research on the use of catalysts in industrial processes. Explain what types of catalysts are used for specific processes, such as the Haber process.

ALTERNATIVE ASSESSMENT

52. Research nitrogen narcosis in the library. What causes nitrogen narcosis, and how does it relate to Le Châtelier's principle?

extension

Graphing Calculator **Chemical Equilibrium**

Go to **go.hrw.com** for a graphing calculator exercise that asks you to calculate the percent ionization for an acid equilibrium.

Keyword: HC6EQUX

Math Tutor DETERMINING EQUILIBRIUM CONSTANTS

For a given temperature, you can write a mathematical equation that describes the equilibrium of a reaction in terms of concentration. The equation defines an equilibrium constant, *K*, as a function of the concentrations of products and reactants at equilibrium.

Consider an equilibrium process in which reactants A and B form products C and D.

$$nA + mB \rightleftharpoons xC + yD$$

The terms *n*, *m*, *x*, and *y* are the coefficients of the balanced equation.

$$K = \frac{[C]^x[D]^y}{[A]^n[B]^m}$$

Problem-Solving *TIPS*

- Always use a balanced chemical equation to write an equilibrium-constant equation.
- To write an equation, place the product concentrations in the numerator and the reactant concentrations in the denominator. Raise each substance's concentration to the power equal to the substance's coefficient in the balanced chemical equation.
- The concentration of any solid or pure liquid that takes part in the reaction is left out because these concentrations never change.

SAMPLE

Write an equation for the equilibrium constant of the reaction in which nitrogen monoxide changes to dinitrogen monoxide and nitrogen dioxide.

To write an equation for an equilibrium constant, you must start with a balanced chemical equation for the equilibrium reaction. By writing the formulas of the compounds mentioned in the description, you get the unbalanced equilibrium equation $NO(g) \rightleftharpoons N_2O(g) + NO_2(g)$.

Balancing the equation requires a coefficient of 3 in front of NO, giving $3NO(g) \rightleftharpoons N_2O(g) + NO_2(g)$. Next, write an equilibrium equation. Remember, each concentration in the equilibrium equation is raised to a power equal to its coefficient in the balanced chemical equation. The product concentrations, $[N_2O]$ and $[NO_2]$, are placed in the numerator. The coefficient of each of the products is 1, so the exponent of each concentration is 1. There is only one reactant, so its concentration, [NO], is written in the denominator. Its coefficient is 3 in the balanced chemical equation, so the concentration of NO is raised to the third power. The exponents with a value of 1 do not have to be written. The resulting equation is

$$K = \frac{[N_2O]^1[NO_2]^1}{[NO]^3} = \frac{[N_2O][NO_2]}{[NO]^3}$$

PRACTICE PROBLEMS

1. Write equations for the equilibrium constant of each of the following hypothetical reactions:
   a. $A(aq) + 2B(aq) \rightleftharpoons AB_2(aq)$
   b. $2DE_2(g) \rightleftharpoons D_2(g) + 2E_2(g)$

2. Use the equilibrium concentrations below to calculate the equilibrium constant for the following decomposition reaction:

$$2BrF_5(g) \rightleftharpoons Br_2(g) + 5F_2(g)$$

$[BrF_5] = 0.000137$ mol/L, $[Br_2] = 0.00050$ mol/L, and $[F_2] = 0.0025$ mol/L

Standardized Test Prep

Answer the following items on a separate piece of paper.

MULTIPLE CHOICE

1. A chemical reaction is in equilibrium when
A. forward and reverse reactions have ceased.
B. the equilibrium constant equals 1.
C. forward and reverse reaction rates are equal.
D. No reactants remain.

2. Which change can cause the value of the equilibrium constant to change?
A. temperature
B. concentration of a reactant
C. concentration of a product
D. None of the above

3. Consider the following reaction:

$$2C(s) + O_2(g) \rightleftharpoons 2CO(g)$$

The equilibrium constant expression for this reaction is

A. $\frac{[CO]^2}{[O_2]}$. **C.** $\frac{2[CO]}{[O_2][2C]}$.
B. $\frac{[CO]^2}{[O_2][C]^2}$. **D.** $\frac{[CO]}{[O_2]^2}$.

4. The solubility product of cadmium carbonate, $CdCO_3$, is 1.0×10^{-12}. In a saturated solution of this salt, the concentration of $Cd^{2+}(aq)$ ions is
A. 5.0×10^{-13} mol/L. **C.** 1.0×10^{-6} mol/L.
B. 1.0×10^{-12} mol/L. **D.** 5.0×10^{-7} mol/L.

5. Consider the following equation for an equilibrium system:

$$2PbS(s) + 3O_2(g) + C(s) \rightleftharpoons 2Pb(s) + CO_2(g) + 2SO_2(g)$$

Which concentration(s) would be included in the denominator of the equilibrium constant expression?
A. $Pb(s)$, $CO_2(g)$, and $SO_2(g)$
B. $PbS(s)$, $O_2(g)$, and $C(s)$
C. $O_2(g)$, $Pb(s)$, $CO_2(g)$, and $SO_2(g)$
D. $O_2(g)$

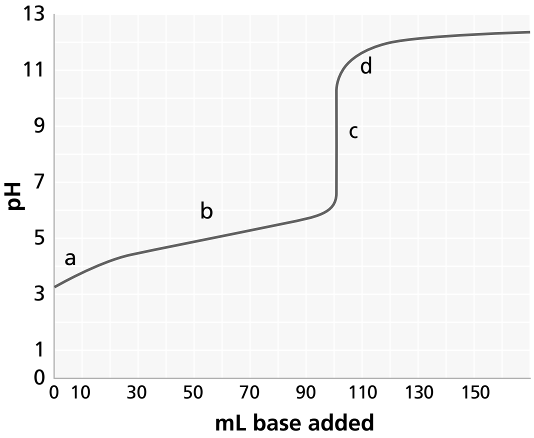
6. If an exothermic reaction has reached equilibrium, then increasing the temperature will
A. favor the forward reaction.
B. favor the reverse reaction.
C. favor both the forward and reverse reactions.
D. have no effect on the equilibrium.

7. Le Châtelier's principle states that
A. at equilibrium, the forward and reverse reaction rates are equal.
B. stresses include changes in concentrations, pressure, and temperature.
C. to relieve stress, solids and solvents are omitted from equilibrium constant expressions.
D. chemical equilibria respond to reduce applied stress.

SHORT ANSWER

8. Describe the conditions that would allow you to conclusively determine that a solution is saturated. You can use only visual observation and cannot add anything to the solution.

9. The graph below shows the neutralization curve for 100 mL of 0.100 M acid with 0.100 M base. Which letter represents the equivalence point? What type of acid and base produced this curve?



EXTENDED RESPONSE

10. Explain how the same buffer can resist a change in pH when either an acid or a base is added. Give an example.

Test TIP Keeping a positive attitude during any test will help you focus on the test and likely improve your score.

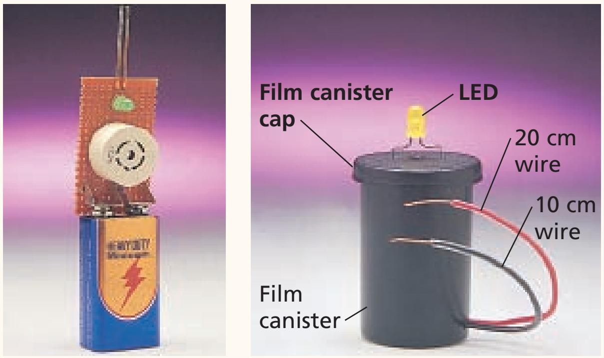
Measuring K_a for Acetic Acid

OBJECTIVES

- ***Compare*** **the conductivities of solutions of known and unknown hydronium ion concentrations.**
- ***Relate*** **conductivity to the concentration of ions in solution.**
- ***Explain*** **the validity of the procedure on the basis of the definitions of strong and weak acids.**
- ***Compute*** **the numerical value of K_a for acetic acid.**

MATERIALS

- **1.0 M acetic acid, CH_3COOH**
- **1.0 M hydrochloric acid, HCl**
- **24-well plate**
- **distilled or deionized water**
- **LED conductivity testers**
- **paper towels**
- **thin-stemmed pipets**



Teacher-made LED conductivity tester

BACKGROUND

The acid dissociation constant, K_a, is a measure of the strength of an acid. Strong acids are completely ionized in water. Because weak acids are only partly ionized, they have a characteristic K_a value. Properties that depend on the ability of a substance to ionize, such as conductivity and colligative properties, can be used to measure K_a. In this experiment, you will compare the conductivity of a 1.0 M solution of acetic acid, CH_3COOH, a weak acid, with the conductivities of solutions of varying concentrations of hydrochloric acid, HCl, a strong acid. From the comparisons you make, you will be able to estimate the concentration of hydronium ions in the acetic acid solution and calculate its K_a.

SAFETY

For review of safety, please see **Safety in the Chemistry Laboratory** in the front of your book.

PREPARATION

1. Create a table with two columns for recording your observations. Head the first column “HCl concentration.” A wide second column can be headed “Observations and comparisons.”

PROCEDURE

1. Obtain samples of 1.0 M HCl solution and 1.0 M CH_3COOH solution.
2. Place 20 drops of HCl in one well of a 24-well plate. Place 20 drops of CH_3COOH in an adjacent well. Label the location of each sample.
3. Test the HCl and CH_3COOH with the conductivity tester. Note the relative intensity of the

tester light for each solution. After testing, rinse the tester probes with distilled water. Remove any excess moisture with a paper towel.

4. Place 18 drops of distilled water in each of six wells in your 24-well plate. Add 2 drops of 1.0 M HCl to the first well to make a total of 20 drops of solution. Mix the contents of this well thoroughly by picking the contents up in a pipet and returning them to the well.

5. Repeat this procedure by taking 2 drops of the previous dilution and placing it in the next well containing 18 drops of water. Return any unused solution in the pipet to the well from which it was taken. Mix the new solution with a new pipet. (You now have 1.0 M HCl in the well from Procedure step 2, 0.10 M HCl in the first dilution well, and 0.010 M HCl in the second dilution.)

6. Continue diluting in this manner until you have six successive dilutions. The $[H_3O^+]$ should now range from 1.0 M to 1.0×10^{-6} M. Write the concentrations in the first column of your data table.

7. Using the conductivity tester, test the cells containing HCl in order from most concentrated to least concentrated. Note the brightness of the tester bulb, and compare it with the brightness of the bulb when it was placed in the acetic acid solution. (Retest the acetic acid well any time for comparison.) After each test, rinse the tester probes with distilled water, and use a paper towel to remove any excess moisture. When the brightness produced by one of the HCl solutions is about the same as that produced by the acetic acid, you can infer that the two solutions have about the same hydronium ion concentration and that the pH of the HCl solution is equal to the pH of the acetic acid. If the glow from the bulb is too faint to see, turn off the lights or build a light shield around your conductivity tester bulb.

8. Record the results of your observations by noting which HCl concentration causes the intensity of the bulb to most closely match that of the bulb when it is in acetic acid. (Hint: If the conductivity of no single HCl concentration matches that of the acetic acid, then estimate the value between the two concentrations that match the best.)

CLEANUP AND DISPOSAL

9. Clean your lab station. Clean all equipment, and return it to its proper place. Dispose of chemicals and solutions in containers designated by your teacher. Do not pour any chemicals down the drain or throw anything in the trash unless your teacher directs you to do so. Wash your hands thoroughly after all work is finished and before you leave the lab.

ANALYSIS AND INTERPRETATION

1. **Resolving Discrepancies:** How did the conductivity of the 1.0 M HCl solution compare with that of the 1.0 M CH_3COOH solution? Why do you think this was so?

2. **Organizing Data:** What is the H_3O^+ concentration of the HCl solution that most closely matched the conductivity of the acetic acid?

3. **Drawing Conclusions:** What was the H_3O^+ concentration of the 1.0 M CH_3COOH solution? Why?

CONCLUSIONS

1. **Applying Models:** The acid ionization expression for CH_3COOH is the following:

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$

Use your answer to Analysis and Interpretation item 3 to calculate K_a for the acetic acid solution.

2. **Applying Models:** Explain how it is possible for solutions of HCl and CH_3COOH to show the same conductivity but have different concentrations.

EXTENSIONS

1. **Evaluating Methods:** Compare the K_a value that you calculated with the value found on page 606 of your text. Calculate the percent error for this experiment.

2. **Predicting Outcomes:** Lactic acid ($HOOCCHOHCH_3$) has a K_a of 1.4×10^{-4}. Predict whether a solution of lactic acid would cause the conductivity tester to glow brighter or dimmer than a solution of acetic acid with the same concentration. How noticeable would the difference be?

CHAPTER 19

Oxidation-Reduction Reactions

Copper oxidizes in air to form the green patina you see on this building.

Oxidation and Reduction

SECTION 1

Objectives

- Assign oxidation numbers to reactant and product species.
- Define *oxidation* and *reduction.*
- Explain what an oxidation-reduction reaction (redox reaction) is.

Oxidation-reduction reactions involve a transfer of electrons. Oxidation involves the loss of electrons, whereas reduction involves the gain of electrons. Reduction and oxidation half-reactions must occur simultaneously. These processes can be identified through the understanding and use of oxidation numbers (oxidation states).

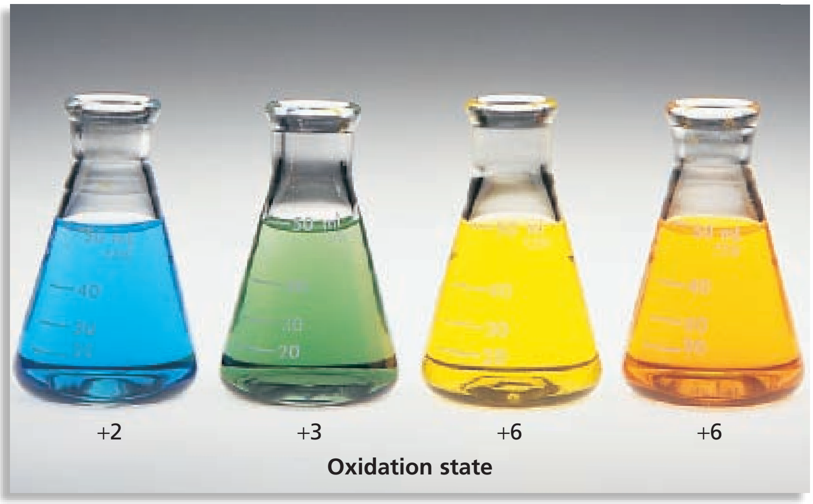
Oxidation States

Oxidation states were defined in Chapter 7. The oxidation number assigned to an element in a molecule is based on the distribution of electrons in that molecule. The rules by which oxidation numbers are assigned were given in Chapter 7. These rules are summarized in **Table 1.**

TABLE 1 ***Rules for Assigning Oxidation Numbers***

Rule	Example
1. The oxidation number of any pure element is 0.	The oxidation number of Na(*s*) is 0.
2. The oxidation number of a monatomic ion equals the charge on the ion.	The oxidation number of Cl^- is –1.
3. The more electronegative element in a binary compound is assigned the number equal to the charge it would have if it were an ion.	The oxidation number of O in NO is –2.
4. The oxidation number of fluorine in a compound is always –1.	The oxidation number of F in LiF is –1.
5. Oxygen has an oxidation number of –2 unless it is combined with F, in which it is +1 or +2, or it is in a peroxide, in which it is –1.	The oxidation number of O in NO_2 is –2.
6. Hydrogen's oxidation state in most of its compounds is +1 unless it is combined with a metal, in which case it is –1.	The oxidation number of H in LiH is –1.
7. In compounds, Group 1 and 2 elements and aluminum have oxidation numbers of +1, +2, and +3, respectively.	The oxidation number of Ca in $CaCO_3$ is +2.
8. The sum of the oxidation numbers of all atoms in a neutral compound is 0.	The oxidation number of C in $CaCO_3$ is +4.
9. The sum of the oxidation numbers of all atoms in a polyatomic ion equals the charge of the ion.	The oxidation number of P in $H_2PO_4^-$ is +5.

FIGURE 1 The color of solutions containing chromium compounds changes with the oxidation state of chromium.



Chromium provides a very visual example of oxidation numbers. Different oxidation states of chromium have dramatically different colors, as can be seen in **Figure 1.** Solutions with the same oxidation state show less dramatic differences. The chromium(II) chloride solution is blue, chromium(III) chloride solution is green, potassium chromate solution is yellow, and potassium dichromate solution is orange.

Oxidation

Processes in which the atoms or ions of an element experience an increase in oxidation state are **oxidation** *processes.* The combustion of metallic sodium in an atmosphere of chlorine gas is shown in **Figure 2.** The sodium ions and chloride ions produced during this strongly exothermic reaction form a cubic crystal lattice in which sodium cations are ionically bonded to chloride anions. The chemical equation for this reaction is written as follows.

$$2\text{Na}(s) + \text{Cl}_2(g) \longrightarrow 2\text{NaCl}(s)$$

FIGURE 2 Sodium and chlorine react violently to form NaCl. The synthesis of NaCl from its elements illustrates the oxidation-reduction process.

The formation of sodium ions illustrates an oxidation process because each sodium atom loses an electron to become a sodium ion. The oxidation state is represented by placing an oxidation number above the symbol of the atom and the ion.

$$\overset{0}{\text{Na}} \longrightarrow \overset{+1}{\text{Na}^+} + e^-$$

The oxidation state of sodium has changed from 0, its elemental state, to the +1 state of the ion (Rules 1 and 7, **Table 1**). *A species whose oxidation number increases is* **oxidized.** The sodium atom is *oxidized* to a sodium ion.

Reduction

Processes in which the oxidation state of an element decreases are **reduction** *processes.* Consider the behavior of chlorine in its reaction with sodium. Each chlorine atom accepts an electron and becomes a chloride ion. The oxidation state of chlorine decreases from 0 to –1 for the chloride ion (Rules 1 and 2, **Table 1**).

$$\overset{0}{\mathrm{Cl}}_2 + 2e^- \longrightarrow 2\overset{-1}{\mathrm{Cl}}{}^-$$

A species that undergoes a decrease in oxidation state is **reduced.** The chlorine atom is reduced to the chloride ion.

FIGURE 3 Copper is oxidized and nitrogen dioxide is produced when this penny is placed in a concentrated nitric acid solution.

Oxidation and Reduction as a Process

Electrons are released in oxidation and acquired in reduction. Therefore, for oxidation to occur during a chemical reaction, reduction must also occur. Furthermore, the number of electrons produced in oxidation must equal the number of electrons acquired in reduction. This makes sense when you recall that electrons are negatively charged and that for charge to be conserved, the number of electrons lost must equal the number of electrons gained. You learned in Chapter 8 that mass is conserved in any chemical reaction. Therefore, the masses of the elements that undergo oxidation and reduction and the electrons that are exchanged are conserved.

A transfer of electrons causes changes in the oxidation states of one or more elements. *Any chemical process in which elements undergo changes in oxidation number is an* **oxidation-reduction reaction.** This name is often shortened to **redox reaction.** An example of a redox reaction can be seen in **Figure 3,** in which copper is being oxidized and NO_3^- from nitric acid is being reduced. *The part of the reaction involving oxidation or reduction alone can be written as a* **half-reaction.** The overall equation for a redox reaction is the sum of two half-reactions. Because the number of electrons involved is the same for oxidation and reduction, they cancel each other out and do not appear in the overall chemical equation. Equations for the reaction between nitric acid and copper illustrate the relationship between half-reactions and the overall redox reaction.

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Topic: Redox Reactions
Code: HC61281

$$\overset{0}{\mathrm{Cu}} \longrightarrow \overset{+2}{\mathrm{Cu}}{}^{2+} + 2e^- \qquad \text{(oxidation half-reaction)}$$

$$2\overset{+5}{\mathrm{N}}\overset{-2}{\mathrm{O}}{}_3^- + 2e^- + 4\overset{+1}{\mathrm{H}}{}^+ \longrightarrow 2\overset{+4}{\mathrm{N}}\overset{-2}{\mathrm{O}}{}_2 + 2\overset{+1}{\mathrm{H}}{}_2\overset{-2}{\mathrm{O}} \qquad \text{(reduction half-reaction)}$$

$$\overset{0}{\mathrm{Cu}} + 2\overset{+5}{\mathrm{N}}\mathrm{O}_3^- + 4\mathrm{H}^+ \longrightarrow \overset{+2}{\mathrm{Cu}}{}^{2+} + 2\overset{+4}{\mathrm{N}}\mathrm{O}_2 + 2\mathrm{H}_2\mathrm{O} \qquad \text{(redox reaction)}$$

Notice that electrons lost in oxidation appear on the product side of the oxidation half-reaction. Electrons are gained in reduction and appear as reactants in the reduction half-reaction. When metallic copper reacts in nitric acid, one copper atom is oxidized to Cu^{2+} as two nitrogen atoms are reduced from a +5 oxidation state to a +4 oxidation state. Atoms are conserved. This is illustrated by the balanced chemical equation for the reaction between copper and nitric acid.

If none of the atoms in a reaction change oxidation state, the reaction is *not* a redox reaction. For example, sulfur dioxide gas, SO_2, dissolves in water to form an acidic solution containing a low concentration of sulfurous acid, H_2SO_3.

$$\overset{+4\;-2}{SO_2} + \overset{+1\;-2}{H_2O} \longrightarrow \overset{+1\;+4\;-2}{H_2SO_3}$$

The oxidation states of all elemental species remain unchanged in this composition reaction. Therefore, it is *not* a redox reaction.

When a solution of sodium chloride is added to a solution of silver nitrate, an ion-exchange reaction occurs and white silver chloride precipitates.

$$\overset{+1}{Na^+} + \overset{-1}{Cl^-} + \overset{+1}{Ag^+} + \overset{+5\;-2}{NO_3^-} \longrightarrow \overset{+1}{Na^+} + \overset{+5\;-2}{NO_3^-} + \overset{+1\;-1}{AgCl}$$

The oxidation state of each monatomic ion remains unchanged. Again, this reaction is not an oxidation-reduction reaction.

Redox Reactions and Covalent Bonds

Both the synthesis of NaCl from its elements and the reaction between copper and nitric acid involve ionic bonding. Substances with covalent bonds also undergo redox reactions. An oxidation number, unlike an ionic charge, has no physical meaning. That is, the oxidation number assigned to a particular atom is based on its electronegativity relative to the other atoms to which it is bonded in a given molecule; it is not based on any real charge on the atom. For example, an ionic charge of 1– results from the complete gain of one electron by an atom or other neutral species, whereas an oxidation state of –1 means an increased attraction for a bonding electron. A change in oxidation number does not require a change in actual charge.

When hydrogen burns in chlorine, a covalent bond forms from the sharing of two electrons. The two bonding electrons in the hydrogen chloride molecule are not shared equally. Rather, the pair of electrons is more strongly attracted to the chlorine atom because of its higher electronegativity.

$$\overset{0}{H_2} + \overset{0}{Cl_2} \longrightarrow \overset{+1\;-1}{2HCl}$$

As specified by Rule 3 in **Table 1,** chlorine in HCl is assigned an oxidation number of –1. Thus, the oxidation number for the chlorine atoms changes from 0, its oxidation number in the elemental state, to –1; chlorine atoms are reduced. As specified by Rule 1, the oxidation number of each hydrogen atom in the hydrogen molecule is 0. As specified by Rule 6, the oxidation state of the hydrogen atom in the HCl molecule is +1; the

Chemistry in Action

Photochromic Lenses

Photochromic eyeglasses darken when exposed to ultraviolet light and become transparent again in the absence of ultraviolet light. This process is the result of oxidation-reduction reactions. Silver chloride and copper(I) chloride are embedded in the lenses. The chloride ions absorb photons, and the silver chloride dissociates and forms chlorine atoms and silver atoms. The elemental silver darkens the lenses. Note that the chlorine ions are oxidized and the silver atoms are reduced. Then, the copper(I) ions reduce the chlorine atoms and form copper(II) ions. In the reverse process, the copper(II) ions oxidize the silver atoms back to the transparent silver ions.

hydrogen atom is oxidized. Neither atom has totally lost or totally gained any electrons. Hydrogen has donated a share of its bonding electron to the chlorine but has not completely transferred that electron. The assignment of oxidation numbers allows an approximation of the electron distribution of a molecule. An element can have different oxidation numbers in different compounds. This difference in oxidation numbers can reveal the difference in electron distribution of the compounds.

Reactants and products in redox reactions are not limited to monatomic ions and uncombined elements. Elements in molecular compounds or polyatomic ions can also be oxidized and reduced if they have more than one nonzero oxidation state. An example of this is provided in the reaction between the copper penny and nitric acid in which the nitrate ion, NO_3^-, is converted to nitrogen dioxide, NO_2. Nitrogen is reduced in this reaction. Usually, we refer to the oxidation or reduction of the entire molecule or ion. Instead of saying that the nitrogen atom is reduced, we say the nitrate ion is reduced to nitrogen dioxide.

$$\cdots + \overset{+5}{NO_3^-} \longrightarrow \overset{+4}{NO_2} + \cdots$$

SECTION REVIEW

1. How are oxidation numbers assigned?

2. Label each of the following half-reactions as either an oxidation or a reduction half-reaction:

   a. $\overset{0}{Br_2} + 2e^- \longrightarrow 2\overset{-1}{Br^-}$

   b. $\overset{0}{Na} \longrightarrow \overset{+1}{Na^+} + e^-$

   c. $2\overset{-1}{Cl^-} \longrightarrow \overset{0}{Cl_2} + 2e^-$

   d. $\overset{0}{Cl_2} + 2e^- \longrightarrow 2\overset{-1}{Cl^-}$

   e. $\overset{+1}{Na^+} + e^- \longrightarrow \overset{0}{Na}$

   f. $\overset{0}{Fe} \longrightarrow \overset{+2}{Fe^{2+}} + 2e^-$

   g. $\overset{+2}{Cu^{2+}} + 2e^- \longrightarrow \overset{0}{Cu}$

   h. $\overset{+3}{Fe^{3+}} + e^- \longrightarrow \overset{+2}{Fe^{2+}}$

3. Which of the following equations represent redox reactions?

   a. $2KNO_3(s) \longrightarrow 2KNO_2(s) + O_2(g)$

   b. $H_2(g) + CuO(s) \longrightarrow Cu(s) + H_2O(l)$

   c. $NaOH(aq) + HCl(aq) \longrightarrow NaCl(aq) + H_2O(l)$

   d. $H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$

   e. $SO_3(g) + H_2O(l) \longrightarrow H_2SO_4(aq)$

4. For each redox equation identified in the previous question, determine which element is oxidized and which is reduced.

Critical Thinking

5. **ANALYZING INFORMATION** Use the following equations for the redox reaction between Al^{3+} and Na to answer the questions below.

$$3\overset{0}{Na} \longrightarrow 3\overset{+1}{Na^+} + 3e^- \qquad \text{(oxidation)}$$

$$\overset{+3}{Al^{3+}} + 3e^- \longrightarrow \overset{0}{Al} \qquad \text{(reduction)}$$

$$3\overset{0}{Na} + \overset{+3}{Al^{3+}} \longrightarrow 3\overset{+1}{Na^+} + \overset{0}{Al} \qquad \text{(redox reaction)}$$

   a. Explain how this reaction illustrates that charge is conserved in a redox reaction.

   b. Explain how this reaction illustrates that mass is conserved in a redox reaction.

   c. Explain why electrons do not appear as reactants or products in the combined equation.

Chemistry in Action

Skunk-Spray Remedy

Have you ever given your pet a tomato juice bath to get rid of the smell of skunk spray on its coat? Chemistry has a much better way of conquering skunk spray.

Paul Krebaum, the inventor of a new "deskunking" formula, says that while working as a materials engineer, he constantly had to deal with the less-than-pleasant smell of the hydrogen sulfide gas that was released from one of his experiments. Venting off the gas only partially solved the problem. A better solution would be to eliminate the smell entirely.

Mr. Krebaum rifled through his old chemistry books and found that hydrogen peroxide could oxidize these sulfur-containing compounds to much less smelly components. He immediately whipped up a hydrogen peroxide mixture, and it worked like a charm.

The equation below shows that hydrogen sulfide reacts with H_2O_2 to form sulfate compounds that do not have a bad odor.

$$2NaOH + 4H_2O_2 + H_2S \longrightarrow Na_2SO_4 + 6H_2O$$

"The receptors that are in your nose are sensitive to sulfur in its low oxidation state," says Mr. Krebaum. "However, they are not sensitive to sulfur in its high oxidation state."

Some time later, a friend of Mr. Krebaum's complained to him that a skunk had sprayed his pet.

▲*Skunk spray gets its odor from chemicals called* mercaptans.

Because the odor in a skunk's spray also comes from compounds containing sulfur in a low oxidation state, Mr. Krebaum thought his solution might also work on this age-old problem. He mixed up a milder version to try out on the pet: 1 qt of a 3% hydrogen peroxide solution, 1/4 cup of baking soda, and 1 tsp of liquid soap. His friend tried it out, and the result was one wet and unhappy—but much less smelly—pet.

Mr. Krebaum says that the hydrogen peroxide in the remedy actually oxidizes the compounds, while the baking soda reduces the acidity of the mixture and the soap helps to wash out the greasy skunk spray. This reaction can be seen in the following equation. The symbol *R* represents all the other elements in the sulfur-containing compound that is in skunk spray.

$$RSH + 3H_2O_2 + NaHCO_3 \longrightarrow RSO_3Na + 4H_2O + CO_2$$

The pet should be thoroughly washed with the mixture, and care should be taken to avoid the eyes. If the mixture is left on for a few minutes—long enough for the reaction to occur—and then rinsed away with tap water, the smell will disappear.

The formula does not bleach or cause any other negative side effects. Mr. Krebaum does have one warning: Mix the formula just before using it, because the mixture breaks down quickly. The reaction releases oxygen, so the formula should not be kept in a sealed container. Pressure will build up, and the lid could eventually blow off. For this reason, bottles of "Krebaum's Skunkinator" will not be appearing on drugstore shelves any time soon.

Questions

1. How did Paul Krebaum's research into the properties of H_2S result in a benefit to dog owners?
2. What are some possible packaging designs that Paul Krebaum could have used if he had wanted to sell his formula?

SECTION 2

Balancing Redox Equations

OBJECTIVES

- Explain what must be conserved in redox equations.
- Balance redox equations by using the half-reaction method.

Equations for simple redox reactions can be balanced by inspection, which you learned to do in Chapter 8. Most redox equations, however, require more systematic methods. The equation-balancing process requires the use of oxidation numbers. In a balanced equation, both charge and mass are conserved. Although oxidation and reduction half-reactions occur together, their reaction equations are balanced separately and then combined to give the balanced redox-reaction equation.

Half-Reaction Method

The *half-reaction method,* or ion-electron method, for balancing redox equations consists of seven steps. Oxidation numbers are assigned to all atoms and polyatomic ions to determine which species are part of the redox process. The oxidation and reduction equations are balanced separately for mass and charge. They are then added together to produce a complete balanced equation. These seven steps are applied to balance the reaction of hydrogen sulfide and nitric acid. Sulfuric acid, nitrogen dioxide, and water are the products of the reaction.

extension

CROSS-DISCIPLINARY

Go to **go.hrw.com** for a full-length article on redox reactions in photosynthesis.

Keyword: HC6OXRX

1. ***Write the formula equation if it is not given in the problem. Then write the ionic equation.***

   Formula equation: $H_2S + HNO_3 \longrightarrow H_2SO_4 + NO_2 + H_2O$

   Ionic equation: $H_2S + H^+ + NO_3^- \longrightarrow 2H^+ + SO_4^{2-} + NO_2 + H_2O$

2. ***Assign oxidation numbers. Delete substances containing only elements that do not change oxidation state.***

$$\overset{+1\ -2}{H_2S} + \overset{+1}{H^+} + \overset{+5\ -2}{NO_3^-} \longrightarrow \overset{+1}{2H^+} + \overset{+6\ -2}{SO_4^{2-}} + \overset{+4\ -2}{NO_2} + \overset{+1\ -2}{H_2O}$$

The sulfur changes oxidation state from −2 to +6. The nitrogen changes oxidation state from +5 to +4. The other substances are deleted.

$$\overset{+1\ -2}{H_2S} + \overset{+5\ -2}{NO_3^-} \longrightarrow \overset{+6\ -2}{SO_4^{2-}} + \overset{+4\ -2}{NO_2}$$

The remaining species are used in step 3.

3. ***Write the half-reaction for oxidation.*** In this example, the sulfur is being oxidized.

$$H_2\overset{-2}{S} \longrightarrow \overset{+6}{S}O_4^{2-}$$

- ***Balance the atoms.*** To balance the oxygen in this half-reaction, H_2O must be added to the left side. This gives 10 extra hydrogen atoms on that side of the equation. Therefore, 10 hydrogen ions are added to the right side. In basic solution, OH^- ions and water may be used to balance atoms.

$$H_2\overset{-2}{S} + 4H_2O \longrightarrow \overset{+6}{S}O_4^{2-} + 10H^+$$

- ***Balance the charge.*** Electrons are added to the side having the greater positive net charge. The left side of the equation has no net charge; the right side has a net charge of 8+. For the charges to balance, each side must have the same net charge. Therefore, 8 electrons are added to the product side so that it has no charge and balances with the reactant side of the equation. Notice that the oxidation of sulfur from a state of –2 to +6 indicates a loss of 8 electrons.

$$H_2\overset{-2}{S} + 4H_2O \longrightarrow \overset{+6}{S}O_4^{2-} + 10H^+ + 8e^-$$

The oxidation half-reaction is now balanced.

4. ***Write the half-reaction for reduction.*** In this example, nitrogen is being reduced from a +5 state to a +4 state.

$$\overset{+5}{N}O_3^- \longrightarrow \overset{+4}{N}O_2$$

- ***Balance the atoms.*** H_2O must be added to the product side of the reaction to balance the oxygen atoms. Therefore, two hydrogen ions must be added to the reactant side to balance the hydrogen atoms.

$$\overset{+5}{N}O_3^- + 2H^+ \longrightarrow \overset{+4}{N}O_2 + H_2O$$

- ***Balance the charge.*** Electrons are added to the side having the greater positive net charge. The left side of the equation has a net charge of 1+. Therefore, 1 electron must be added to this side to balance the charge.

$$\overset{+5}{N}O_3^- + 2H^+ + e^- \longrightarrow \overset{+4}{N}O_2 + H_2O$$

The reduction half-reaction is now balanced.

5. ***Conserve charge by adjusting the coefficients in front of the electrons so that the number lost in oxidation equals the number gained in reduction.*** Write the ratio of the number of electrons lost to the number of electrons gained.

$$\frac{e^- \text{ lost in oxidation}}{e^- \text{ gained in reduction}} = \frac{8}{1}$$

This ratio is already in its lowest terms. If it were not, it would need to be reduced. Multiply the oxidation half-reaction by 1 (it remains unchanged) and the reduction half-reaction by 8. The number of electrons lost now equals the number of electrons gained.

$$1\left(\overset{-2}{H_2S} + 4H_2O \longrightarrow \overset{+6}{SO_4^{2-}} + 10H^+ + 8e^-\right)$$

$$8\left(\overset{+5}{NO_3^-} + 2H^+ + e^- \longrightarrow \overset{+4}{NO_2} + H_2O\right)$$

6. ***Combine the half-reactions, and cancel out anything common to both sides of the equation.***

$$\begin{array}{c} \overset{-2}{H_2S} + 4H_2O \longrightarrow \overset{+6}{SO_4^{2-}} + 10H^+ + 8e^- \\ \overset{+5}{8NO_3^-} + 16H^+ + 8e^- \longrightarrow \overset{+4}{8NO_2} + 8H_2O \\ \hline \end{array}$$

$$\overset{+5}{8NO_3^-} + \overset{6}{\cancel{16}}H^+ + \cancel{8e^-} + \overset{-2}{H_2S} + \cancel{4H_2O} \longrightarrow$$

$$\overset{+4}{8NO_2} + \overset{4}{\cancel{8}}H_2O + \overset{+6}{SO_4^{2-}} + \cancel{10H^+} + \cancel{8e^-}$$

Each side of the above equation has $10H^+$, $8e^-$, and $4H_2O$. These cancel each other out and do not appear in the balanced equation.

$$\overset{+5}{8NO_3^-} + \overset{-2}{H_2S} + 6H^+ \longrightarrow \overset{+4}{8NO_2} + 4H_2O + \overset{+6}{SO_4^{2-}}$$

7. ***Combine ions to form the compounds shown in the original formula equation. Check to ensure that all other ions balance.*** The NO_3^- ion appeared as nitric acid in the original equation. There are only 6 hydrogen ions to pair with the 8 nitrate ions. Therefore, 2 hydrogen ions must be added to complete this formula. If 2 hydrogen ions are added to the left side of the equation, 2 hydrogen ions must also be added to the right side of the equation.

$$8HNO_3 + H_2S \longrightarrow 8NO_2 + 4H_2O + SO_4^{2-} + 2H^+$$

The sulfate ion appeared as sulfuric acid in the original equation. The hydrogen ions added to the right side are used to complete the formula for sulfuric acid.

$$8HNO_3 + H_2S \longrightarrow 8NO_2 + 4H_2O + H_2SO_4$$

A final check must be made to ensure that all elements are correctly balanced.

FIGURE 4 As a $KMnO_4$ solution is titrated into an acidic solution of $FeSO_4$, deep purple MnO_4^- ions are reduced to colorless Mn^{2+} ions. When all Fe^{2+} ions are oxidized, MnO_4^- ions are no longer reduced to colorless Mn^{2+} ions. Thus, the first faint appearance of the MnO_4^- color indicates the end point of the titration.

SAMPLE PROBLEM A

For more help, go to the Math Tutor at the end of this chapter.

Write a balanced equation for the reaction shown in Figure 4. A deep purple solution of potassium permanganate is titrated with a colorless solution of iron(II) sulfate and sulfuric acid. The products are iron(III) sulfate, manganese(II) sulfate, potassium sulfate, and water—all of which are colorless.

SOLUTION

1. *Write the formula equation if it is not given in the problem. Then write the ionic equation.*

$$KMnO_4 + FeSO_4 + H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + MnSO_4 + K_2SO_4 + H_2O$$

$$K^+ + MnO_4^- + Fe^{2+} + SO_4^{2-} + 2H^+ + SO_4^{2-} \longrightarrow 2Fe^{3+} + 3SO_4^{2-} + Mn^{2+} + SO_4^{2-} + 2K^+ + SO_4^{2-} + H_2O$$

2. *Assign oxidation numbers to each element and ion. Delete substances containing an element that does not change oxidation state.*

$$\overset{+1}{K}{}^+ + \overset{+7}{Mn}\overset{-2}{O}{}_4^- + \overset{+2}{Fe}{}^{2+} + \overset{+6}{S}\overset{-2}{O}{}_4^{2-} + 2\overset{+1}{H}{}^+ + \overset{+6}{S}\overset{-2}{O}{}_4^{2-} \longrightarrow 2\overset{+3}{Fe}{}^{3+} + 3\overset{+6}{S}\overset{-2}{O}{}_4^{2-} + \overset{+2}{Mn}{}^{2+} + \overset{+6}{S}\overset{-2}{O}{}_4^{2-} + 2\overset{+1}{K}{}^+ + \overset{+6}{S}\overset{-2}{O}{}_4^{2-} + \overset{+1}{H}{}_2\overset{-2}{O}$$

Only ions or molecules whose oxidation numbers change are retained.

$$\overset{+7}{Mn}\overset{-2}{O}{}_4^- + \overset{+2}{Fe}{}^{2+} \longrightarrow \overset{+3}{Fe}{}^{3+} + \overset{+2}{Mn}{}^{2+}$$

3. *Write the half-reaction for oxidation.* The iron shows the increase in oxidation number. Therefore, it is oxidized.

$$\overset{+2}{Fe}{}^{2+} \longrightarrow \overset{+3}{Fe}{}^{3+}$$

- *Balance the mass.* The mass is already balanced.

- *Balance the charge.*

$$\overset{+2}{Fe}{}^{2+} \longrightarrow \overset{+3}{Fe}{}^{3+} + e^-$$

4. *Write the half-reaction for reduction.* Manganese shows a change in oxidation number from +7 to +2. It is reduced.

$$\overset{+7}{Mn}O_4^- \longrightarrow \overset{+2}{Mn}{}^{2+}$$

- *Balance the mass.* Water and hydrogen ions must be added to balance the oxygen atoms in the permanganate ion.

$$\overset{+7}{Mn}O_4^- + 8H^+ \longrightarrow \overset{+2}{Mn}{}^{2+} + 4H_2O$$

- *Balance the charge.*

$$\overset{+7}{Mn}O_4^- + 8H^+ + 5e^- \longrightarrow \overset{+2}{Mn}{}^{2+} + 4H_2O$$

5. *Adjust the coefficients to conserve charge.*

$$\frac{e^- \text{ lost in oxidation}}{e^- \text{ gained in reduction}} = \frac{1}{5}$$

$$5(Fe^{2+} \longrightarrow Fe^{3+} + e^-)$$

$$1(MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O)$$

6. *Combine the half-reactions and cancel.*

$$\begin{array}{r}
5Fe^{2+} \longrightarrow 5Fe^{3+} + 5e^- \\
MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O \\
\hline
MnO_4^- + 5Fe^{2+} + 8H^+ + \cancel{5e^-} \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O + \cancel{5e^-}
\end{array}$$

7. *Combine ions to form compounds from the original equation.* The iron(III) product appears in the original equation as $Fe_2(SO_4)_3$. Every iron(III) sulfate molecule requires two iron ions. Therefore, the entire equation must be multiplied by 2 to provide an even number of iron ions.

$$2(5Fe^{2+} + MnO_4^- + 8H^+ \longrightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O)$$
$$10Fe^{2+} + 2MnO_4^- + 16H^+ \longrightarrow 10Fe^{3+} + 2Mn^{2+} + 8H_2O$$

The iron(II), iron(III), manganese(II), and 2 hydrogen ions in the original equation are paired with sulfate ions. Iron(II) sulfate requires 10 sulfate ions, and sulfuric acid requires 8 sulfate ions. To balance the equation, 18 sulfate ions must be added to each side. On the product side, 15 of these ions form iron(III) sulfate, and 2 of them form manganese(II) sulfate. That leaves 1 sulfate ion unaccounted for. The permanganate ion requires the addition of 2 potassium ions to each side. These 2 potassium ions form potassium sulfate on the product side of the reaction.

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 \longrightarrow 5Fe_2(SO_4)_3 + 2MnSO_4 + K_2SO_4 + 8H_2O$$

Final inspection shows that atoms and charges are balanced.

PRACTICE

Answers in Appendix E

1. Copper reacts with hot, concentrated sulfuric acid to form copper(II) sulfate, sulfur dioxide, and water. Write and balance the equation for this reaction.
2. Write and balance the equation for the reaction between nitric acid and potassium iodide. The products are potassium nitrate, iodine, nitrogen monoxide, and water.

extension

Go to **go.hrw.com** for more practice problems that ask you to balance redox equations.

Keyword: HC6OXRX

SECTION REVIEW

1. What two quantities are conserved in redox equations?
2. Why do we add H^+ and H_2O to some half-reactions and OH^- and H_2O to others?
3. Balance the following redox reaction:

$$Na_2SnO_2 + Bi(OH)_3 \longrightarrow Bi + Na_2SnO_3 + H_2O$$

Critical Thinking

4. **RELATING IDEAS** When heated, elemental phosphorus, P_4, produces phosphine, PH_3, and phosphoric acid, H_3PO_4. How many grams of phosphine are produced if 56 g P_4 have reacted?

SECTION 3

Oxidizing and Reducing Agents

OBJECTIVES

- Relate chemical activity to oxidizing and reducing strength.
- Explain the concept of disproportionation.

A **reducing agent** *is a substance that has the potential to cause another substance to be reduced*. Reducing agents lose electrons; they attain a more positive oxidation state during an oxidation-reduction reaction. Therefore, the reducing agent is the oxidized substance.

An **oxidizing agent** *is a substance that has the potential to cause another substance to be oxidized.* Oxidizing agents gain electrons and attain a more negative oxidation state during an oxidation-reduction reaction. The oxidizing agent is the reduced substance. **Table 2** helps clarify the terms describing the oxidation-reduction process.

Strengths of Oxidizing and Reducing Agents

Different substances can be compared and rated by their relative potential as reducing and oxidizing agents. For example, the order of the elements in the activity series (see **Table 3** on page 286) is related to each element's tendency to lose electrons. Elements in this series lose electrons to the positively charged ions of any element below them in the series. The more active an element is, the greater its tendency to lose electrons and the better a reducing agent it is. The greater the distance is between two elements in the list, the more likely it is that a redox reaction will take place between them.

These elements and some other familiar substances are arranged in **Table 3** according to their activity as oxidizing and reducing agents. The fluorine atom is the most highly electronegative atom. It is also the most

TABLE 2 Oxidation-Reduction Terminology

Term	Change in oxidation number	Change in electron population
Oxidation	in a positive direction	loss of electrons
Reduction	in a negative direction	gain of electrons
Oxidizing agent	in a negative direction	gains electrons
Reducing agent	in a positive direction	loses electrons

active oxidizing agent. Because of its strong attraction for its own electrons, the fluoride ion is the weakest reducing agent. The negative ion of a strong oxidizing agent is a weak reducing agent.

The positive ion of a strong reducing agent is a weak oxidizing agent. As shown in **Table 3,** Li atoms are strong reducing agents because Li is a very active metal. When Li atoms oxidize, they produce Li^+ ions, which are unlikely to reacquire electrons, so Li^+ ions are weak oxidizing agents.

The left column of each pair also shows the relative abilities of metals listed in the table to displace other metals from their compounds. Zinc, for example, appears above copper. Thus, zinc is the more active reducing agent, and it displaces copper ions from solutions of copper compounds, as illustrated in **Figure 5.** The copper(II) ion, on the other hand, is a more active oxidizing agent than the zinc ion.

Nonmetals and some important ions also are included in the series in **Table 3.** Any reducing agent is oxidized by the oxidizing agents below it. Observe that F_2 displaces Cl^-, Br^-, and I^- ions from their solutions. Cl_2 displaces Br^- and I^- ions, and Br_2 displaces I^- ions. The equation for the displacement of Br^- by Cl_2 is as follows.

$$Cl_2 + 2Br^-(aq) \longrightarrow 2Cl^-(aq) + Br_2$$

$$2\overset{-1}{Br^-} \longrightarrow \overset{0}{Br_2} + 2e^- \qquad \text{(oxidation)}$$

$$\overset{0}{Cl_2} + 2e^- \longrightarrow 2\overset{-1}{Cl^-} \qquad \text{(reduction)}$$

In every redox reaction, there is one reducing agent and one oxidizing agent. In the preceding example, Br^- is the reducing agent and Cl_2 is the oxidizing agent.

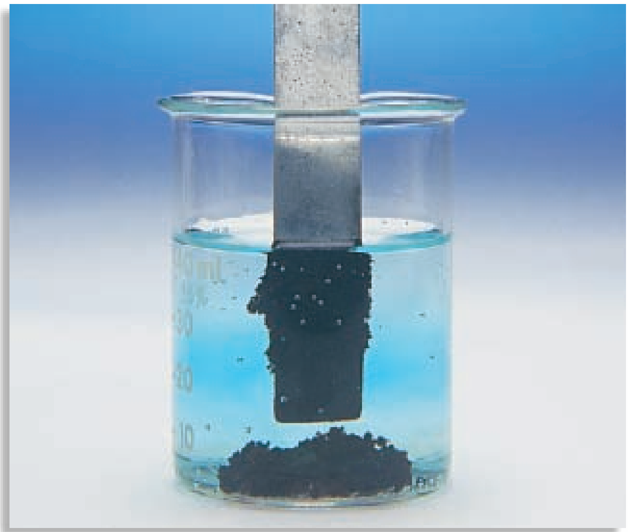


FIGURE 5 Zinc displaces copper ions from a copper(II) sulfate solution. Metallic copper precipitates.

TABLE 3 ***Relative Strength of Oxidizing and Reducing Agents***

Reducing agents	Oxidizing agents
Li	Li^+
K	K^+
Ca	Ca^{2+}
Na	Na^+
Mg	Mg^{2+}
Al	Al^{3+}
Zn	Zn^{2+}
Cr	Cr^{3+}
Fe	Fe^{2+}
Ni	Ni^{2+}
Sn	Sn^{2+}
Pb	Pb^{2+}
H_2	H_3O^+
H_2S	S
Cu	Cu^{2+}
I^-	I_2
MnO_4^{2-}	MnO_4^-
Fe^{2+}	Fe^{3+}
Hg	Hg_2^{2+}
Ag	Ag^+
NO_2^-	NO_3^-
Br^-	Br_2
Mn^{2+}	MnO_2
SO_2	H_2SO_4 (conc.)
Cr^{3+}	$Cr_2O_7^{2-}$
Cl^-	Cl_2
Mn^{2+}	MnO_4^-
F^-	F_2

Increasing strength ↑

Increasing strength ↓

QuickLAB

Wear safety goggles and an apron.

Redox Reactions

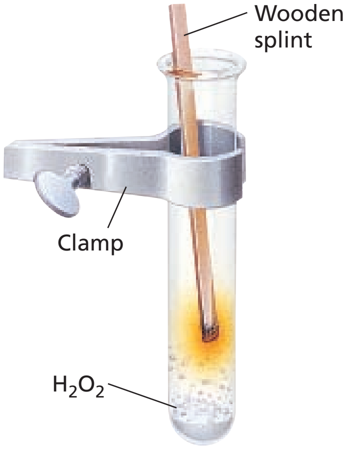
Procedure

Record all of your results in a data table.

1. Put 10 mL of hydrogen peroxide in a test tube, and add a small amount of manganese dioxide (equal to the size of about half a pea). What is the result?
2. Insert a glowing wooden splint into the test tube (see diagram). What is the result? If oxygen is produced, a glowing wooden splint inserted into the test tube will glow brighter.
3. Fill the 250 mL beaker halfway with the copper(II) chloride solution.
4. Cut foil into 2 cm × 12 cm strips.
5. Add the aluminum strips to the copper(II) chloride solution. Use a glass rod to stir the mixture, and observe for 12 to 15 minutes. What is the result?

Discussion

1. Write balanced equations showing what happened in each of the reactions.
2. Write a conclusion for the two experiments.



Materials

- **aluminum foil**
- **beaker, 250 mL**
- **1 M copper(II) chloride solution, $CuCl_2$**
- **3% hydrogen peroxide**
- **manganese dioxide**
- **metric ruler**
- **scissors**
- **test-tube clamp**
- **test tube, 16 × 150 mm**
- **wooden splint**

Disproportionation

Some substances can be both reduced and oxidized easily. For example, peroxide ions, O_2^{2-}, have a relatively unstable covalent bond between the two oxygen atoms. The electron-dot formula is written as follows.

$$\left[:\ddot{\underset{\cdot\cdot}{O}}:\ddot{\underset{\cdot\cdot}{O}}:\right]^{2-}$$

Each oxygen atom has an oxidation number of –1. The peroxide ion structure represents an intermediate oxidation state between O_2 and O^{2-}. Therefore, the peroxide ion is highly reactive.

Hydrogen peroxide, H_2O_2, is a covalent compound. It decomposes into water and molecular oxygen, as shown in the equation below.

$$2H_2\overset{-1}{O}_2 \longrightarrow 2H_2\overset{-2}{O} + \overset{0}{O}_2$$

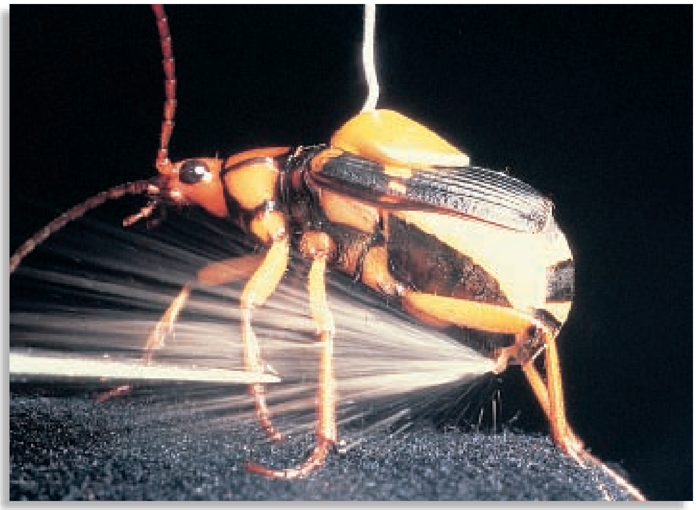


FIGURE 6 A bombardier beetle can repel large predators such as frogs with a chemical defense mechanism that uses the disproportionation of hydrogen peroxide.

Notice that in this reaction, hydrogen peroxide is both oxidized and reduced. Oxygen atoms that become part of gaseous oxygen molecules are oxidized. The oxidation number of these oxygen atoms increases from −1 to 0. Oxygen atoms that become part of water are reduced. The oxidation number of these oxygen atoms decreases from −1 to −2. *A process in which a substance acts as both an oxidizing agent and a reducing agent is called* **disproportionation.** A substance that undergoes disproportionation is both *self-oxidizing* and *self-reducing.*

The bombardier beetle defends itself by spraying its enemies with an unpleasant hot chemical mixture, as shown in **Figure 6.** The catalyzed disproportionation of hydrogen peroxide produces hot oxygen gas. This gas gives the insect an ability to eject irritating chemicals from its abdomen with explosive force.

SECTION REVIEW

1. Describe the chemical activity of the alkali metals and of the halogens on the basis of oxidizing and reducing strength.

2. The photo on the left depicts two redox reactions. Both nails are in a sulfuric acid solution. Answer the following questions:
   a. When zinc is wrapped around an iron nail, is the iron or zinc oxidized?
   b. When copper is wrapped around an iron nail, is the iron or copper oxidized?

3. Would Cl_2 be reduced by I^-? Explain.

4. Which is the stronger oxidizing agent in each of the following pairs: Cu^{2+} or Al^{3+}, I_2 or S, F_2 or Li^+?

5. What is meant by *disproportionation*?

Critical Thinking

6. **ORGANIZING IDEAS** In general, where in the periodic table are the elements found that in elemental form are the strongest oxidizing agents? Explain.

CHAPTER HIGHLIGHTS

Oxidation and Reduction

Vocabulary
oxidation
oxidized
reduction
reduced
oxidation-reduction reaction
redox reaction
half-reaction

- Oxidation numbers are assigned by the set of rules listed in **Table 1.** Oxidation numbers are based on the distribution of electrons in a molecule.
- Oxidation-reduction reactions consist of two half-reactions that must occur simultaneously.
- Oxidation-reduction reactions are identified by examining the changes in the oxidation numbers of atoms in the reactants and products.
- Oxidation involves the loss of electrons, and reduction involves the gain of electrons.
- A species whose oxidation number increases is oxidized. A species whose oxidation number decreases is reduced.

Balancing Redox Equations

- Charge and mass are conserved in a balanced redox equation.
- In the half-reaction method for balancing equations, the atoms and charge of oxidation and reduction equations are balanced separately. Then, they are combined to give a complete balanced equation.
- In a half-reaction, the charge on the reactant side must equal the charge on the product side, but these charges do not need to be zero.
- For the half-reaction method, the atoms in each half-reaction are balanced by adding H^+ ions and H_2O molecules in acidic solutions. If the solution is basic, OH^- ions and H_2O molecules are added to balance the atoms in each half-reaction.
- The number of electrons lost in the oxidation half-reaction must equal the number of electrons gained in the reduction half-reaction. The two half-reactions must be multiplied by appropriate factors to ensure that the same number of electrons are transferred.

Oxidizing and Reducing Agents

Vocabulary
reducing agent
oxidizing agent
disproportionation

- The substance that is *reduced* in redox reactions is the *oxidizing agent* because it *acquires* electrons from the substance that is oxidized.
- The substance that is *oxidized* in a redox reaction is the *reducing agent* because it *supplies* the electrons to the substance that is reduced.
- Strong reducing agents are substances that easily give up electrons.
- Disproportionation is a process in which a substance is both an oxidizing agent and a reducing agent.

CHAPTER REVIEW

For more practice, go to the Problem Bank in Appendix D.

Oxidation and Reduction

SECTION 1 REVIEW

1. a. Distinguish between the processes of oxidation and reduction.
   b. Write an equation to illustrate each process.

2. Which of the following are redox reactions?
   a. $2Na + Cl_2 \longrightarrow 2NaCl$
   b. $C + O_2 \longrightarrow CO_2$
   c. $2H_2O \longrightarrow 2H_2 + O_2$
   d. $NaCl + AgNO_3 \longrightarrow AgCl + NaNO_3$
   e. $NH_3 + HCl \longrightarrow NH_4^+ + Cl^-$
   f. $2KClO_3 \longrightarrow 2KCl + 3O_2$
   g. $H_2 + Cl_2 \longrightarrow 2HCl$
   h. $H_2SO_4 + 2KOH \longrightarrow K_2SO_4 + 2H_2O$
   i. $Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu$

3. For each oxidation-reduction reaction in the previous question, identify what is oxidized and what is reduced.

PRACTICE PROBLEMS

4. Each of the following atom/ion pairs undergoes the oxidation number change indicated below. For each pair, determine whether oxidation or reduction has occurred, and then write the electronic equation indicating the corresponding number of electrons lost or gained.
   a. $K \longrightarrow K^+$
   b. $S \longrightarrow S^{2-}$
   c. $Mg \longrightarrow Mg^{2+}$
   d. $F^- \longrightarrow F_2$
   e. $H_2 \longrightarrow H^+$
   f. $O_2 \longrightarrow O^{2-}$
   g. $Fe^{3+} \longrightarrow Fe^{2+}$
   h. $Mn^{2+} \longrightarrow MnO_4^-$

5. Identify the following reactions as redox or nonredox:
   a. $2NH_4Cl(aq) + Ca(OH)_2(aq) \longrightarrow 2NH_3(aq) + 2H_2O(l) + CaCl_2(aq)$
   b. $2HNO_3(aq) + 3H_2S(g) \longrightarrow 2NO(g) + 4H_2O(l) + 3S(s)$
   c. $[Be(H_2O)_4]^{2+}(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + [Be(H_2O)_3OH]^+(aq)$

6. Arrange the following in order of increasing oxidation number of the xenon atom: $CsXeF_8$, Xe, XeF_2, $XeOF_2$, XeO_3, and XeF.

7. Determine the oxidation number of each atom indicated in the following:
   a. H_2
   b. H_2O
   c. Al
   d. MgO
   e. Al_2S_3
   f. HNO_3
   g. H_2SO_4
   h. $Ca(OH)_2$
   i. $Fe(NO_3)_2$
   j. O_2

Balancing Redox Equations

SECTION 2 REVIEW

8. Label the following half-reactions as either reduction or oxidation half-reactions.
   a. $H_2S \longrightarrow S + 2e^- + 2H^+$
   b. $SO_2 + 4e^- + 2H_2O \longrightarrow S + 4OH^-$
   c. $ClO_3^- + 6H^+ + 6e^- \longrightarrow Cl^- + 3H_2O$
   d. $Mn(CN)_6^{4-} \longrightarrow Mn(CN)_6^{3-} + e^-$

9. What are the oxidation states of the elements that changed oxidation states in the half-reactions in the above question?

10. Balance the equation for the following reaction in a basic solution. Give balanced equations for both half-reactions and the balanced equation for the overall reaction.
$KMnO_4 + NaIO_3 \longrightarrow MnO_2 + NaIO_4$

PRACTICE PROBLEMS

11. For each requested step, use the half-reaction method to balance the oxidation-reduction equation below. (Hint: See Sample Problem A.)

$$K + H_2O \longrightarrow KOH + H_2$$

   a. Write the ionic equation, and assign oxidation numbers to all atoms to determine what is oxidized and what is reduced.
   b. Write the equation for the reduction, and balance it for both atoms and charge.
   c. Write the equation for the oxidation, and balance it for both atoms and charge.
   d. Multiply the coefficients of the oxidation and reduction equations so that the number of electrons lost equals the number of electrons gained. Add the two equations.
   e. Add species as necessary to balance the overall formula equation.

12. Use the method in the previous problem to balance each of the reactions below.
a. $HI + HNO_2 \longrightarrow NO + I_2 + H_2O$
b. $FeCl_3 + H_2S \longrightarrow FeCl_2 + HCl + S$

13. Balance the equation for the reaction in which hot, concentrated sulfuric acid reacts with zinc to form zinc sulfate, hydrogen sulfide, and water.

Oxidizing and Reducing Agents

SECTION 3 REVIEW

14. a. Identify the most active reducing agent among all common elements.
b. Why are all of the elements in its group in the periodic table very active reducing agents?
c. Identify the most active oxidizing agent among the common elements.

15. Use **Table 3** to identify the strongest and weakest reducing agents among the substances listed within each of the following groupings:
a. Ca, Ag, Sn, Cl^-
b. Fe, Hg, Al, Br^-
c. F^-, Pb, Mn^{2+}, Na

16. Use **Table 3** to respond to each of the following:
a. Would Al be oxidized by Ni^{2+}?
b. Would Cu be oxidized by Ag^+?
c. Would Pb be oxidized by Na^+?
d. Would F_2 be reduced by Cl^-?
e. Would Br_2 be reduced by Cl^-?

MIXED REVIEW

17. Identify the following reactions as redox or nonredox:
a. $Mg(s) + ZnCl_2(aq) \longrightarrow Zn(s) + MgCl_2(aq)$
b. $2H_2(g) + OF_2(g) \longrightarrow H_2O(g) + 2HF(g)$
c. $2KI(aq) + Pb(NO_3)_2(aq) \longrightarrow PbI_2(s) + 2KNO_3(aq)$
d. $CaO(s) + H_2O(l) \longrightarrow Ca(OH)_2(aq)$
e. $3CuCl_2(aq) + 2(NH_4)_3PO_4(aq) \longrightarrow 6NH_4Cl(aq) + Cu_3(PO_4)_2(s)$
f. $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g)$

18. Arrange the following in order of decreasing oxidation number of the nitrogen atom: N_2, NH_3, N_2O_4, N_2O, N_2H_4, and NO_3^-.

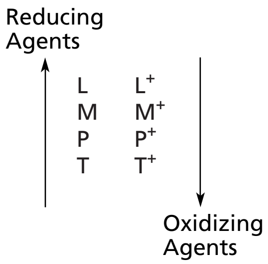
19. Balance the following redox equations:
a. $SbCl_5 + KI \longrightarrow KCl + I_2 + SbCl_3$
b. $Ca(OH)_2 + NaOH + ClO_2 + C \longrightarrow NaClO_2 + CaCO_3 + H_2O$

20. Balance the following equations in basic solution:
a. $PbO_2 + KCl \longrightarrow KClO + KPb(OH)_3$
b. $KMnO_4 + KIO_3 \longrightarrow MnO_2 + KIO_4$
c. $K_2MnO_4 \longrightarrow MnO_2 + KMnO_4$

21. Balance the following equations in acidic solution:
a. $MnO_4^- + Cl^- \longrightarrow Mn^{2+} + HClO$
b. $NO_3^- + I_2 \longrightarrow IO_3^- + NO_2$
c. $NO_2^- \longrightarrow NO + NO_3^-$

CRITICAL THINKING

22. Interpreting Graphics Given the activity table below, determine whether a reaction will occur or not. If the reaction will occur, give the products.



a. L and M^+
b. P and M^+
c. P and T^+

23. Drawing Conclusions A substance has an element in one of its highest possible oxidation states. Is this substance more likely to be an oxidizing agent or a reducing agent? Explain your reasoning.

24. **Drawing Conclusions** Use **Table 3** to decide if a redox reaction would occur between the two species, and if so, write the balanced equation. Explain your reasoning.
   a. Cl_2 and Br_2
   b. Sn^{2+} and Zn

25. **Drawing Conclusions** An element that disproportionates must have at least how many different oxidation states? Explain your reasoning.

USING THE HANDBOOK

26. Several reactions of aluminum are shown in the common reactions section for Group 13 of the *Elements Handbook*. Use these reactions to answer the following:
   a. Which of the five reactions shown are oxidation-reduction reactions? How do you know?
   b. For each redox reaction you listed in item **a,** identify what is oxidized and what is reduced.
   c. Write half-reactions for each equation you listed in item **a.**

27. Aluminum is described in Group 13 of the *Elements Handbook* as a self-protecting metal. This property of aluminum results from a redox reaction.
   a. Write the redox equation for the oxidation of aluminum.
   b. Write the half-reactions for this reaction, and show the number of electrons transferred.
   c. What problems are associated with the buildup of aluminum oxide on electrical wiring made of aluminum?

RESEARCH & WRITING

28. Oxidizing agents are used in the cleaning industry. Research three different oxidizing agents used in this area, and write a report on the advantages and disadvantages of these compounds.

29. Oxidizing and reducing agents play important roles in biological systems. Research the role of one of these agents in a biological process. Write a report describing the process and the role of oxidation and reduction.

ALTERNATIVE ASSESSMENT

30. Boilers are used to convert water to steam in electric power plants. Dissolved oxygen in the water promotes corrosion of the steel used in boiler parts. Explain how dissolved oxygen is removed from the water in boilers.

31. **Performance** For one day, record situations that show evidence of oxidation-reduction reactions. Identify the reactants and the products, and determine whether there is proof that a chemical reaction has taken place.

Math Tutor BALANCING REDOX EQUATIONS

A redox equation must conserve both mass and charge. So, to balance a redox equation, you must balance both atoms and charge (electrons). The problem-solving tips and sample below show how to balance an equation for a redox reaction in *basic* solution.

Problem-Solving TIPS

To balance redox equations for reactions in *basic* solution:

- Add OH^- and H_2O to balance oxygen and hydrogen in the redox half-reactions.
- Add OH^- ions to the side of the equation that needs oxygen atoms. Make sure you add enough OH^- ions so that the number of oxygen atoms added is twice the number needed.
- Then, add enough H_2O molecules to the other side of the equation to balance the hydrogen atoms.

SAMPLE

The following unbalanced equation represents a redox reaction that takes place in a basic solution containing KOH. Balance the redox equation.

$$Br_2(l) + KOH(aq) \longrightarrow KBr(aq) + KBrO_3(aq)$$

Write the full ionic equation, assign oxidation numbers, and eliminate species whose oxidation numbers do not change. The result is the following equation:

$$\overset{0}{Br_2} \longrightarrow \overset{-1}{Br^-} + \overset{+5}{Br}O_3^-$$

Divide this equation into half-reactions. Note that Br_2 is the reactant in both half-reactions.

Reduction: $Br_2 \longrightarrow Br^-$ Oxidation: $Br_2 \longrightarrow BrO_3^-$

Add H_2O and OH^- to balance atoms in basic solution. Then, add electrons to balance charge.

Reduction: $Br_2 + 2e^- \longrightarrow 2Br^-$ (no need to add H_2O or OH^-)

Oxidation: $12OH^- + Br_2 \longrightarrow 2BrO_3^- + 6H_2O + 10e^-$

To balance transferred electrons, you must multiply the reduction half-reaction by 5 so that both reactions have $10e^-$.

$$5 \times (Br_2 + 2e^- \longrightarrow 2Br^-) = 5Br_2 + 10e^- \longrightarrow 10Br^-$$

Combining the two half-reactions gives

$$5Br_2 + 12OH^- + Br_2 + 10e^- \longrightarrow 10Br^- + 2BrO_3^- + 6H_2O + 10e^-$$

Canceling common species gives

$$6Br_2 + 12OH^- \longrightarrow 10Br^- + 2BrO_3^- + 6H_2O$$

Returning the potassium ions to the equation gives

$$6Br_2 + 12KOH \longrightarrow 10KBr + 2KBrO_3 + 6H_2O, \text{ or } 3Br_2 + 6KOH \longrightarrow 5KBr + KBrO_3 + 3H_2O$$

PRACTICE PROBLEMS

1. Balance the following equation for a redox reaction that takes place in basic solution:
$MnO_2(s) + NaClO_3(aq) + NaOH(aq) \longrightarrow NaMnO_4(aq) + NaCl(aq) + H_2O(l)$

2. Balance the following equation for a redox reaction that takes place in basic solution:
$N_2O(g) + KClO(aq) + KOH(aq) \longrightarrow KCl(aq) + KNO_2(aq) + H_2O(l)$

Standardized Test Prep

Answer the following items on a separate piece of paper.

MULTIPLE CHOICE

1. In the following reaction, which species is reduced?

$$2K + Br_2 \longrightarrow 2K^+ + 2Br^-$$

A. K
B. Br_2
C. All of the above
D. None of the above

2. The oxidation number of the sulfur atom in the SO_4^{2-} ion is

A. +2.
B. –2.
C. +6.
D. +4.

3. A half-reaction

A. involves a change in the oxidation state of an element.
B. always contains H_2O molecules.
C. always contains H^+ ions.
D. All of the above

4. In the following reaction, which is the oxidizing agent?

$$AgNO_2 + Cl_2 + 2KOH \longrightarrow AgNO_3 + 2KCl + H_2O$$

A. $AgNO_2$
B. Cl_2
C. KOH
D. KCl

5. What are the oxidation states (in increasing order) of the element that undergoes disproportionation in the following reaction:

$$Cl_2 + H_2O \longrightarrow HCl + HOCl$$

A. –1, 0, +2
B. –1, 0, +1
C. –2, –1, 0
D. None of the above

6. Which reaction is a redox reaction?

A. $Al_2O_3 + 6HCl \longrightarrow 2AlCl_3 + 3H_2O$
B. $2HCO_3^- \longrightarrow CO_2 + CO_3^{2-} + H_2O$
C. $SiBr_4 + 3H_2O \longrightarrow H_2SiO_3 + 4HBr$
D. $H_2O + PbO_2 + NaOH + KCl \longrightarrow KClO + NaPb(OH)_3$

7. Arrange the following in order of increasing oxidation number of the sulfur atom: $S_2O_3^{2-}$, $S_4O_6^{2-}$, HSO_4^-, and H_2S.

A. H_2S, $S_2O_3^{2-}$, $S_4O_6^{2-}$, HSO_4^-
B. $S_2O_3^{2-}$, H_2S, $S_4O_6^{2-}$, HSO_4^-
C. H_2S, $S_2O_3^{2-}$, HSO_4^-, $S_4O_6^{2-}$
D. HSO_4^-, $S_2O_3^{2-}$, $S_4O_6^{2-}$, H_2S

8. Which answer contains the correct information about the following reaction:

$$2Pb(NO_3)_2 \longrightarrow 2PbO + 4NO_2 + O_2$$

A. This reaction is a decomposition reaction and not a redox reaction.
B. This reaction is a redox reaction in which the lead is reduced and the oxygen is oxidized.
C. This reaction is a disproportionation reaction.
D. This reaction is a redox reaction in which the nitrogen is reduced and the oxygen is oxidized.

SHORT ANSWER

9. Determine the oxidation numbers for Cu in the superconductor $YBa_2Cu_3O_7$. Yttrium (Y) has an oxidation number of +3. (Cu does not have oxidation numbers greater than +3.) Give only integer oxidation numbers.

10. What is an oxidizing agent?

EXTENDED RESPONSE

11. B, F, K, and L are four unknown reducing agents that oxidize to singly charged cations. Using the following information, construct a table showing the relative strengths of the oxidizing and reducing agents. Data: F reduces K^+, B^+, and L^+. B^+ oxidizes K and F, but not L.

12. Balance the equation for the following reaction in basic solution:

$$ClO_2 \longrightarrow KClO_3 + KClO_2$$

Give the balanced equation for each half-reaction and for the overall reaction. Give the oxidizing agent and the reducing agent.

Test TIP If you are short on time, quickly scan the unanswered questions to see which might be easiest to answer.

CHAPTER LAB

SEE PRE-LAB
VOLUMETRIC ANALYSIS

MICRO LAB

Reduction of Manganese in Permanganate Ion

OBJECTIVES

- ***Demonstrate*** **proficiency in performing redox titrations and recognizing end points of a redox reaction.**
- ***Write*** **a balanced oxidation-reduction equation for a redox reaction.**
- ***Determine*** **the concentration of a solution by using stoichiometry and volume data from a titration.**

MATERIALS

- **0.0200 M $KMnO_4$**
- **1.0 M H_2SO_4**
- **100 mL graduated cylinder**
- **125 mL Erlenmeyer flasks, 4**
- **250 mL beakers, 2**
- **400 mL beaker**
- **burets, 2**
- **distilled water**
- **double buret clamp**
- **$FeSO_4$ solution**
- **ring stand**
- **wash bottle**

BACKGROUND

In Chapter 15, you studied acid-base titrations in which an unknown amount of acid is titrated with a carefully measured amount of base. In this procedure, a similar approach called a *redox titration* is used. In a redox titration, the reducing agent, Fe^{2+}, is oxidized to Fe^{3+} by the oxidizing agent, MnO_4^-. When this process occurs, the Mn in MnO_4^- changes from a +7 to a +2 oxidation state and has a noticeably different color. You can use this color change to signify a redox reaction "end point." When the reaction is complete, any excess MnO_4^- added to the reaction mixture will give the solution a pink or purple color. The volume data from the titration, the known molarity of the $KMnO_4$ solution, and the mole ratio from the balanced redox equation will give you the information you need to calculate the molarity of the $FeSO_4$ solution.

SAFETY

For review of safety, please see **Safety in the Chemistry Laboratory** in the front of your book.

PREPARATION

1. In your lab notebook, prepare a data table like the one shown on the next page.
2. Clean two 50 mL burets with a buret brush and distilled water. Rinse each buret at least three times with distilled water to remove contaminants.
3. Label one 250 mL beaker "0.0200 M $KMnO_4$" and the other "$FeSO_4$." Label three of the flasks "1," "2," and "3." Label the 400 mL beaker "Waste." Label one buret "$KMnO_4$" and the other "$FeSO_4$."

DATA TABLE

Trial	Initial $KMnO_4$ volume (mL)	Final $KMnO_4$ volume (mL)	Initial $FeSO_4$ volume (mL)	Final $FeSO_4$ volume (mL)
1				
2				
3				

4. Measure approximately 75 mL of 0.0200 M $KMnO_4$, and pour it into the appropriately labeled beaker. Obtain approximately 75 mL of $FeSO_4$ solution, and pour it into the appropriately labeled beaker.

5. Rinse one buret three times with a few milliliters of 0.0200 M $KMnO_4$ from the appropriately labeled beaker. Collect these rinses in the waste beaker. Rinse the other buret three times with small amounts of $FeSO_4$ solution from the appropriately labeled beaker. Collect these rinses in the waste beaker.

6. Set up the burets as instructed by your teacher. Fill one buret with approximately 50 mL of 0.0200 M $KMnO_4$ from the beaker, and fill the other buret with approximately 50 mL of the $FeSO_4$ solution from the other beaker.

7. With the waste beaker underneath its tip, open the $KMnO_4$ buret long enough to be sure the buret tip is filled. Repeat the process for the $FeSO_4$ buret.

8. Add 50 mL of distilled water to one of the 125 mL Erlenmeyer flasks, and add one drop of 0.0200 M $KMnO_4$ to the flask. Set this mixture aside to use as a color standard. It can be compared with the titration mixture to determine the end point.

PROCEDURE

1. Record in your data table the initial buret readings for both solutions. Add 10 mL of the hydrated iron(II) sulfate solution, $FeSO_4{\bullet}7H_2O$, to the flask labeled “1.” Add 5 mL of 1 M H_2SO_4 to the $FeSO_4$ solution in this flask. The acid will help keep the Fe^{2+} ions in the reduced state, which will allow you time to titrate.

2. Slowly add $KMnO_4$ from the buret to the $FeSO_4$ in the flask while swirling the flask. When the color of the solution matches the color standard you prepared in Preparation step 8, record in your data table the final readings of the burets.

3. Empty the titration flask into the waste beaker. Repeat the titration procedure in steps 1 and 2 with the flasks labeled “2” and “3.”

CLEANUP AND DISPOSAL

4. Dispose of the contents of the waste beaker in the container designated by your teacher. Also, pour the color-standard flask into this container. Wash your hands thoroughly after cleaning up the area and equipment.

ANALYSIS AND INTERPRETATION

1. Organizing Ideas: Write the balanced equation for the redox reaction of $FeSO_4$ and $KMnO_4$.

2. Evaluating Data: Calculate the number of moles of MnO_4^- reduced in each trial.

3. Analyzing Information: Calculate the number of moles of Fe^{2+} oxidized in each trial.

4. Applying Conclusions: Calculate the average concentration (molarity) of the iron(II) sulfate solution.

EXTENSIONS

1. Designing Experiments: What possible sources of error can you identify with this procedure? If you can think of ways to eliminate them, ask your teacher to approve your plan, and run the procedure again.