CHAPTER 17

Chemical Equilibrium

BIG Idea **Many reactions and processes reach a state of chemical equilibrium in which both reactants and products are formed at equal rates.**

17.1 A State of Dynamic Balance

MAIN Idea Chemical equilibrium is described by an equilibrium constant expression that relates the concentrations of reactants and products.

17.2 Factors Affecting Chemical Equilibrium

MAIN Idea When changes are made to a system at equilibrium, the system shifts to a new equilibrium position.

17.3 Using Equilibrium Constants

MAIN Idea Equilibrium constant expressions can be used to calculate concentrations and solubilities.

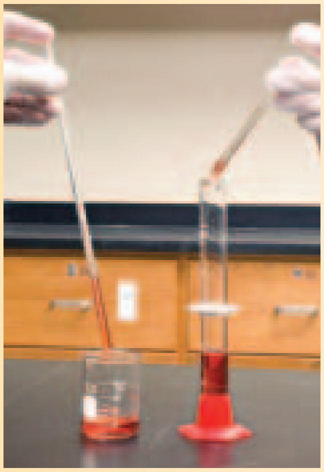
ChemFacts

- No other human activity causes as much air pollution as the use of motor vehicles.
- On some days at the Grand Canyon in Arizona, visitors cannot see to the other side of the canyon because of smog generated in California.
- Every day 50 million Americans experience harmful levels of ozone (O_3), a component of smog.
- Catalytic converters and changes in gasoline additives have made cars 40% cleaner than a decade ago.

LAUNCH Lab

What is equal about equilibrium?

Equilibrium is a point of balance in which opposing changes cancel each other.



Procedure

1. Read and complete the lab safety form.
2. Measure 20 mL of water in a **graduated cylinder** and pour it into a **100-mL beaker.** Fill the graduated cylinder to the 20-mL mark with water. Add two drops of **food coloring** to the water in each container.
3. Obtain **two glass tubes of equal diameter.** Place one tube in the graduated cylinder and the other in the beaker.
4. Work with a partner. With the ends of the tubes at the bottoms of their containers, cover the open ends of the glass tubes with your index fingers so that water becomes trapped in the tubes. Simultaneously, move each tube to the other container and release your fingers to release the water.
5. Repeat the transfer process about 25 times. Record your observations.

Analysis

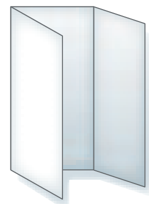
1. **Describe** your observations during the transfer process.
2. **Explain** Would the final result be different if you had continued the transfer process for a longer time?

Inquiry Could you illustrate equilibrium using glass tubes of different diameters? Explain.

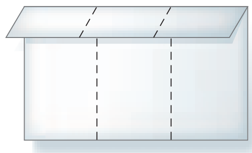
FOLDABLES™ Study Organizer

Changes Affecting Equilibrium Make the following Foldable to help you organize information about the factors that affect equilibrium.

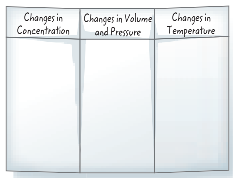
STEP 1 Fold a sheet of paper into thirds horizontally.



STEP 2 Unfold and fold the top edge down about 2 cm.



STEP 3 Unfold and draw lines along all folds. Label the columns as follows: *Changes in Concentration, Changes in Volume and Pressure,* and *Changes in Temperature.*



FOLDABLES Use this Foldable with Section 17.2. As you read this section, summarize how these changes shift the equilibrium of a system. Include sample equations.

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Matt Meadows

Section 17.1

Objectives

- **List** the characteristics of chemical equilibrium.
- **Write** equilibrium expressions for systems that are at equilibrium.
- **Calculate** equilibrium constants from concentration data.

Review Vocabulary

free energy: the energy that is available to do work—the difference between the change in enthalpy and the product of the entropy change and the absolute temperature

New Vocabulary

reversible reaction
chemical equilibrium
law of chemical equilibrium
equilibrium constant
homogeneous equilibrium
heterogeneous equilibrium

A State of Dynamic Balance

MAIN Idea Chemical equilibrium is described by an equilibrium constant expression that relates the concentrations of reactants and products.

Real-World Reading Link Imagine a tug-of-war between two teams. Because the rope between them is not moving, it might seem that neither team is pulling. In fact, both teams are pulling, but the forces exerted by the two teams are equal and opposite, so they are in complete balance.

What is equilibrium?

Often, chemical reactions reach a point of balance or equilibrium. If you performed the Launch Lab on the previous page, you found that a point of balance was reached in the transfer of water from the beaker to the graduated cylinder and from the graduated cylinder to the beaker.

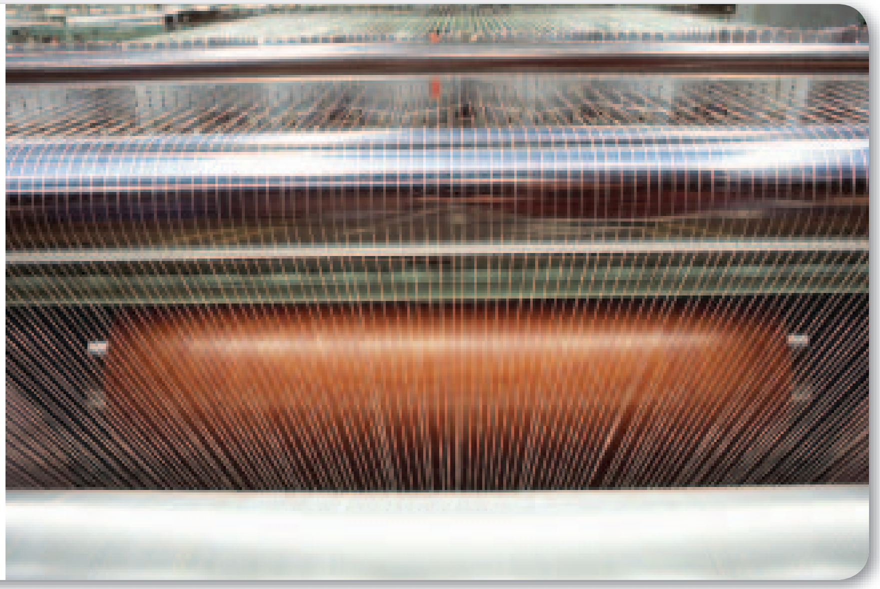
Consider the reaction for the formation of ammonia from nitrogen and hydrogen that you read about in Chapter 15.

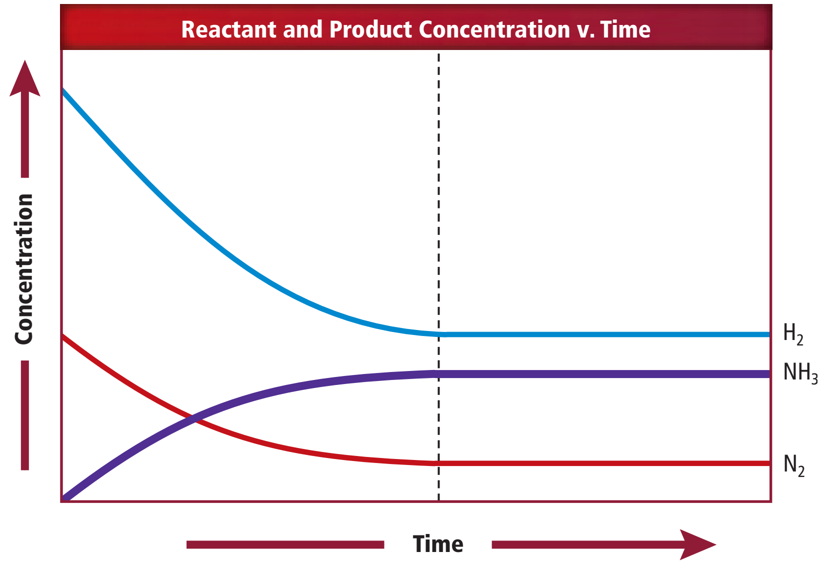
$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g) \quad \Delta G° = -33.1 \text{ kJ}$$

Ammonia is important in agriculture as a fertilizer and an additive to animal feed grains. In industry, it is a raw material for the manufacture of many products such as nylon, as shown in **Figure 17.1.**

The equation for the production of ammonia has a negative standard free energy, $\Delta G°$. Recall that a negative sign for $\Delta G°$ indicates that the reaction is spontaneous under standard conditions, defined as 298 K and 1 atm, but spontaneous reactions are not always fast. When carried out under standard conditions, this ammonia-forming reaction is much too slow. To produce ammonia at a rate that is practical, the reaction must be carried out at a much higher temperature and pressure.

Figure 17.1 Ammonia reacts with both ends of a six-carbon molecule to form a diamine (1,6-diaminohexane). This is one step in the formation of the polymer nylon. Here nylon fibers, to be used in tire manufacturing, are being wound onto a spool.





■ **Figure 17.2** The concentrations of the reactants (H_2 and N_2) decrease at first, while the concentration of the product (NH_3) increases. Then, before the reactants are used up, all concentrations become constant.

Graph Check
Explain how the graph shows that the concentrations of the reactants and products become constant.

What happens when 1 mol of nitrogen and 3 mol of hydrogen, the number of moles shown as coefficients in the chemical equation, are placed in a closed reaction vessel at 723 K? Because the reaction is spontaneous, nitrogen and hydrogen react. **Figure 17.2** illustrates the progress of the reaction. Note that the concentration of the product, NH_3, is zero at the start and gradually increases with time. The reactants, H_2 and N_2, are consumed in the reaction, so their concentrations gradually decrease. After a period of time, however, the concentrations of H_2, N_2, and NH_3 no longer change. All concentrations become constant, as shown by the horizontal lines on the right side of the diagram. The concentrations of H_2 and N_2 are not zero, so not all of the reactants were converted to product, even though $\Delta G°$ for this reaction is negative.

Graph Check **Describe** the slopes of the curves for the reactants and for the product on the left of the vertical dotted line. How do the slopes differ on the right of the dotted line?

Reversible reactions and chemical equilibrium When a reaction results in an almost complete conversion of reactants to products, chemists say that the reaction goes to completion—but most reactions do not go to completion. The reactions appear to stop because they are reversible. A **reversible reaction** is a chemical reaction that can occur in both the forward and the reverse directions.

$$\text{Forward: } N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$
$$\text{Reverse: } N_2(g) + 3H_2(g) \longleftarrow 2NH_3(g)$$

Chemists combine these two equations into a single equation that uses a double arrow to show that both reactions occur.

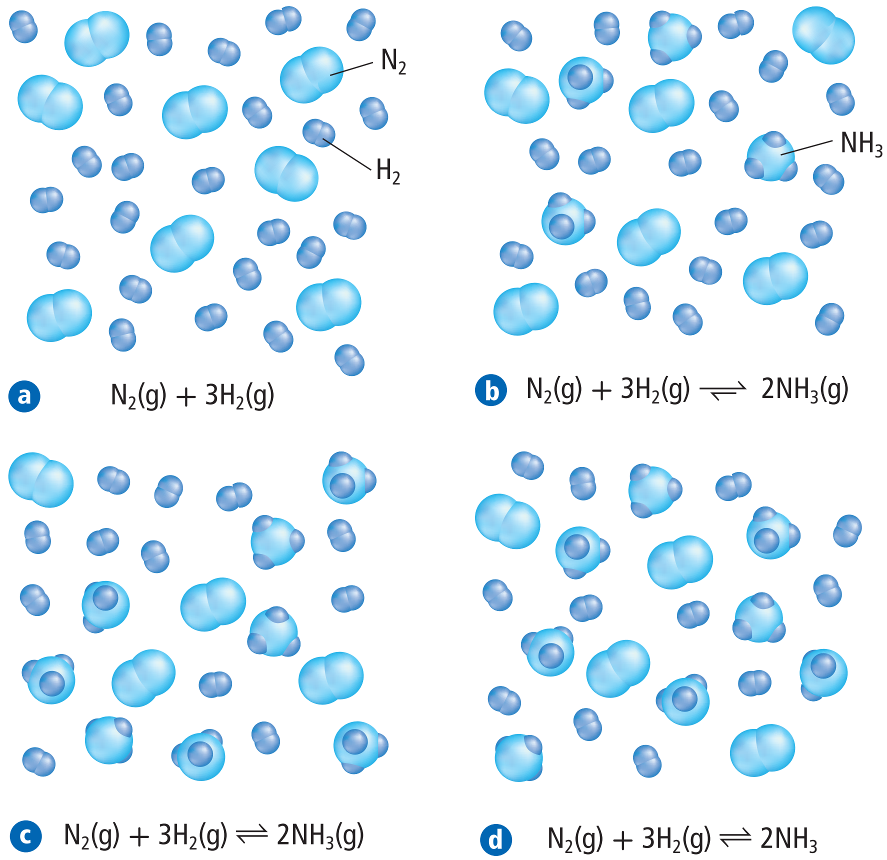
$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

The reactants in the forward reaction are on the left of the arrows. The reactants in the reverse reaction are on the right of the arrows. In the forward reaction, hydrogen and nitrogen combine to form the product ammonia. In the reverse reaction, ammonia decomposes into the products hydrogen and nitrogen.

VOCABULARY
ACADEMIC VOCABULARY
Convert
to change from one form or function to another
She converted a spare bedroom into an office.

■ **Figure 17.3** The progress of a reaction to produce ammonia from hydrogen and nitrogen is shown in **a.** through **d.**

Interpret *Study the diagrams to answer the following questions. In* **a,** *how do you know that the reaction has not yet begun? In* **b,** *what evidence indicates that the reverse reaction has begun? Compare* **c** *with* **d.** *How do you know that equilibrium has been reached?*



How does the reversibility of this reaction affect the production of ammonia? **Figure 17.3a** shows a mixture of nitrogen and hydrogen just as the reaction begins at a definite, initial rate. No ammonia is present, therefore only the forward reaction can occur.

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

As hydrogen and nitrogen combine to form ammonia, their concentrations decrease, as shown in **Figure 17.3b.** Recall from Chapter 16 that the rate of a reaction depends on the concentration of the reactants. The decrease in the concentration of the reactants causes the rate of the forward reaction to slow. As soon as ammonia is present, the reverse reaction can occur, slowly at first, but at an increasing rate as the concentration of ammonia increases.

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

As the reaction proceeds, the rate of the forward reaction continues to decrease and the rate of the reverse reaction continues to increase until the two rates are equal. At that point, ammonia is produced at the same rate it is decomposed, so the concentrations of N_2, H_2, and NH_3 remain constant, as shown in **Figures 17.3c** and **17.3d.** The system has reached a state of balance or equilibrium. The word *equilibrium* means that opposing processes are in balance. **Chemical equilibrium** is a state in which the forward and reverse reactions balance each other because they take place at equal rates.

$$\text{Rate}_{\text{forward reaction}} = \text{Rate}_{\text{reverse reaction}}$$

You can recognize that the ammonia-forming reaction reaches a state of chemical equilbrium because its chemical equation is written with a double arrow like this.

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

At equilibrium, the concentrations of reactants and products are constant, as shown in **Figures 17.3c** and **17.3d.** However, that doesn't mean that the amounts or concentrations of reactants and products are equal. That is seldom the case. In fact, it is not unusual for the equilibrium concentrations of a reactant and product to differ by a factor of one million or more.

Reading Check **Explain** the meaning of a double arrow in chemical equations.

Connection to Physics **The dynamic nature of equilibrium** A push or pull on an object is a force. When you push on a door or pull on a dog's leash, you exert a force. When two or more forces are exerted on the same object in the same direction, they add together. One force subtracts from the other if the forces are in opposite directions. Thus, in a tug-of-war, when two teams pull on a rope with equal force, the resulting force has a magnitude of zero and the rope does not move. The system is said to be in equilibrium. Similarly, the people on the seesaw in **Figure 17.4a** represent a system in equilibrium. The equal-and-opposite forces on both ends of the seesaw are called balanced forces. If, instead, one force is greater in magnitude than the other, the combined force is greater than zero and is called an unbalanced force. An unbalanced force causes an object to accelerate, which is what has happened in **Figure 17.4b.**

Figure 17.4 In **a,** all the forces are in perfect balance, so the position of the seesaw remains steady. In **b,** the unbalanced force on the left causes the seesaw to change its position.

Explain *this analogy in terms of chemical equilibrium.*

■ **Figure 17.5** Suppose a certain number of people are confined to the two buildings connected by this walkway and that people can walk back and forth between the buildings. The number of people in each building will remain constant only if the same number of people cross the bridge in one direction as cross in the opposite direction.

Decide ***whether the same people will always be in the same building. How does your answer apply to chemical equilibrium?***

Like equal forces opposing each other, equilibrium is a state of action, not inaction. For example, consider this analogy: The glassed-in walkway, shown in **Figure 17.5,** connects two buildings. Suppose that all entrances and exits for the buildings, except the walkway, are closed for a day. And suppose that the same number of persons cross the walkway in each direction every hour. Given these circumstances, the number of persons in each building remains constant even though people continue to cross between the two buildings. Note that the numbers of persons in the two buildings do not have to be equal. Equilibrium requires only that the number of persons crossing the walkway in one direction is equal to the number crossing in the opposite direction.

The dynamic nature of chemical equilibrium can be illustrated by placing equal masses of iodine crystals in two interconnected flasks, as shown in **Figure 17.6a.** The flask on the left contain iodine molecules made up entirely of the nonradioactive isotope I-127. The flask on the right contain iodine molecules made up of the radioactive isotope I-131. The radiation counters indicate the difference in the levels of radioactivity within each flask.

Each flask is a closed system. No reactant or product can enter or leave. At 298 K and 1 atm, this equilibrium is established in both flasks.

$$I_2(s) \rightleftharpoons I_2(g)$$

In the forward process, called sublimation, iodine molecules change directly from the solid phase to the gas phase. In the reverse process, gaseous iodine molecules return to the solid phase. A solid-vapor equilibrium is established in each flask.

When the stopcock in the tube connecting the two flasks is opened, as in **Figure 17.6b,** iodine vapor can travel back and forth between the two flasks. After a period of time, the readings on the radiation counters indicate that the flask on the left contains as many radioactive I-131 molecules as the flask on the right in both the vapor and the solid phases.

The evidence suggests that iodine molecules constantly change from the solid phase to the gas phase according to the forward process, and that gaseous iodine molecules convert back to the solid phase according to the reverse process. The constant readings on both radiation detectors indicate that equilibrium has been established in the combined volume of the two flasks.

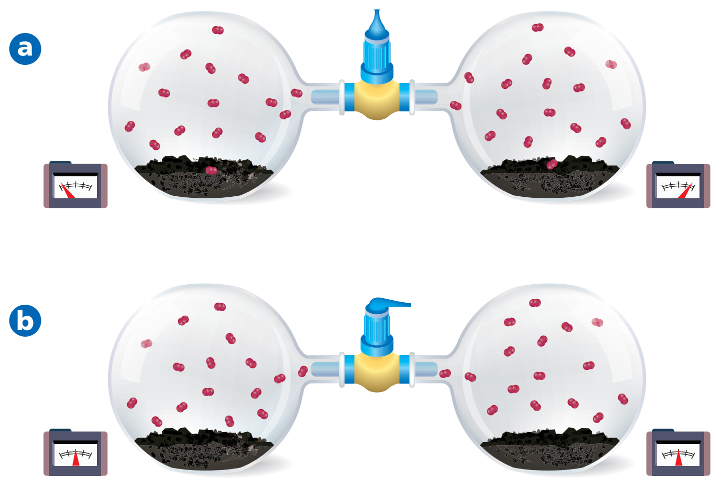


Figure 17.6 **a.** Radioactive iodine molecules in the solid in the flask on the right are separated from nonradioactive iodine in the flask on the left. Note the readings on the radiation monitors. **b.** After the stopcock has been open for a time, the radiation monitors show that radioactive molecules are in both flasks. The particles must have moved back and forth between the flasks and between the solid and the gaseous phases.

Equilibrium Expressions

Some chemical systems have little tendency to react. Others go to completion. The majority of reactions reach a state of equilibrium with some of the reactants unconsumed. If the reactants are not all consumed, then the amount of products produced is less than the amount predicted by the balanced chemical equation. According to the equation for the ammonia-producing reaction, 2 mol of ammonia should be produced when 1 mol of nitrogen and 3 mol of hydrogen react. However, because the reaction reaches a state of equilibrium, less than 2 mol of ammonia are obtained.

The law of chemical equilibrium In 1864, Norwegian chemists Cato Maximilian Guldberg and Peter Waage jointly proposed and developed the **law of chemical equilibrium,** which states that at a given temperature, a chemical system might reach a state in which a particular ratio of reactant and product concentrations has a constant value. The general equation for a reaction at equilibrium is as follows.

$$aA + bB \rightleftharpoons cC + dD$$

If the law of chemical equilibrium is applied to this reaction, the following ratio is obtained.

The Equilibrium Constant Expression

$$K_{eq} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

[A] and [B] are the molar concentrations of the reactants. [C] and [D] are the molar concentrations of the products.

The exponents *a*, *b*, *c*, and *d*, are the coefficients in the balanced equation.

The equilibrium constant expression is the ratio of the molar concentrations of the products to the molar concentrations of the reactants with each concentration raised to a power equal to its coefficient in the balanced chemical equation.

The **equilibrium constant,** K_{eq}, is the numerical value of the ratio of product concentrations to reactant concentrations, with each concentration raised to the power equal to its coefficient in the balanced equation. The value of K_{eq} is constant only at a specified temperature.

Vocabulary

Word origin

Completion
comes from the Latin verb *completus,* which means *having all necessary parts, elements, or steps.*

How can you interpret the size of the equilibrium constant? Recall that a fraction with a numerator greater than its denominator has a value greater than 1. And a fraction with a numerator less than its denominator has a value less than 1. For example, compare the ratios 5/1 and 1/5. Five is a larger number than one-fifth. Because the product concentrations are in the numerator of the equilibrium expression, a numerically large K_{eq} means that the equilibrium mixture contains more products than reactants. Similarly, a numerically small K_{eq} means that the equilibrium mixture contains more reactants than products.

$K_{eq} > 1$: Products are favored at equilibrium.

$K_{eq} < 1$: Reactants are favored at equilibrium.

Expressions for homogeneous equilibria Gaseous hydrogen iodide is produced by the equilibrium reaction of hydrogen gas with iodine. Iodine and some of its compounds have important uses in medicine, as illustrated in **Figure 17.7.** How would you write the equilibrium constant expression for this reaction in which hydrogen and iodine react to form hydrogen iodide?

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

This reaction is a **homogeneous equilibrium,** which means that all the reactants and products are in the same physical state. All participants are gases. First, place the product concentration in the numerator and the reactant concentrations in the denominator.

$$\frac{[HI]}{[H_2][I_2]}$$

The expression becomes equal to K_{eq} when you add the coefficients from the balanced chemical equation as exponents.

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

K_{eq} for this equilibrium at 731 K is 49.7. Note that 49.7 has no units. When writing equilibrium constant expressions, it is customary to omit units.

Figure 17.7 Because of iodine's antibacterial properties, solutions of iodine and iodine compounds are used externally as antiseptics. Some iodine compounds are used internally. For example, doctors use potassium iodide (KI) in the treatment of goiter, a condition characterized by the enlargement of the thyroid gland.

EXAMPLE Problem 17.1

Equilibrium Constant Expressions for Homogeneous Equilibria Millions of tons of ammonia (NH_3) are produced each year for use in the manufacture of products such as explosives, fertilizers, and synthetic fibers. You might have used ammonia in your home as a household cleaner, which is particularly useful for cleaning glass. Ammonia is manufactured from its elements, hydrogen and nitrogen, using the Haber process. Write the equilibrium constant expression for the following reaction.

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

1 Analyze the Problem

The equation for the reaction provides the information needed to write the equilibrium constant expression. The equilibrium is homogeneous because the reactants and product are in the same physical state.

The general form of the equilibrium constant expression is

$$K_{eq} = \frac{[C]^c}{[A]^a[B]^b}$$

Known

$[A] = [N_2]$, coefficient $N_2 = 1$

$[B] = [H_2]$, coefficient $H_2 = 3$

$[C] = [NH_3]$, coefficient $NH_3 = 2$

Unknown

$K_{eq} = ?$

2 Solve for the Unknown

Form a ratio of product concentration to reactant concentrations.

$$K_{eq} = \frac{[C]^c}{[A]^a[B]^b}$$ **State the general form of the equilibrium constant expression.**

$$K_{eq} = \frac{[NH_3]^c}{[N_2]^a[H_2]^b}$$ **Substitute A = N_2, B = H_2, and C = NH_3.**

$$K_{eq} = \frac{[NH_3]^2}{[N_2][H_2]^3}$$ **Substitute a = 1, b = 3, and c = 2.**

3 Evaluate the Answer

The product concentration is in the numerator and the reactant concentrations are in the denominator. Product and reactant concentrations are raised to powers equal to their coefficients.

PRACTICE Problems

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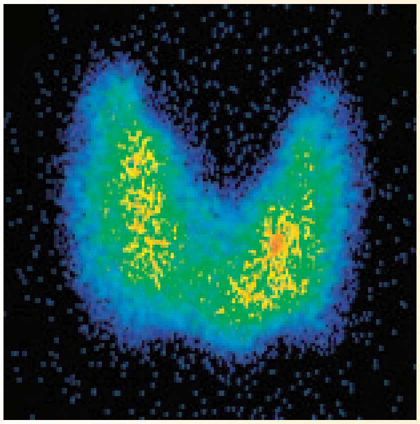
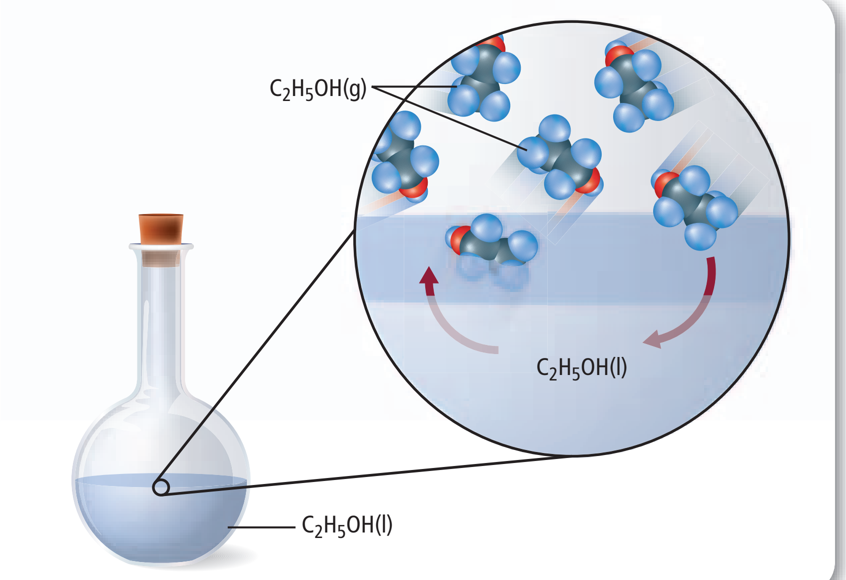
1. Write equilibrium constant expressions for these equilibria.
   - **a.** $N_2O_4(g) \rightleftharpoons 2NO_2(g)$
   - **b.** $2H_2S(g) \rightleftharpoons 2H_2(g) + S_2(g)$
   - **c.** $CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$
   - **d.** $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$
   - **e.** $CH_4(g) + 2H_2S(g) \rightleftharpoons CS_2(g) + 4H_2(g)$
2. **Challenge** Write the chemical equation that has the equilibrium constant expression $K_{eq} = \frac{[CO]^2[O_2]}{[CO_2]^2}$.

Real-World Chemistry
Thyroid Health



Nuclear Medicine Iodine-131 is a radioactive isotope that is absorbed by the thyroid gland. It is used in medicine to diagnose and treat diseases of the thyroid. When iodine-131 is administered to a patient, radiation from the isotope creates an image of the gland on film that reveals abnormalities. The image above shows the thyroid of a patient with Graves' disease, a treatable disease that is a common cause of an overactive thyroid gland.

Figure 17.8 At equilibrium the rate of evaporation of ethanol (C_2H_5OH) equals the rate of condensation. This two-phase equilibrium is called a heterogeneous equilibrium. K_{eq} depends only on $[C_2H_5OH(g)]$.



Expressions for heterogeneous equilibria You have learned to write K_{eq} expressions for homogeneous equilibria, those in which all reactants and products are in the same physical state. When the reactants and products are present in more than one physical state, the equilibrium is called a **heterogeneous equilibrium.** When ethanol is placed in a closed flask, a liquid-vapor equilibrium is established, as illustrated in **Figure 17.8.**

$$C_2H_5OH(l) \rightleftharpoons C_2H_5OH(g)$$

To write the equilibrium constant expression for this process, you would form a ratio of the product to the reactant. At a given temperature, the ratio would have a constant value K.

$$K = \frac{[C_2H_5OH(g)]}{[C_2H_5OH(l)]}$$

Note that the concentration of liquid ethanol is in the denominator. Liquid ethanol is a pure substance, so its concentration is its density expressed in moles per liter. Recall that at any given temperature, density is constant. No matter how much or how little C_2H_5OH is present, its concentration remains constant. Therefore, the term in the denominator is a constant and can be combined with K in the expression for K_{eq}.

$$\mathrm{K}[C_2H_5OH(l)] = [C_2H_5OH(g)] = K\,\mathrm{eq}$$

The equilibrium constant expression for this phase change is

$$K_{eq} = [C_2H_5OH(g)]$$

Solids are also pure substances with unchanging concentrations, so equilibria involving solids are simplified in the same way. Recall the experiment involving the sublimation of iodine crystals in **Figure 17.6.**

$$I_2(s) \rightleftharpoons I_2(g)$$
$$K_{eq} = [I_2(g)]$$

The equilibrium constant, K_{eq}, depends only on the concentration of gaseous iodine in the system.

EXAMPLE Problem 17.2

Equilibrium Constant Expressions for Heterogeneous Equilibria In addition to its uses in baking and as an antacid and cleaning agent, baking soda is often placed in open boxes in refrigerators to freshen the air as shown in **Figure 17.9.** Write the equilibrium constant expression for the decomposition of baking soda (sodium hydrogen carbonate).

$$2NaHCO_3(s) \rightleftharpoons Na_2CO_3(s) + CO_2(g) + H_2O(g)$$

1 Analyze the Problem

You are given a heterogeneous equilibrium involving gases and solids. Solids are omitted from the equilibrium constant expression.

Known

$[C] = [Na_2CO_3]$, coefficient $Na_2CO_3 = 1$
$[D] = [CO_2]$, coefficient $CO_2 = 1$
$[E] = [H_2O]$, coefficient $H_2O = 1$
$[A] = [NaHCO_3]$, coefficient $NaHCO_3 = 2$

Unknown

equilibrium constant expression = **?**

2 Solve for the Unknown

Form a ratio of product concentrations to reactant concentrations.

$$K_{eq} = \frac{[C]^c[D]^d[E]^e}{[A]^a[B]^b}$$

State the general form of the equilibrium constant expression.

$$K_{eq} = \frac{[NaCO_3]^c[CO_2]^d[H_2O]^e}{[NaHCO_3]^a}$$

Substitute A = $NaHCO_3$, C = Na_2CO_3, D = CO_2, and E = H_2O.

$$K_{eq} = \frac{[NaCO_3]^1[CO_2]^1[H_2O]^1}{[NaHCO_3]^2}$$

Substitute a = 2, c = 1, d = 1, and e = 1.

$$K_{eq} = [CO_2][H_2O]$$

Omit terms involving solid substances.

3 Evaluate the Answer

The expression correctly applies the law of chemical equilibrium to the equation.

PRACTICE Problems

Extra Practice Page 988 and glencoe.com

3. Write equilibrium constant expressions for these heterogeneous equilibria.
   - **a.** $C_{10}H_8(s) \rightleftharpoons C_{10}H_8(g)$
   - **b.** $H_2O(l) \rightleftharpoons H_2O(g)$
   - **c.** $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$
   - **d.** $C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$
   - **e.** $FeO(s) + CO(g) \rightleftharpoons Fe(s) + CO_2(g)$
4. **Challenge** Solid iron reacts with chlorine gas to form solid iron(III) chloride ($FeCl_3$). Write the balanced equation and the equilibrium constant expression for the reaction.

Figure 17.9 Sodium hydrogen carbonate (baking soda) absorbs odors and freshens the air in a refrigerator. It is also a key ingredient in some toothpastes.

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Equilibrium Constants

For a given reaction at a given temperature, K_{eq} will always be the same regardless of the initial concentrations of reactants and products. To test this statement, three experiments were carried out using the following reaction.

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

The results are summarized in **Table 17.1.** In Trial 1, 1.0000 mol H_2 and 2.0000 mol I_2 were placed in a 1.0000-L vessel. No HI was present at the beginning of Trial 1. In Trial 2, only HI was present at the start of the experiment. In Trial 3, each of the three substances had the same initial concentration. The reactions were carried out at 731 K.

Equilibrium concentrations When equilibrium was established, the concentration of each substance was determined experimentally. Note that the equilibrium concentrations are not the same in the three trials, yet when each set of equilibrium concentrations is put into the equilibrium constant expression, the value of K_{eq} is the same. Each set of equilibrium concentrations represents an equilibrium position.

The value of K_{eq} Although an equilibrium system has only one value for K_{eq} at a particular temperature, it has an unlimited number of equilibrium positions. Equilibrium positions depend on the initial concentrations of the reactants and products. The large value of K_{eq} for the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ means that at equilibrium the product is present in larger amount than the reactants. However, many equilibria have small K_{eq} values. For the equilibrium $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$, K_{eq} equals 4.6×10^{-31} at 298 K. A K_{eq} this small means that the product, NO, is practically nonexistent at equilibrium.

Equilibrium characteristics You might have noticed certain characteristics of all chemical reactions that reach equilibrium. First, the reaction must take place in a closed system—no reactant or product can enter or leave the system. Second, the temperature must remain constant. Third, all reactants and products are present, and they are in constant dynamic motion. This means that equilibrium is dynamic, not static.

Reading Check **Explain** why it is important that all reactants and products be present at equilibrium.

Table 17.1 Experimental Data for HI Reaction Equilibrium

	Initial Concentrations			Equilibrium Concentrations			K_{eq}
Trial	$[H_2]_0$ (*M*)	$[I_2]_0$ (*M*)	$[HI]_0$ (*M*)	$[H_2]_{eq}$ (*M*)	$[I_2]_{eq}$ (*M*)	$[HI]_{eq}$ (*M*)	$\frac{[HI]^2}{[H_2][I_2]} = K_{eq}$
1	1.0000	2.0000	0	0.06587	1.0659	1.8682	$\frac{[1.8682]^2}{[0.06587][1.0659]} = 49.70$
2	0	0	5.0000	0.5525	0.5525	3.8950	$\frac{[3.8950]^2}{[0.5525][0.5525]} = 49.70$
3	1.0000	1.0000	1.0000	0.2485	0.2485	1.7515	$\frac{[1.7515]^2}{[0.2485][0.2485]} = 49.70$

EXAMPLE Problem 17.3

Math Handbook
Solving Algebraic Equations
pages 954–955

The Value of Equilibrium Constants Calculate the value of K_{eq} for the equilibrium constant expression $K_{eq} = \frac{[NH_3]^2}{[N_2][H_2]^3}$ given concentration data at one equilibrium position: $[NH_3] = 0.933$ mol/L, $[N_2] = 0.533$ mol/L, $[H_2] = 1.600$ mol/L.

1 Analyze the Problem

You have been given the equilibrium constant expression and the concentration of each reactant and product. You must calculate the equilibrium constant.

Known

$K_{eq} = \frac{[NH_3]^2}{[N_2][H_2]^3}$

$[NH_3] = 0.933$ mol/L

$[N_2] = 0.533$ mol/L

$[H_2] = 1.600$ mol/L

Unknown

$K_{eq} = ?$

2 Solve for the Unknown

$$K_{eq} = \frac{[0.933]^2}{[0.533][1.600]^3} = 0.399$$

Substitute $[NH_3] = 0.933$ mol/L, $[N_2] = 0.533$ mol/L, and $[H_2] = 1.600$ mol/L.

3 Evaluate the Answer

The answer is correctly stated with three digits. The largest concentration value is in the denominator and raised to the third power, so a value less than 1 is reasonable.

PRACTICE Problems

Extra Practice Page 988 and glencoe.com

5. Calculate K_{eq} for the equilibrium in Practice Problem 1a on page 601 using the data $[N_2O_4] = 0.0185$ mol/L and $[NO_2] = 0.0627$ mol/L.

6. Calculate K_{eq} for the equilibrium in Practice Problem 1c on page 601 using the data $[CO] = 0.0613$ mol/L, $[H_2] = 0.1839$ mol/L, $[CH_4] = 0.0387$ mol/L, and $[H_2O] = 0.0387$ mol/L.

7. Challenge The reaction $COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$ reaches equilibrium at 900 K. K_{eq} is 8.2×10^{-2}. If the equilibrium concentrations of CO and Cl_2 are 0.150*M*, what is the equilibrium concentration of $COCl_2$?

Section 17.1 Assessment

Section Summary

- A reaction is at equilibrium when the rate of the forward reaction equals the rate of the reverse reaction.
- The equilibrium constant expression is a ratio of the molar concentrations of the products to the molar concentrations of the reactants with each concentration raised to a power equal to its coefficient in the balanced chemical equation.
- The value of the equilibrium constant expression, K_{eq}, is a constant for a given temperature.

8. MAIN Idea **Explain** how the size of the equilibrium constant relates to the amount of product formed at equilibrium.

9. Compare homogeneous and heterogeneous equilibria.

10. List three characteristics a reaction mixture must have if it is to attain a state of chemical equilibrium.

11. Calculate Determine the value of K_{eq} at 400 K for this equation: $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ if $[PCl_5] = 0.135$ mol/L, $[PCl_3] = 0.550$ mol/L, and $[Cl_2] = 0.550$ mol/L.

12. Interpret Data The table below shows the value of the equilibrium constant for a reaction at three different temperatures. At which temperature is the concentration of the products the greatest? Explain your answer.

K_{eq} and Temperature

263 K	273 K	373 K
0.0250	0.500	4.500

Section 17.2

Objectives

- **Describe** how various factors affect chemical equilibrium.
- **Explain** how Le Châtelier's principle applies to equilibrium systems.

Review Vocabulary

reaction rate: the change in concentration of a reactant or product per unit time, generally calculated and expressed in moles per liter per second.

New Vocabulary

Le Châtelier's principle

Factors Affecting Chemical Equilibrium

MAIN Idea When changes are made to a system at equilibrium, the system shifts to a new equilibrium position.

Real-World Reading Link When demand for a product equals the available supply, the price remains constant. If demand exceeds supply, the price of the product increases. The price becomes constant again when supply and demand regain a state of balance. Systems at equilibrium behave in a similar way.

Le Châtelier's Principle

Suppose the by-products of an industrial process are the gases carbon monoxide and hydrogen, and a company chemist believes these gases can be combined to produce the fuel methane (CH_4). When CO and H_2 are placed in a closed vessel at 1200 K, this exothermic reaction ($\Delta H = -06.5$ kJ) establishes equilibrium (Equilibrium Position 1).

$$\begin{array}{ccccccccc} CO(g) & + & 3H_2(g) & \rightleftharpoons & CH_4(g) & + & H_2O(g) & & \Delta H^\circ = -206.5\text{ kJ} \\ 0.30000M & & 0.10000M & & 0.05900M & & 0.02000M & & \end{array}$$

Inserting these concentrations into the equilibrium expression gives an equilibrium constant equal to 3.933.

$$K_{eq} = \frac{[CH_4][H_2O]}{[CO][H_2]^3} = \frac{(0.05900)(0.02000)}{(0.30000)(0.10000)^3} = 3.933$$

Unfortunately, a methane concentration of 0.05900 mol/L in the equilibrium mixture is too low to be of any practical use. Could the chemist change the equilibrium position and thereby increase the amount of methane? An analogy might be the runner on a treadmill shown in **Figure 17.10.** If the runner increases the speed of the treadmill, she must also increase her speed to restore equilibrium.

Figure 17.10 A runner gradually increases the speed of the treadmill. With each change, she must increase her running speed in order to restore her equilibrium at the new treadmill setting. Similarly, a chemist can change the conditions of a reaction at equilibrium in order to increase the amount of product.

In 1888, French chemist Henri-Louis Le Châtelier discovered that there are ways to control equilibria to make reactions more productive. He proposed what is now called **Le Châtelier's principle:** If a stress is applied to a system at equilibrium, the system shifts in the direction that relieves the stress. A stress is any kind of change in a system at equilibrium that upsets the equilibrium.

FOLDABLES Incorporate information from this section into your Foldable.

Applying LeChâtelier's Principle

How could the industrial chemist apply LeChâtelier's principle to increase her yield of methane? She will need to adjust any factors that will shift the equilibrium to the product side of the reaction.

Changes in concentration

Adjusting the concentrations of either the reactants or the products puts a stress on the equilibrium. In Chapter 16, you read about collision theory, which states that particles must collide in order to react. The number of collisions between reacting particles depends on the concentration of the particles, so perhaps the chemist can change the equilibrium by changing concentrations.

VOCABULARY
SCIENCE USAGE V. COMMON USAGE
Stress
Science usage: any kind of change in a system at equilibrium that upsets the equilibrium
The stress of the addition of more reactant to the reaction mixture caused the rate of the forward reaction to increase.

Common usage: physical or mental strain or pressure
He felt that the stress of taking on another task would be too great.

Adding reactants Suppose additional carbon monoxide is injected into the reaction vessel, raising the concentration of carbon monoxide from 0.30000*M* to 1.00000*M*. The higher carbon monoxide concentration immediately increases the number of effective collisions between CO and H_2 molecules and upsets the equilibrium. The rate of the forward reaction increases, as indicated by the longer arrow to the right.

$$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$$

In time, the rate of the forward reaction slows down as the concentrations of CO and H_2 decrease. Simultaneously, the rate of the reverse reaction increases as more CH_4 and H_2O molecules are produced. Eventually, a new equilibrium position (Position 2) is established.

$$\begin{array}{ccccccc} CO(g) & + & 3H_2(g) & \rightleftharpoons & CH_4(g) & + & H_2O(g) \\ 0.99254M & & 0.07762M & & 0.06648M & & 0.02746M \end{array}$$

$$K_{eq} = \frac{[CH_4][H_2O]}{[CO][H_2]^3} = \frac{(0.06648)(0.02746)}{(0.99254)(0.07762)^3} = 3.933$$

Note that although K_{eq} has not changed, the new equilibrium position results in the desired effect—an increased concentration of methane. The results of this experiment are summarized in **Table 17.2.**

Could you have predicted this result using Le Châtelier's principle? Yes. Think of the increased concentration of CO as a stress on the equilibrium. The equilibrium system reacts to the stress by consuming CO at an increased rate. This response, called a shift to the right, forms more CH_4 and H_2O. Any increase in the concentration of a reactant results in a shift to the right and additional product.

Table 17.2 At Equilibrium: $CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$

Equilibrium position	$[CO]_{eq}$ (*M*)	$[H_2]_{eq}$ (*M*)	$[CH4]_{eq}$ (*M*)	$[H_2O]_{eq}$ (*M*)	K_{eq}
1	0.30000	0.10000	0.05900	0.02000	3.933
2	0.99254	0.07762	0.06648	0.02746	3.933

■ **Figure 17.11** Storekeepers know that all products should be available at all times, so when stocks get low, they must be replaced.

Explain *this analogy in terms of Le Châtelier's principle.*

Removing products Suppose that rather than injecting more reactant, the chemist decides to remove a product (H_2O) by adding a desiccant to the reaction vessel. Recall from Chapter 10 that a desiccant is a substance that absorbs water. What does Le Châtelier's principle predict the equilibrium will do in response to a decrease in the concentration of water? The equilibrium shifts in the direction that will tend to bring the concentration of water back up. That is, the equilibrium shifts to the right and results in additional product.

Think about how supermarket shelves are kept stocked, as shown in **Figure 17.11.** As customers buy items from the shelves, it is someone's job to replace whatever is removed. Similarly, the equilibrium reaction restores some of the lost water by producing more water. In any equilibrium, the removal of a product results in a shift to the right and the production of more product.

Adding products The equilibrium position can also be shifted to the left, toward the reactants. Le Châtelier's principle predicts that if additional product is added to a reaction at equilibrium, the reaction will shift to the left. The stress is relieved by converting products to reactants. If one of the reactants is removed, a similar shift to the left will occur.

When predicting the results of a stress on an equilibrium using Le Châtelier's principle, have the equation for the reaction in view. The effects of changing concentrations are summarized in **Figure 17.12.**

Reading Check **Describe** how an equilibrium shifts if a reactant is removed.

Changes in volume and pressure Consider again the reaction for making methane from by-product gases.

$$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$$

Can this reaction be forced to produce more methane by changing the volume of the reaction vessel? Suppose the volume can be changed using a pistonlike device similar to the one shown in **Figure 17.13.** If the piston is forced downward, the volume of the system decreases. Recall from Chapter 13 that Boyle's law states that decreasing the volume at constant temperature increases the pressure. The increased pressure is a stress on the reaction at equilibrium. How does the equilibrium respond to the disturbance and relieve the stress?

■ **Figure 17.12** The addition or removal of a reactant or product shifts the equilibrium in the direction that relieves the stress. Note the unequal arrows, which indicate the direction of the shift.

Describe *how the reaction would shift if you added H_2. If you removed CH_4.*

$$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$$

Equilibrium shifts to the right.

1 $CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$

CO(g) Add a reactant.

2 $CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$

Remove a product.

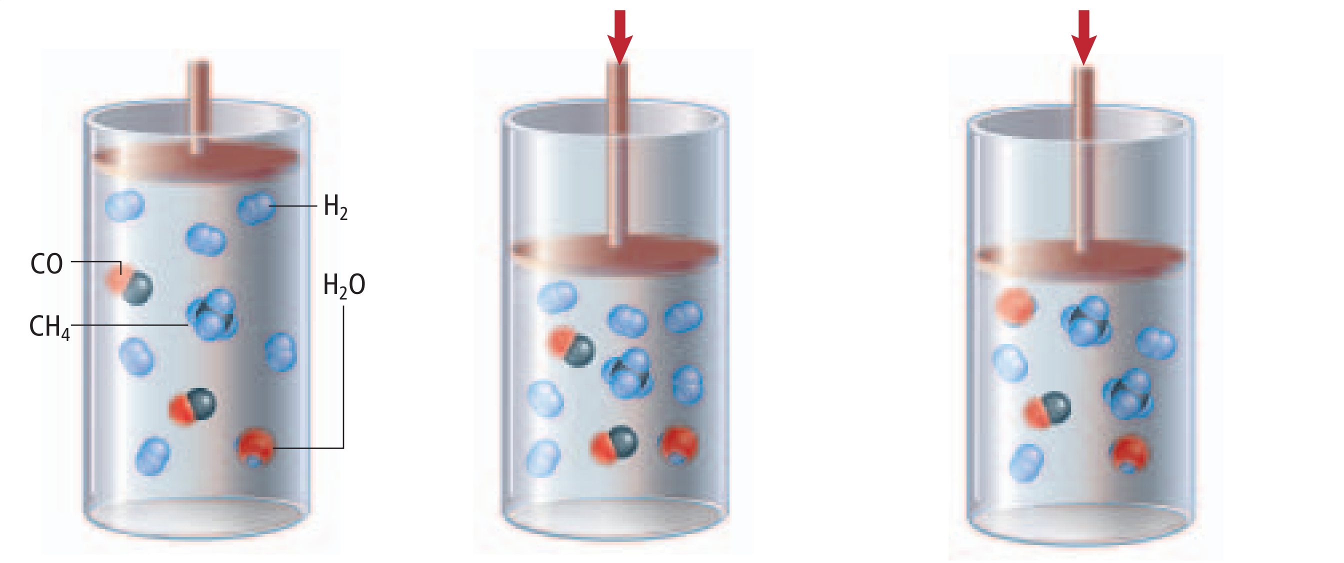
Equilibrium shifts to the left.

3 $CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$

Remove a reactant.

4 $CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$

Add a product. $H_2O(g)$



The reaction between CO and H_2 is at equilibrium.

Lowering the piston decreases the volume and increases the pressure.

As a result, more molecules of the products form. Their formation relieves the stress on the system.

Figure 17.13 For the reaction between CO and H_2 at constant temperature, changing the volume of the reaction vessel changes the concentrations of gaseous reactants and products. Increasing the pressure shifts the equilibrium to the right and increases the amount of product.

Compare ***the numbers of product molecules on the left with the numbers on the right.***

The pressure exerted by an ideal gas depends on the number of gas particles that collide with the walls of the vessel. The more gas particles contained in the vessel, the greater the pressure will be. If the number of gas particles is increased at constant temperature, the pressure of the gas increases. If the number of gas particles is decreased, the pressure decreases. How does this relationship between numbers of gas particles and pressure apply to the reaction for making methane?

Moles of reactant versus moles of product Compare the number of moles of gaseous reactants in the equation to the number of moles of gaseous products. For every two moles of gaseous products, four moles of gaseous reactants are consumed, a net decrease of two moles. If you apply Le Châtelier's principle, you can see that the equilibrium can relieve the stress of increased pressure by shifting to the right. **Figure 17.13** shows that this shift decreases the total number of moles of gas, and thus the pressure inside the reaction vessel decreases. Although the shift to the right does not reduce the pressure to its original value, it has the desired effect—more methane is produced.

Changing the volume (and pressure) of an equilibrium system shifts the equilibrium only if the number of moles of gaseous reactants is different from the number of moles of gaseous products. If the number of moles of gas is the same on both sides of the equation, changes in volume and pressure have no effect on the equilibrium.

Changes in temperature A change in temperature alters both the equilibrium position and the equilibrium constant. Recall that virtually every chemical reaction is either endothermic or exothermic. The reaction for making methane has a negative $\Delta H°$, which means that the forward reaction is exothermic and the reverse reaction is endothermic.

$$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g) \quad \Delta H° = -206.5\ kJ$$

In this case, you can think of heat as a product in the forward reaction and a reactant in the reverse reaction.

$$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g) + heat$$

■ **Figure 17.14** When placed in a warm-water bath, the equilibrium shifts in the endothermic direction, to the right, which produces more reddish-brown NO_2. The mixture becomes lighter in color when placed in an ice bath because the equilibrium shifts in the exothermic direction, to the left, in which more NO_2 is converted to colorless N_2O_4.

Concepts In Motion

Interactive Figure To see an animation of equilibrium shifts, visit glencoe.com.

Heat and equilibrium position According to Le Châtelier's principle, if heat is added to an equilibrium system, the equilibrium shifts in the direction in which heat is used up; that is, the equilibrium shifts to the left and decreases the concentration of methane (CH_4). Lowering the temperature shifts the equilibrium to the right because the forward reaction liberates heat and relieves the stress. In shifting to the right, the equilibrium produces more methane.

Temperature and *K* eq Any change in temperature results in a change in K_{eq}. Recall that the larger the value of K_{eq}, the more product is found in the equilibrium mixture. Thus, for the methane-producing reaction, K_{eq} increases in value when the temperature is lowered and decreases in value when the temperature is raised.

The conversion between dinitrogen tetroxide (N_2O_4) and nitrogen dioxide (NO_2) responds to changes in temperature in an observable way. This endothermic equilibrium is described by the following equation.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \quad \Delta H° = 55.3 \text{ kJ}$$

N_2O_4 is a colorless gas; NO_2 is a reddish-brown gas. **Figure 17.14** shows that the color of the equilibrium mixture, when cooled in an ice bath, is much lighter than when the mixture is heated in warm water. The removal of heat by cooling shifts the equilibrium to the left and creates more colorless N_2O_4. Adding heat shifts the equilibrium to the right and creates more reddish-brown NO_2. **Figure 17.15** shows the effects of heating and cooling on the reactions you have been reading about.

■ **Figure 17.15** For the exothermic reaction between CO and H_2, raising the temperature shifts the equilibrium to the left (Equation 1). Lowering the temperature results in a shift to the right (Equation 2). The opposite is true for the endothermic reaction involving NO and N_2O_4 (Equations 3 and 4).

Exothermic Reaction

Equilibrium shifts to the left. heat — Raise the temperature.

1. $CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g) + \text{heat}$

Equilibrium shifts to the right. Lower the temperature.

2. $CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g) + \text{heat}$

Endothermic Reaction

Equilibrium shifts to the right.

3. $\text{heat} + N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$

heat — Raise the temperature.

Equilibrium shifts to the left.

4. $\text{heat} + N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$

Lower the temperature.

MiniLab

Observe Shifts in Equilibrium

If a stress is placed on a reaction at equilibrium, how will the system shift to relieve the stress?

Procedure

1. Read and complete the lab safety form.
2. Place about 2 mL of **0.1*M* $CoCl_2$ solution** in a **test tube.** Record the color of the solution.
3. Add about 3 mL of **concentrated HCl** to the test tube. Record the color of the solution. **WARNING:** *HCl can burn skin and clothing.*
4. Add enough **water** to the test tube to make a color change occur. Record the color.
5. Add about 2 mL of 0.1*M* $CoCl_2$ to another test tube. Add concentrated HCl a drop at a time until the solution turns purple. If the solution becomes blue, add water until it turns purple.
6. Place the test tube in an **ice bath** that has had some **table salt** sprinkled into the ice water. Record the color of the solution in the test tube.
7. Place the test tube in a hot water bath. Use a **nonmercury thermometer** to determine that the temperature is at least 70°C. Record the solution's color.

Analysis

1. **Interpret** Use the equation for the reaction you just observed to explain your observations of color in Steps 2–4. The equation is as follows.

$$\underset{\text{pink}}{Co(H_2O)_6^{2+}} + 4Cl^- \rightleftharpoons \underset{\text{blue}}{CoCl_4^{2-}} + 6H_2O$$

2. **Describe** how the equilibrium shifts when energy is added or removed.
3. **Interpret** From your observations of color in Steps 6 and 7, determine whether the reaction is exothermic or endothermic.

Catalysts and equilibrium Changes in concentration, volume, and temperature make a difference in the amount of product formed in a reaction. Can a catalyst also affect product concentration? A catalyst speeds up a reaction, but it does so equally in both directions. Therefore, a catalyzed reaction reaches equilibrium more quickly but with no change in the amount of product formed.

Section 17.2 Assessment

Section Summary

- Le Châtelier's principle describes how an equilibrium system shifts in response to a stress or a disturbance.
- When an equilibrium shifts in response to a change in concentration or volume, the equilibrium position changes but K_{eq} remains constant. A change in temperature, however, alters both the equilibrium position and the value of K_{eq}.

13. MAIN Idea **Explain** how a system at equilibrium responds to a stress and list factors that can be stresses on an equilibrium system.
14. **Explain** how decreasing the volume of the reaction vessel affects each equilibrium.

    a. $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ **b.** $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$
15. **Decide** whether higher or lower temperatures will produce more CH_3CHO in the following equilibrium. $C_2H_2(g) + H_2O(g) \rightleftharpoons CH_3CHO(g)$ $\Delta H° = -151$ kJ
16. **Demonstrate** The table below shows the concentrations of Substances A and B in two reaction mixtures. A and B react according to the equation $2A \rightleftharpoons B$; $K_{eq} = 200$. Are the two mixtures at different equilibrium positions?

Concentration Data in mol/L

Reaction	[A]	[B]
1	0.0100	0.0200
2	0.0500	0.500

17. **Design** a concept map that shows ways in which Le Châtelier's principle can be applied to increase the products in a system at equilibrium and to increase the reactants in such a system.

Section 17.3

Objectives

- **Determine** equilibrium concentrations of reactants and products.
- **Calculate** the solubility of a compound from its solubility product constant.
- **Explain** the common ion effect.

Review Vocabulary

solubility: the maximum amount of solute that will dissolve in a given amount of solvent at a specific temperature and pressure

New Vocabulary

solubility product constant
common ion
common ion effect

Using Equilibrium Constants

MAIN Idea Equilibrium constant expressions can be used to calculate concentrations and solubilities.

Real-World Reading Link If you have ever tried to squeeze yourself into the backseat of a car already occupied by several of your friends, you know there is a limit to how many people the seat can hold. An ionic compound encounters a similar situation when being dissolved in a solution.

Calculating Equilibrium Concentrations

How can the equilibrium constant expression be used to calculate the concentration of a product? The K_{eq} for the reaction that forms CH_4 from H_2 and CO is 3.933 at 1200 K. If the concentrations of H_2, CO, and H_2O are known, the concentration of CH_4 can be calculated.

$$\begin{array}{cccc} CO(g) & + \; 3H_2(g) \rightleftharpoons & CH_4(g) \; + & H_2O(g) \\ 0.850M & 1.333M & ?M & 0.286M \end{array}$$

$$K_{eq} = \frac{[CH_4][H_2O]}{[CO][H_2O]^3}$$

Solve the expression for the unknown $[CH_4]$ by multiplying both sides of the equation by $[CO][H_2]^3$ and dividing both sides by $[H_2O]$.

$$[CH_4] = K_{eq} \times \frac{[CO][H_2]^3}{[H_2O]}$$

Substitute the known concentrations and the value of K_{eq} (3.933).

$$[CH_4] = 3.933 \times \frac{(0.850)(1.333)^3}{(0.286)} = 27.7 \text{ mol/L}$$

The equilibrium concentration of CH_4 is 27.7 mol/L.

Is a yield of of 27.7 mol/L sufficient to make the conversion of waste CO and H_2 to methane practical? That depends on the cost of methane. **Figure 17.16** shows a tanker transporting natural gas, which is primarily methane, to ports around the world.

Figure 17.16 New port terminals are being planned to accommodate tankers, which carry increasing amounts of natural gas around the world to meet both industrial and home needs. Natural gas, which is primarily methane, is used for heating and cooking.

EXAMPLE Problem 17.4

Math Handbook
Square and Cube Roots
page 949

Calculating Equilibrium Concentrations At 1405 K, hydrogen sulfide, which has a foul odor resembling rotten eggs, decomposes to form hydrogen and a diatomic sulfur molecule, S_2. The equilibrium constant for the reaction is 2.27×10^{-3}.

$$2H_2S(g) \rightleftharpoons 2H_2(g) + S_2(g)$$

What is the concentration of hydrogen gas if $[S_2] = 0.0540$ mol/L and $[H_2S] = 0.184$ mol/L?

1 Analyze the Problem

You have been given K_{eq} and two of the three variables in the equilibrium constant expression. The equilibrium expression can be solved for $[H_2]$. K_{eq} is less than one, so more reactants than products are in the equilibrium mixture. Thus, you can predict that $[H_2]$ will be less than 0.184 mol/L, the concentration of the reactant H_2S.

Known	**Unknown**
$K_{eq} = 2.27 \times 10^{-3}$	$[H_2]$ = ? mol/L
$[S_2] = 0.0540$ mol/L	
$[H_2S] = 0.184$ mol/L	

2 Solve for the Unknown

$$\frac{[H_2]^2[S_2]}{[H_2S]^2} = K_{eq}$$ **State the equilibrium constant expression.**

Solve the equation for $[H_2]$.

$$[H_2]^2 = K_{eq} \times \frac{[H_2S]^2}{[S_2]}$$ **Multiply both sides by $[H_2S]^2$. Divide both sides by $[S_2]$.**

$$[H_2] = \sqrt{K_{eq} \times \frac{[H_2S]^2}{[S_2]}}$$ **Take the square root of both sides.**

$$[H_2] = \sqrt{(2.27 \times 10^{-3}) \times \frac{(0.184)^2}{(0.0540)}}$$ **Substitute $K_{eq} = 2.27 \times 10^{-3}$, $[H_2S] = 0.184$ mol/L, and $[S_2] = 0.0540$ mol/L.**

$$[H_2] = 0.0377 \text{ mol/L}$$ **Multiply and divide.**

The equilibrium concentration of H_2 is 0.0377 mol/L.

3 Evaluate the Answer

The answer is correctly stated with three significant figures. As predicted, the equilibrium concentration of H_2 is less than 0.184 mol/L.

PRACTICE Problems

Extra Practice Page 988 and glencoe.com

18. At a certain temperature, $K_{eq} = 10.5$ for the equilibrium $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$. Calculate the following concentrations:

a. [CO] in an equilibrium mixture containing 0.933 mol/L H_2 and 1.32 mol/L CH_3OH

b. $[H_2]$ in an equilibrium mixture containing 1.09 mol/L CO and 0.325 mol/L CH_3OH

c. $[CH_3OH]$ in an equilibrium mixture containing 0.0661 mol/L H_2 and 3.85 mol/L CO

19. Challenge In a generic reaction $A + B \rightleftharpoons C + D$, 1.00 mol of A and 1.00 mol of B are allowed to react in a 1-L flask until equilibrium is established. If the equilibrium concentration of A is 0.450 m/L, what is the equilibrium concentration of each of the other substances? What is K_{eq}?

■ **Figure 17.17** The water of the Great Salt Lake is much saltier than sea water. The high concentration of salt makes the water dense enough that most people can float in it. The Salar de Uyuni, or Uyuni Salt Flats, at right, were left behind when a similar prehistoric lake dried.

The Solubility Product Constant

Some ionic compounds, such as sodium chloride, dissolve readily in water, and some, such as barium sulfate ($BaSO_4$) barely dissolve at all. On dissolving, all ionic compounds dissociate into ions.

$$NaCl(s) \longrightarrow Na^{+}(aq) + Cl^{-}(aq)$$

Connection to Earth Science Because of the high solubility of NaCl, the oceans and some lakes contain large amounts of salt. **Figure 17.17** shows the Great Salt Lake next to one of the Uyuni flats in Bolivia, which were left behind when a prehistoric lake dried.

Sometimes low solubility is also important. Although barium ions are toxic to humans, patients must ingest barium sulfate prior to having an X ray of the digestive tract taken. Can patients safely ingest $BaSO_4$?

Barium sulfate dissociates in water according to this equation.

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

As soon as the first product ions form, the reverse reaction begins.

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

In time, equilibrium is established.

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

For sparingly soluble compounds such as $BaSO_4$, the rates become equal when the concentrations of the aqueous ions are exceedingly small. Nevertheless, the solution at equilibrium is a saturated solution.

Writing solubility product constant expressions The equilibrium constant expression for the dissolving of a sparingly soluble compound is called the **solubility product constant,** K_{sp}. The solubility product constant expression is the product of the concentrations of the dissolved ions, each raised to the power equal to the coefficient of the ion in the chemical equation. Recall from page 602 that the concentration of a pure substance is its density in moles per liter, which is constant at a given temperature. Therefore, in heterogeneous equilibria, pure solids and liquids are omitted from equilibrium expressions.

Now you can write the solubility product constant expression for the dissolving of barium sulfate ($BaSO_4$) in water. The K_{sp} for the process is 1.1×10^{-10} at 298 K.

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

The small value of K_{sp} for $BaSO_4$ indicates that products are not favored at equilibrium. The concentration of barium ions at equilibrium is only $1.0 \times 10^{-5}M$, and a patient, such as the one shown in **Figure 17.18,** can safely ingest a barium sulfate solution.

The solubility product constant for the antacid magnesium hydroxide ($Mg(OH)_2$) provides another example.

$$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$$

$$K_{sp} = [Mg^{2+}][OH^-]^2$$

K_{sp} depends only on the concentrations of the ions in the saturated solution. However, some of the undissolved solid, no matter how small the amount, must be present in the equilibrium mixture.

The solubility product constants for some ionic compounds are listed in **Table 17.3.** Note that they are all small numbers. Solubility product constants are measured and recorded only for sparingly soluble compounds.

Using solubility product constants The solubility product constants in **Table 17.3** have been determined through careful experiments. K_{sp} values are important because they can be used to determine the solubility of a sparingly soluble compound. Recall that the solubility of a compound in water is the amount of the substance that will dissolve in a given volume of water at a given temperature.

Figure 17.18 Greater definition is possible in a gastrointestinal X ray when patients drink a thick mixture containing barium sulfate. Barium sulfate is a poisonous substance, but it has such low solubility that only a minimal amount can dissolve in the patient's body.

Table 17.3 Solubility Product Constants at 298 K

Compound	K_{sp}	Compound	K_{sp}	Compound	K_{sp}
Carbonates		**Halides**		**Hydroxides**	
$BaCO_3$	2.6×10^{-9}	CaF_2	3.5×10^{-11}	$Al(OH)_3$	4.6×10^{-33}
$CaCO_3$	3.4×10^{-9}	$PbBr_2$	6.6×10^{-6}	$Ca(OH)_2$	5.0×10^{-6}
$CuCO_3$	2.5×10^{-10}	$PbCl_2$	1.7×10^{-5}	$Cu(OH)_2$	2.2×10^{-20}
$PbCO_3$	7.4×10^{-14}	PbF_2	3.3×10^{-8}	$Fe(OH)_3$	4.9×10^{-17}
$MgCO_3$	6.8×10^{-6}	PbI_2	9.8×10^{-9}	$Fe(OH)_3$	2.8×10^{-39}
Ag_2CO_3	8.5×10^{-12}	$AgCl$	1.8×10^{-10}	$Mg(OH)_2$	5.6×10^{-12}
$ZnCO_3$	1.5×10^{-10}	$AgBr$	5.4×10^{-13}	$Zn(OH)_2$	3×10^{-17}
Hg_2CO_3	3.6×10^{-17}	AgI	8.5×10^{-17}	**Sulfates**	
Chromates		**Phosphates**		$BaSO_4$	1.1×10^{-10}
$BaCrO_4$	1.2×10^{-10}	$AlPO_4$	9.8×10^{-21}	$CaSO_4$	4.9×10^{-5}
$PbCrO_4$	2.3×10^{-13}	$Ca_3(PO_4)_2$	2.1×10^{-33}	$PbSO_4$	2.5×10^{-8}
Ag_2CrO_4	1.1×10^{-12}	$Mg_3(PO_4)_2$	1.0×10^{-24}	Ag_2SO_4	1.2×10^{-5}

Suppose you wish to determine the solubility of silver iodide (AgI) in mol/L at 298 K. The equilibrium equation and solubility product constant expression are as follows.

$$AgI(s) \rightleftharpoons Ag^+(aq) + I^-(aq)$$
$$K_{sp} = [Ag^+][I^-] = 8.5 \times 10^{-17} \text{ at } 298 \text{ K}$$

It is convenient to let *s* represent the solubility of AgI, that is, the number of moles of AgI that dissolves in one liter of solution. The equation indicates that for every mole of AgI that dissolves, an equal number of moles of Ag^+ ions forms in solution. Therefore, $[Ag^+]$ equals *s*. Every Ag^+ has an accompanying I^- ion, so $[I^-]$ also equals *s*. Substituting *s* for $[Ag^+]$ and $[I^-]$, the K_{sp} expression becomes the following.

$$[Ag^+][I^-] = (s)(s) = s^2 = 8.5 \times 10^{-17}$$
$$s = \sqrt{8.5 \times 10^{-17}} = 9.2 \times 10^{-9} \text{ mol/L}$$

The solubility of AgI is 9.2×10^{-9} mol/L at 298 K.

EXAMPLE Problem 17.5

Calculating Molar Solubility Use the K_{sp} value from **Table 17.5** to calculate the solubility in mol/L of copper(II) carbonate ($CuCO_3$) at 298 K.

1 Analyze the Problem

You have been given the solubility product constant for $CuCO_3$. The copper and carbonate ion concentrations are in a one-to-one relationship with the molar solubility of $CuCO_3$. Use *s* to represent the molar solubility of $CuCO_3$. Then use the solubility product constant expression to solve for the solubility. Because K_{sp} is of the order of 10^{-10}, you can predict that the solubility will be the square root of K_{sp}, or about 10^{-5}.

Known	**Unknown**
K_{sp} ($CuCO_3$) $= 2.5 \times 10^{-10}$	**s = ? mol/L**

2 Solve for the Unknown

$CuCO_3(s) \rightleftharpoons Cu^{2+}(aq) + CO_3^{2-}(aq)$	**State the balanced chemical equation for the solubility equilibrium.**
$K_{sp} = [Cu^{2+}][CO_3^{2-}] = 2.5 \times 10^{-10}$	**State the solubility product constant expression.**
$s = [Cu^{2+}] = [CO_3^{2-}]$	**Relate $[Cu^{2+}]$ and $[CO_3^{2-}]$ to the solubility of $CuCO_3$, s.**
$(s)(s) = s^2 = 2.5 \times 10^{-10}$	**Substitute s for $[Cu^{2+}]$ and $[CO_3^{2-}]$ in the expression for K_{sp}.**
$s = \sqrt{2.5 \times 10^{-10}} = \mathbf{1.6 \times 10^{-5}}$ **mol/L**	**Solve for s, and calculate the answer.**

The molar solubility of $CuCO_3$ in water at 298 K is 1.6×10^{-5} mol/L.

3 Evaluate the Answer

The K_{sp} value has two significant figures, so the answer is correctly expressed with two digits. As predicted, the molar solubility of $CuCO_3$ is approximately 10^{-5} mol/L.

PRACTICE Problems

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20. Use the data in **Table 17.3** to calculate the solubility in mol/L of the following ionic compounds at 298 K.

a. $PbCrO_4$ **b.** AgCl **c.** $CaCO_3$

21. Challenge The K_{sp} of lead carbonate ($PbCO_3$) is 7.40×10^{-14} at 298 K. What is the solubility of lead carbonate in g/L?

You have read that the solubility product constant can be used to determine the molar solubility of an ionic compound. You can apply this information as you perform the ChemLab at the end of this chapter. K_{sp} can also be used to find the concentrations of the ions in a saturated solution.

EXAMPLE Problem 17.6

Calculating Ion Concentration Magnesium hydroxide is a white solid obtained from seawater and used in the formulation of many medications, in particular those whose function is to neutralize excess stomach acid. Determine the hydroxide ion concentration in a saturated solution of $Mg(OH)_2$ at 298 K. The K_{sp} equals 5.6×10^{-12}.

1 Analyze the Problem

You have been given the K_{sp} for $Mg(OH)_2$. The moles of Mg^{2+} ions in solution equal the moles of $Mg(OH)_2$ that dissolved, but the moles of OH^- ions in solution are two times the moles of $Mg(OH)_2$ that dissolved. You can use these relationships to write the solubility product constant expression in terms of one unknown. Because the equilibrium expression is a third-power equation, you can predict that $[OH^-]$ will be approximately the cube root of 10^{-12}, or approximately 10^{-4}.

Known	**Unknown**
$K_{sp} = 5.6 \times 10^{-12}$	**$[OH^-]$ = ? mol/L**

2 Solve for the Unknown

$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$ — **State the equation for the solubility equilibrium.**

$K_{sp} = [Mg^{2+}][OH^-]^2 = 5.6 \times 10^{-12}$ — **State the K_{sp} expression.**

Let $x = [Mg^{2+}]$. Because there are two OH^- ions for every Mg^{2+} ion, $2x = [OH^-]$.

$(x)(2x)^2 = 5.6 \times 10^{-12}$ — **Substitute $x = [Mg^{2+}]$ and $2x = [OH^-]$**

$(x)(4)(x)^2 = 5.6 \times 10^{-12}$ — **Square the terms.**

$4x^3 = 5.6 \times 10^{-12}$ — **Combine the terms.**

$x^3 = \dfrac{5.6 \times 10^{-12}}{4} = 1.4 \times 10^{-12}$ — **Divide.**

$x = [Mg^{2+}] = \sqrt[3]{1.4 \times 10^{-12}} = 1.1 \times 10^{-4}$ mol/L — **Use your calculator to determine the cube root.**

Multiply $[Mg^{2+}]$ by 2 to obtain $[OH^-]$.

$[OH^-] = 2[Mg^{2+}] = 2(1.1 \times 10^{-4}\ \text{mol/L}) = \mathbf{2.2 \times 10^{-4}\ mol/L}$

3 Evaluate the Answer

The given K_{sp} has two significant figures, so the answer is correctly stated with two digits. As predicted, $[OH^-]$ is about 10^{-4} mol/L.

PRACTICE Problems

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22. Use K_{sp} values from **Table 17.3** to calculate the following.

a. $[Ag^+]$ in a solution of AgBr at equilibrium

b. $[F^-]$ in a saturated solution of CaF_2

c. $[Ag^+]$ in a solution of Ag_2CrO_4 at equilibrium

23. Calculate the solubility of Ag_3PO_4 ($K_{sp} = 2.6 \times 10^{-18}$).

24. **Challenge** The solubility of silver chloride (AgCl) is 1.86×10^{-4} g/100 g of H_2O at 298 K. Calculate the K_{sp} for AgCl.

Table 17.4	Ion Concentrations
Original Solutions (mol/L)	Mixture (mol/L)
$[Fe^{3+}] = 0.10$	$[Fe^{3+}] = 0.050$
$[Cl^-] = 0.30$	$[Cl^-] = 0.15$
$[K^+] = 0.40$	$[K^+] = 0.20$
$[Fe(CN)_6{}^{4-}] = 0.10$	$[Fe(CN)_6{}^{4-}] = 0.050$

Predicting precipitates Suppose equal volumes of 0.10*M* aqueous solutions of iron(III) chloride ($FeCl_3$) and potassium hexacyanoiron(II) ($K_4Fe(CN)_6$) are combined. Will a precipitate form as shown in **Figure 17.19?** The following double-replacement reaction might occur.

$$4FeCl_3 + 3K_4Fe(CN)_6 \longrightarrow 12KCl + Fe_4(Fe(CN)_6)_3$$

You can use K_{sp} to predict whether a precipitate will form when any two ionic solutions are mixed.

For the reaction above, a precipitate is likely to form only if either product, KCl or $Fe_4(Fe(CN)_6)_3$, has low solubility. You might know that KCl is a soluble compound and would be unlikely to precipitate. But K_{sp} for $Fe_4(Fe(CN)_6)_3$ is a very small number, 3.3×10^{-41}, which suggests that $Fe_4(Fe(CN)_6)_3$ might precipitate if the concentrations of its ions are large enough. How large is large enough?

The following equilibrium is possible between solid $Fe_4(Fe(CN)_6)_3$—a precipitate—and its ions in solution, Fe^{3+} and $Fe(CN)_6{}^{4-}$.

$$Fe_4(Fe(CN)_6)_3(s) \rightleftharpoons 4Fe^{3+}(aq) + 3Fe(CN)_6{}^{4-}(aq)$$

When the $FeCl_3$ and $Fe_4(Fe(CN)_6)_3(s)$ solutions are mixed, if the concentrations of the ions Fe^{3+} and $Fe(CN)_6{}^{4-}$ are greater than those that can exist in a saturated solution of $Fe_4(Fe(CN)_6)_3$, the equilibrium will shift to the left and $Fe_4(Fe(CN)_6)_3(s)$ will precipitate. To predict whether a precipitate will form when the two solutions are mixed, you must first calculate the concentrations of the ions.

Reading Check **Explain** the conditions under which you would predict that a precipitate would form.

Calculating ion concentrations **Table 17.4** shows the concentrations of the ions of reactants and products in the original solutions (0.10*M* $FeCl_3$ and 0.10*M* $K_4Fe(CN)_6$) and in the mixture immediately after equal volumes of the two solutions were mixed. Note that $[Cl^-]$ is three times as large as $[Fe^{3+}]$ because the ratio of Cl^- to Fe^{3+} in $FeCl_3$ is 3:1. Also note that $[K^+]$ is four times as large as $[Fe(CN)_6{}^{4-}]$ because the ratio of K^+ to $Fe(CN)_6{}^{4-}$ in $K_4Fe(CN)_6$ is 4:1. In addition, note that the concentration of each ion in the mixture is one-half its original concentration. This is because when equal volumes of two solutions are mixed, the same number of ions are dissolved in twice as much solution. Therefore, the concentration is reduced by one-half.

You can now use the data in the table to make a trial to see if the concentrations of Fe^{3+} and $Fe(CN)_6{}^{4-}$ in the mixed solution exceed the value of K_{sp} when substituted into the solubility product constant expression.

$$K_{sp} = [Fe^{3+}]^4[Fe(CN)_6{}^{4-}]^3$$

Remember that you have not determined whether the solution is saturated. When you make this substitution, it will not necessarily give the solubility product constant. Instead, it provides a number called the ion product (Q_{sp}). Q_{sp} is a trial value that can be compared with K_{sp}.

$$Q_{sp} = [Fe^{3+}]^4[Fe(CN)_6{}^{4-}]\ 3 = (0.050)^4(0.050)^3 = 7.8 \times 10^{-10}$$

You can now compare Q_{sp} and K_{sp}. This comparison can have one of three outcomes: Q_{sp} can be less than K_{sp}, equal to K_{sp}, or greater than K_{sp}.

Figure 17.19 Because its ion-product constant (Q_{sp}) is greater than K_{sp}, you could predict that this precipitate of $Fe_4(Fe(CN)_6)_3$ would form.

Concepts In Motion

Interactive Figure To see an animation of a precipitation reaction, visit glencoe.com.

1. If $Q_{sp} < K_{sp}$, the solution is unsaturated. No precipitate will form.
2. If $Q_{sp} = K_{sp}$, the solution is saturated, and no change will occur.
3. If $Q_{sp} > K_{sp}$, a precipitate will form, reducing the concentrations of the ions in the solution until the product of their concentrations in the K_{sp} expression equals the numerical value of K_{sp}. Then the system is in equilibrium, and the solution is saturated.

In the case of the $Fe_4(Fe(CN)_6)_3$ equilibrium, Q_{sp} (7.8×10^{-10}) is larger than K_{sp}(3.3×10^{-41}) and a deeply colored blue precipitate of $Fe_4(Fe(CN)_6)_3$ forms, as shown in **Figure 17.19.**

EXAMPLE Problem 17.7

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Solving Algebraic Equations
pages 954–955

Predicting a Precipitate Predict whether a precipitate of $PbCl_2$ will form if 100 mL of 0.0100*M* NaCl is added to 100 mL of 0.0200*M* $Pb(NO_3)_2$.

1 Analyze the Problem

You have been given equal volumes of two solutions with known concentrations. The concentrations of the initial solutions allow you to calculate the concentrations of Pb^{2+} and Cl^- ions in the mixed solution.

Known	Unknown
100 mL 0.0100*M* NaCl	$Q_{sp} > K_{sp}$?
100 mL 0.0200*M* $Pb(NO_3)_2$	
$K_{sp} = 1.7 \times 10^{-5}$	

2 Solve for the Unknown

$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$ — **State the equation for the dissolving of $PbCl_2$.**

$Q_{sp} = [Pb^{2+}][Cl^-]^2$ — **State the ion product expression, Q_{sp}.**

Mixing the solutions dilutes their concentrations by one-half.

$[Pb^{2+}] = \frac{0.0200M}{2} = 0.0100M$ — **Divide $[Pb^{2+}]$ by 2.**

$[Cl^-] = \frac{0.0100M}{2} = 0.00500M$ — **Divide $[Cl^-]$ by 2.**

$Q_{sp} = (0.0100)(0.00500)^2 = 2.5 \times 10^{-7}$ — **Substitute $[Pb^{2+}] = 0.0100M$ and $[Cl^-] = 0.00500M$ into Q_{sp}.**

$\mathbf{Q_{sp}\ (2.5 \times 10^{-7}) < K_{sp}\ (1.7 \times 10^{-5})}$ — **Compare Q_{sp} with K_{sp}.**

A precipitate will not form.

3 Evaluate the Answer

Q_{sp} is less than K_{sp}. The Pb^{2+} and Cl^- ions are not present in high enough concentrations in the mixed solution to cause precipitation to occur.

PRACTICE Problems

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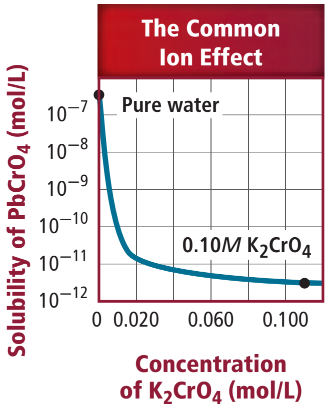
25. Use K_{sp} values from **Table 17.3** to predict whether a precipitate will form when equal volumes of the following solutions are mixed.
  a. 0.10*M* $Pb(NO_3)_2$ and 0.030*M* NaF
  b. 0.25*M* K_2SO_4 and 0.010*M* $AgNO_3$

26. Challenge Will a precipitate form when 250 mL of 0.20*M* $MgCl_2$ is added to 750 mL of 0.0025*M* NaOH?



Pure water: $[Pb^{2+}] = 4.8 \times 10^{-7}$ mol/L
$[CrO_4{}^{2-}] = 4.8 \times 10^{-7}$ mol/L
0.10*M* K_2CrO_4: $[Pb^{2+}] = 2.3 \times 10^{-12}$ mol/L
$[CrO_4{}^{2-}] = 1.00 \times 10^{-1}$ mol/L

■ **Figure 17.20** The solubility of lead chromate becomes lower as the concentration of the potassium chromate solution in which it is dissolved increases. The change is due to the presence of $CrO_4{}^{2-}$ in both lead chromate and potassium chromate.

Graph Check
Verify that K_{sp} does not change as the concentration of potassium chromate increases.

The Common Ion Effect

The solubility of lead chromate ($PbCrO_4$) in water is 4.8×10^{-7} mol/L at 298 K. That means you can dissolve 4.8×10^{-7} mol $PbCrO_4$ in 1.00 L of pure water. However, you cannot dissolve 4.8×10^{-7} mol $PbCrO_4$ in 1.00 L of 0.10*M* aqueous potassium chromate (K_2CrO_4) solution at that temperature. Why is $PbCrO_4$ less soluble in an aqueous K_2CrO_4 solution than in pure water?

The equation for the $PbCrO_4$ solubility equilibrium and the solubility product constant expression are as follows.

$$PbCrO_4(s) \rightleftharpoons Pb^{2+}(aq) + CrO_4{}^{2-}(aq)$$
$$K_{sp} = [Pb^{2+}][CrO_4{}^{2-}] = 2.3 \times 10^{-13}$$

Recall that K_{sp} is a constant at any given temperature, so if the concentration of either Pb^{2+} or $CrO_4{}^{2-}$ increases when the system is at equilibrium, the concentration of the other ion must decrease. The product of the concentrations of the two ions must always equal K_{sp}. The K_2CrO_4 solution contains $CrO_4{}^{2-}$ ions before any $PbCrO_4$ dissolves. In this example, the $CrO_4{}^{2-}$ ion is called a common ion because it is part of both $PbCrO_4$ and K_2CrO_4. **Figure 17.20** shows the effect of the common ion, the $CrO_4{}^{2-}$ ion, on the solubility of $PbCrO_4$. A **common ion** is an ion that is common to two or more ionic compounds. The lowering of the solubility of a substance because of the presence of a common ion is called the **common ion effect.**

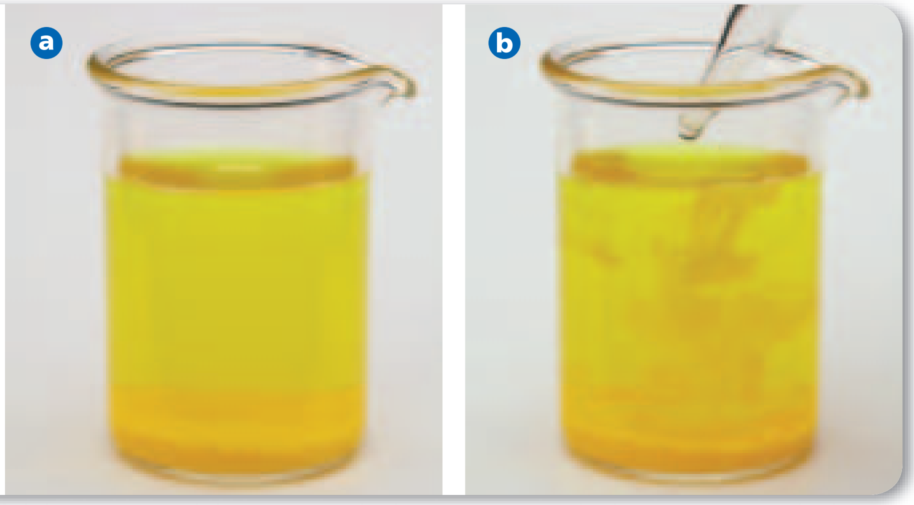
Applying Le Châtelier's principle

A saturated solution of lead chromate ($PbCrO_4$) is shown in **Figure 17.21a.** Note the solid-yellow $PbCrO_4$ in the bottom of the beaker. The solution and solid are in equilibrium according to the following equation.

$$PbCrO_4(s) \rightleftharpoons Pb^{2+}(aq) + CrO_4{}^{2-}(aq)$$

When a solution of $Pb(NO_3)$ is added to the saturated $PbCrO_4$ solution, more solid $PbCrO_4$ precipitates, as shown in **Figure 17.21b.** The Pb^{2+} ion, common to both $Pb(NO_3)_2$ and $PbCrO_4$, reduces the solubility of $PbCrO_4$. Can this precipitation of $PbCrO_4$ be explained by Le Châtelier's principle? Adding Pb^{2+} ion to the solubility equilibrium stresses the equilibrium. To relieve the stress, the equilibrium shifts to the left to form more solid $PbCrO_4$.

■ **Figure 17.21** Refer to **Figure 17.20** to see the effect of additional chromate ions on the solubility of lead chromate. Adding P b^{2+} ions in the form of lead nitrate (Pb(NO$_3$)$_2$) also affects the solubility of lead chromate. **a.** $PbCrO_4(s)$ is in equilibrium with its ions in solution. **b.** The equilibrium is stressed by the addition of $Pb(NO_3)_2$ and more $PbCrO_4$ precipitate forms.



The common ion effect also plays a role in the use of $BaSO_4$ when X rays of the digestive system are taken. The low solubility of $BaSO_4$ helps ensure that the amount of the toxic barium ion absorbed into patient's system is small enough to be harmless. The procedure is further safeguarded by the addition of sodium sulfate (Na_2SO_4), a soluble ionic compound that provides a common ion, SO_4^{2-} .

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

Le Châtelier's principle tells you that additional SO_4^{2-} from theNa_2SO_4 shifts the equilibrium to the left to produce more solid $BaSO_4$ and reduces the number of harmful Ba^{2+} ions in solution.

Problem-Solving Strategy

Using Assumptions

In Example Problem 17.5, you calculated the molar solubility of $CuCO_3$ in pure water as 1.6×10^{-5} mol/L. But suppose that $CuCO_3$ is dissolved in a solution of 0.10*M* K_2CO_3? A common ion is in solution. If you set up the problem the same way you did in Example Problem 17.5, you will need to solve a quadratic equation. Solving the quadratic equation results in the correct answer, but you can make a simple assumption that streamlines the problem-solving process.

Concentration	$CuCO_3$ (s) →	Cu^{2+} (aq) +	CO_3^{2-} (aq)
(*M*)			
Initial	—	0	0.10
Change	—	$+ s$	$+ s$
Equilibrium	—	s	$0.10 + s$

Using the Quadratic Equation

1. Set up the problem

$[Cu^{2+}][CO_3^{2-}] = 2.5 \times 10^{-10}$

$(s)(0.10 + s) = 2.5 \times 10^{-10}$

2. Solve the quadratic

$0.10s + s^2 = 2.5 \times 10^{-10}$

$s^2 + 0.10s - 2.5 \times 10^{-10} = 0$

$$s = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$= \frac{-0.10 \pm \sqrt{0.10^2 - (4)(1)(-2.5 \times 10^{-10})}}{2(1)}$$

$s = 2.5 \times 10^{-9}$ mol/L and $s = -0.10$ mol/L

Using the Simplifying Assumption

1. Set up the problem

$[Cu^{2+}][CO_3^{2-}] = 2.5 \times 10^{-10}$

$(s)(0.10 + s) = 2.5 \times 10^{-10}$

Because K_{sp} is small (2.5×10^{-10}), assume that s is negligible compared to 0.10*M*. Thus, $0.10 + s \approx 0.10$.

$(s)(0.10) = 2.5 \times 10^{-10}$

2. Solve the problem

$(s)(0.10) = 2.5 \times 10^{-10}$

$$s = \frac{2.5 \times 10^{-10}}{(0.10)} = 2.5 \times 10^{-9} \text{ mol/L}$$

The root of the quadratic that makes sense is $s = 2.5 \times 10^{-9}$ mol/L. As you can see by comparing the two answers, the assumption gave good results more quickly and easily. However, this assumption works only for sparingly soluble compounds.

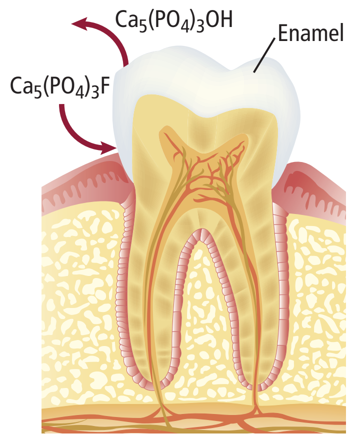
Apply the Strategy

Calculate the molar solubility of lead(II) fluoride in a 0.20 *M* $Pb(NO_3)_2$ solution.

PROBLEM-SOLVING LAB

Apply Scientific Explanations

How does the fluoride ion prevent tooth decay? During the last half century, tooth decay has decreased significantly because minute quantities of fluoride ion ($6 \times 10^{-5}M$) are being added to most public drinking-water systems, and most people are using toothpastes containing sodium fluoride or tin(II) fluoride. Use what you know about the solubility of ionic compounds and reversible reactions to explore the role of the fluoride ion in maintaining cavity-free teeth.



Analysis

Enamel, the hard, protective outer layer of the tooth, is 98% hydroxyapatite ($Ca_5(PO_4)_3OH$). Although insoluble in water ($K_{sp} = 6.8 \times 10^{-37}$), demineralization, which is the dissolving of hydroxyapatite, does occur, especially when the saliva contains acids. The reverse reaction, remineralization, also occurs. Remineralization is the redepositing of tooth enamel. When hydroxyapatite is in solution with fluoride ions, a double-replacement reaction can occur. A fluoride ion replaces the hydroxide ion to form fluoroapatite ($Ca_5(PO_4)_3F$), ($K_{sp} = 1 \times 10^{-60}$). Fluoroapatite remineralizes the tooth enamel, thus partially displacing hydroxyapatite. Because fluoroapatite is less soluble than hydroxyapatite, destructive demineralization is reduced.

Think Critically

1. **State** the equation for the dissolving of hydroxyapatite and its equilibrium constant expression. How do the conditions in the mouth differ from those of a true equilibrium?
2. **State** the equation that describes the double-replacement reaction that occurs between hydroxyapatite and sodium fluoride.
3. **Calculate** the solubility of hydroxyapatite and fluoroapatite in water. Compare the solubilities.
4. **Calculate** the ion product constant (Q_{sp}) for the reaction if $0.00050M$ NaF is mixed with an equal volume of $0.000015M$ $Ca_5(PO_4)_3OH$. Will a precipitate form (re-mineralization)?

Section 17.3 Assessment

Section Summary

- Equilibrium concentrations and solubilities can be calculated using equilibrium constant expressions.
- K_{sp} describes the equilibrium between a sparingly soluble ionic compound and its ions in solution.
- If the ion product, Q_{sp}, exceeds the K_{sp} when two solutions are mixed, a precipitate will form.
- The presence of a common ion in a solution lowers the solubility of a dissolved substance.

27. MAIN Idea **List** the information you would need in order to calculate the concentration of a product in a reaction mixture at equilibrium.
28. **Explain** how to use the solubility product constant to calculate the solubility of a sparingly soluble ionic compound.
29. **Describe** how the presence of a common ion reduces the solubility of an ionic compound.
30. **Explain** the difference between K_{sp} and Q_{sp}. Is Q_{sp} an equilibrium constant?
31. **Calculate** The K_{sp} of magnesium carbonate ($MgCO_3$) is 2.6×10^{-9}. What is the solubility of $MgCO_3$ in pure water?
32. **Design an experiment** based on solubilities to demonstrate which of two ions, Mg^{2+} or Pb^{2+}, is contained in an aqueous solution. Solubility information about ionic compounds is given in **Tables R-3** and **R-8** on pages 969 and 974 respectively.

Chemistry & Health

Hemoglobin Rises to the Challenge

When people travel to the mountains, they often feel tired and light-headed for a time. That's because the mountain air contains fewer oxygen molecules, as shown in **Figure 1.** Over time, the fatigue lessens. The body adapts by producing more of a protein called hemoglobin.

Hemoglobin-oxygen equilibrium

Hemoglobin (Hgb) binds with oxygen molecules that enter your bloodstream, producing oxygenated hemoglobin ($Hgb(O_2)_4$). The equilibrium of Hgb and O_2 is represented as follows.

$$Hgb(aq) + 4O_2(g) \rightleftharpoons Hgb(O_2)_4(aq)$$

In the lungs When you breathe, oxygen molecules move into your blood. The equilibrium reacts to the stress by consuming oxygen molecules at an increased rate. The equilibrium shifts to the right, increasing the blood concentration of $Hgb(O_2)_4$.

$$Hgb(aq) + 4O_2(g) \rightleftharpoons Hgb(O_2)_4(aq)$$

In the tissues When the $Hgb(O_2)_4$ reaches body tissues where oxygen concentrations are low, the equilibrium shifts to the left, releasing oxygen to enable the metabolic processes that produce energy.

$$Hgb(aq) + 4O_2(g) \leftrightharpoons Hgb(O_2)_4(aq)$$

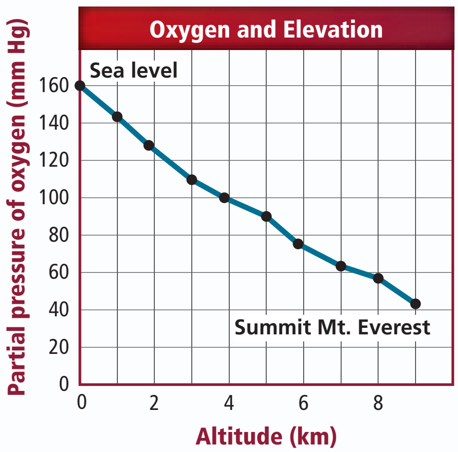


Figure 1 On the summit, the partial pressure of O_2 is much lower. Each breath a person draws contains fewer O_2 molecules.

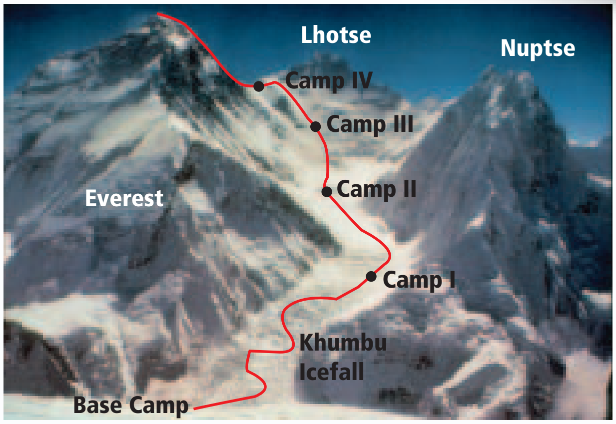


Figure 2 On Mount Everest, a climber might ascend to Camp II, descend to Base Camp, and then ascend to Camp III over the course of several days to prepare for a summit bid.

In the mountains The equilibrium reacts to the stress of thin mountain air by producing oxygen at an increased rate. The shift to the left releases oxygen molecules in your lungs, leaving less oxygenated hemoglobin in your blood.

$$Hgb(aq) + 4O_2(g) \leftrightharpoons Hgb(O_2)_4(aq)$$

The lower blood concentration of oxygenated hemoglobin means that fewer oxygen molecules are released in other parts of your body. Because less energy is produced, you feel tired.

The body adjusts. Your body responds to the lower oxygen concentration by producing more hemoglobin, part of a process known as acclimatization. More hemoglobin shifts the equilibrium position back to the right.

$$Hgb(aq) + 4O_2(g) \rightleftharpoons Hgb(O_2)_4(aq)$$

The increased concentration of $Hgb(O_2)_4(aq)$ means that more oxygen molecules can be released in your body tissues. **Figure 2** shows where climbers might adjust their bodies to high elevations before beginning their summit bid.

WRITING in Chemistry

Research the sleep disorder apnea. How would an incident of apnea affect the body's hemoglobin equilibrium? Visit glencoe.com to learn more about hemoglobin and its function in the human body.

CHEMLAB

SMALL SCALE

COMPARE TWO SOLUBILITY PRODUCT CONSTANTS

Background: **By observing the formation of two precipitates in the same system, you can infer the relationship between the solubilities of the two ionic compounds and the numerical values of their solubility product constants (K_{sp}).**

Question: *How can you use Le Châtelier's principle to evaluate the relative solubilities of two precipitates?*

Materials

$AgNO_3$ solution
NaCl solution
Na_2S solution
24-well microplate
thin-stem pipettes (3)

Safety Precautions

WARNING: ***Silver nitrate is highly toxic and will stain skin and clothing. Sodium sulfide is a skin irritant and should be kept away from acids.***

Procedure

1. Read and complete the lab safety form.
2. Place 10 drops of $AgNO_3$ solution in Well A1 of a 24-well microplate. Place 10 drops of the same solution in Well A2.
3. Add 10 drops of NaCl solution to Well A1 and 10 drops to Well A2.
4. Allow the precipitates to form. Observe the wells from the top and the side and record your observations.
5. To Well A2, add 10 drops of Na_2S solution.
6. Allow the precipitate to form. Record your observations of the precipitate.
7. Compare the contents of Wells A1 and A2, and record your observations.
8. **Cleanup and Disposal** Use a wash bottle to transfer the contents of the well plate into a waste beaker.

Analyze and Conclude

1. **Analyze** Write the complete equation for the reaction that occurred when you mixed NaCl and $AgNO_3$ in Step 3. Write the net ionic equation.
2. **Analyze** Write the solubility product constant expression for the equilibrium established in Wells A1 and A2 in Step 3. K_{sp} (AgCl) $= 1.8 \times 10^{-10}$.
3. **Analyze** Write the equation for the equilibrium that was established in Well A2 when you added Na_2S. K_{sp} $(Ag_2S) = 8 \times 10^{-48}$.
4. **Identify** the two precipitates by color.
5. **Compare** the K_{sp} values for the two precipitates. Which of the two ionic compounds is more soluble?
6. **Recognize Cause and Effect** Use Le Châtelier's principle to explain how the addition of Na_2S in Step 5 affected the equilibrium established in Well A2.
7. **Calculate** the molar solubilities of the two precipitates using the K_{sp} values. Which of the precipitates is more soluble?
8. **Identify** What evidence from this experiment supports your answer to Question 7? Explain.
9. **Error Analysis** Compare your observations of the well plate from the side with your observations from the top. What did you notice?
10. **Research** how industries use precipitation to remove hazardous chemicals from wastewater.

INQUIRY EXTENSION

Soluble v. Insoluble The reactants that you used in this ChemLab are all soluble ionic compounds, and the precipitates are insoluble. How does soluble Na_2S differ from insoluble Ag_2S? How does soluble NaCl differ from insoluble AgCl? Use this information, K_{sp} data from **Table 17.3,** and other reference sources to develop general rules for solubility.

Matt Meadows

CHAPTER 17 Study Guide

BIG Idea Many reactions and processes reach a state of chemical equilibrium in which both reactants and products are formed at equal rates.

Section 17.1 A State of Dynamic Balance

MAIN Idea Chemical equilibrium is described by an equilibrium constant expression that relates the concentrations of reactants and products.

Vocabulary

- chemical equilibrium (p. 596)
- equilibrium constant (p. 599)
- heterogeneous equilibrium (p. 602)
- homogeneous equilibrium (p. 600)
- law of chemical equilibrium (p. 599)
- reversible reaction (p. 595)

Key Concepts

- A reaction is at equilibrium when the rate of the forward reaction equals the rate of the reverse reaction.
- The equilibrium constant expression is a ratio of the molar concentrations of the products to the molar concentrations of the reactants with each concentration raised to a power equal to its coefficient in the balanced chemical equation.

$$K_{eq} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

- The value of the equilibrium constant expression, K_{eq}, is a constant for a given temperature.

Section 17.2 Factors Affecting Chemical Equilibrium

MAIN Idea When changes are made to a system at equilibrium, the system shifts to a new equilibrium position.

Vocabulary

- Le Châtelier's principle (p. 607)

Key Concepts

- Le Châtelier's principle describes how an equilibrium system shifts in response to a stress or a disturbance.
- When an equilibrium shifts in response to a change in concentration or volume, the equilibrium position changes but K_{eq} remains constant. A change in temperature, however, alters both the equilibrium position and the value of K_{eq}.

Section 17.3 Using Equilibrium Constants

MAIN Idea Equilibrium constant expressions can be used to calculate concentrations and solubilities.

Vocabulary

- common ion (p. 620)
- common ion effect (p. 620)
- solubility product constant (p. 614)

Key Concepts

- Equilibrium concentrations and solubilities can be calculated using equilibrium constant expressions.
- K_{sp}, describes the equilibrium between a sparingly soluble ionic compound and its ions in solution.
- If the ion product, Q_{sp}, exceeds the K_{sp} when two solutions are mixed, a precipitate will form.
- The presence of a common ion in a solution lowers the solubility of a dissolved substance.

CHAPTER 17 Assessment

Section 17.1

Mastering Concepts

33. Describe an equilibrium in everyday life that illustrates a state of balance between two opposing processes.

34. Given the fact that the concentrations of reactants and products are not changing, why is the word *dynamic* used to describe chemical equilibrium?

35. Explain how a person bailing out a row boat with a leak could represent a state of physical equilibrium.

36. Does the following equation represent a homogeneous equilibrium or a heterogeneous equilibrium? Explain. your answer.

$$H_2O(s) \rightleftharpoons H_2O(l)$$

37. What is an equilibrium position?

38. Explain how to write an equilibrium constant expression.

39. Why should you pay attention to the physical states of reactants and products when writing equilibrium constant expressions?

40. Why does a numerically large K_{eq} mean that the products are favored in an equilibrium system?

41. What happens to K_{eq} for an equilibrium system if the equation for the reaction is rewritten in the reverse?

42. How can an equilibrium system contain small and unchanging amounts of products yet have large amounts of reactants? What can you say about the relative size of K_{eq} for such an equilibrium?

43. A system, which contains only molecules as reactants and products, is at equilibrium. Describe what happens to the concentrations of the reactants and products and what happens to individual reactant and product molecules.

Mastering Problems

44. Write equilibrium constant expressions for these homogeneous equilibria.
a. $2N_2H_4(g) + 2NO_2(g) \rightleftharpoons 3N_2(g) + 4H_2O(g)$
b. $2NbCl_4(g) \rightleftharpoons NbCl_3(g) + NbCl_5(g)$

45. Write equilibrium constant expressions for these heterogeneous equilibria.
a. $2NaHCO_3(s) \rightleftharpoons Na_2CO_3(s) + H_2O(g) + CO_2(g)$
b. $C_6H_6(l) \rightleftharpoons C_6H_6(g)$

46. Heating limestone ($CaCO_3(s)$) forms quicklime ($CaO(s)$) and carbon dioxide gas. Write the equilibrium constant expression for this reversible reaction.

47. Suppose you have a cube of pure manganese metal measuring 5.25 cm on each side. You find that the mass of the cube is 1076.6 g. What is the molar concentration of manganese in the cube?

48. K_{eq} is 3.63 for the reaction $A + 2B \rightleftharpoons C$. **Table 17.5** shows the concentrations of the reactants and product in two different reaction mixtures at the same temperature. Determine whether both reactions are at equilibrium.

Table 17. 5 Concentrations of A, B, and C

A (mol/L)	B (mol/L)	C (mol/L)
0.500	0.621	0.700
0.250	0.525	0.250

49. When steam is passed over iron filings, solid iron(III) oxide and gaseous hydrogen are produced in a reversible reaction. Write the balanced chemical equation and the equilibrium constant expression for the reaction, which yields iron(III) oxide and hydrogen gas.

Section 17.2

Mastering Concepts

50. What is meant by a stress on a reaction at equilibrium?

51. How does Le Châtelier's principle describe an equilibrium's response to a stress?

52. Why does removing a reactant cause an equilibrium shift to the left?

53. When an equilibrium shifts to the right, what happens to each of the following?
a. the concentration of the reactants
b. the concentration of the products

54. **Carbonated Beverages** Use Le Châtelier's principle to explain how a shift in the equilibrium $H_2CO_3(aq) \rightleftharpoons H_2O(l) + CO_2(g)$ causes a soft drink to go flat when its container is left open.

55. How would each of the following changes affect the equilibrium position of the system used to produce methanol from carbon monoxide and hydrogen?

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g) + \text{heat}$$

a. adding CO to the system
b. cooling the system
c. adding a catalyst to the system
d. removing CH_3OH from the system
e. decreasing the volume of the system

56. Explain how a temperature increase would affect the equilibrium represented by the following equation.

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g) + \text{heat}$$

57. A liquid solvent for chlorine is poured into a flask in which the following reaction is at equilibrium: $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g) + \text{heat}$. How is the equilibrium affected when some of the chlorine gas dissolves?

■ **Figure 17.22**

58. **Figure 17.22** shows the following endothermic reaction at equilibrium at room temperature.

$Co(H_2O)_6^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons CoCl_4^{2-}(aq) + 6H_2O(l)$

Given that $Co(H_2O)_6^{2+}(aq)$ is pink and $CoCl_4^{2-}(aq)$ is blue, what visual change would you expect to see if the flask were placed in an ice bath? Explain.

59. For the equilibrium described in Question 54, what visual change would you expect to see if 10 g of solid potassium chloride were added and dissolved? Explain.

60. Given two reactions at equilibrium:

a. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
b. $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$,

explain why changing the volume of the systems alters the equilibrium position of **a** but has no effect on **b.**

61. Would you expect the numerical value of K_{eq} for the following equilibrium to increase or decrease with increasing temperature? Explain your answer.

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g) + \text{heat}$$

62. Explain how you would regulate the pressure to favor the products in the following equilibrium system.

$$MgCO_3(s) \rightleftharpoons MgO(s) + CO_2(g)$$

63. Ethylene (C_2H_4) reacts with hydrogen to form ethane (C_2H_6).

$$C_2H_4(g) + H_2(g) \rightleftharpoons C_2H_6(g) + \text{heat}$$

How would you regulate the temperature of this equilibrium in order to accomplish each of the following?

a. increase the yield of ethane
b. decrease the concentration of ethylene
c. increase the amount of hydrogen in the system

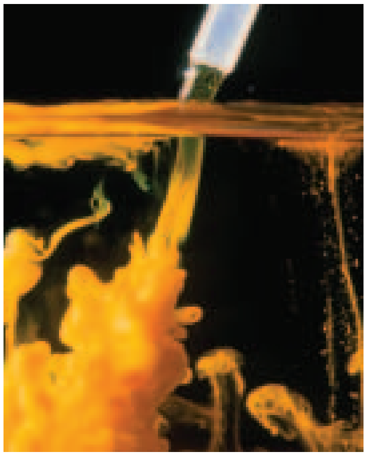
Section 17.3

Mastering Concepts

64. What does it mean to say that two solutions have a common ion? Give an example.

65. Why are compounds such as sodium chloride usually not given K_{sp} values?

66. **X rays** Why is barium sulfate a better choice than barium chloride for adding definition to X rays? At 26°C, 37.5 g of $BaCl_2$ can be dissolved in 100 mL of water.



■ **Figure 17.23**

67. Explain what is happening in **Figure 17.23** in terms of Q_{sp} and K_{sp}.

68. Explain why a common ion lowers the solubility of an ionic compound.

69. Describe the solution that results when two solutions are mixed and Q_{sp} is found to equal K_{sp}. Does a precipitate form?

Mastering Problems

70. Write the K_{sp} expression for lead chromate ($PbCrO_4$), and calculate its solubility in mol/L. $K_{sp} = 2.3 \times 10^{-13}$

71. At 350°C, $K_{eq} = 1.67 \times 10^{-2}$ for the reversible reaction $2HI(g) \rightleftharpoons H^2(g) + I^2(g)$. What is the concentration of HI at equilibrium if $[H^2]$ is 2.44×10^{-3} M and $[I^2]$ is 7.18×10^{-5} M?

72. K_{sp} for scandium fluoride (ScF_3) at 298 K is 4.2×10^{-18}. Write the chemical equation for the solubility equilibrium of scandium fluoride in water. What concentration of Sc^{3+} ions is required to cause a precipitate to form if the fluoride-ion concentration is 0.076M?

73. Will a precipitate form when 62.6 mL of 0.0322M $CaCl_2$ and 31.3 mL of 0.0145M NaOH are mixed? Use data from **Table 17.4** on page 615. Explain your logic.

74. **Manufacturing** Ethyl acetate ($CH_3COOCH_2CH_3$), a solvent used in making varnishes and lacquers, can be produced by the reaction between ethanol and acetic acid. The equilibrium system is described by the equation

$$CH_3COOH + CH_3CH_2OH \rightleftharpoons CH_3COOCH_2CH_3 + H_2O.$$

Calculate K_{eq} using these equilibrium concentrations: $[CH_3COOCH_2CH_3] = 2.90M$, $[CH_3COOH] = 0.316M$, $[CH_3CH_2OH] = 0.313M$, and $[H_2O] = 0.114M$.

Mixed Review

75. Ethyl acetate ($CH_3COOCH_2CH_3$) is produced in the equilibrium system described by the following equation.

$$CH_3COOH + CH_3CH_2OH \rightleftharpoons CH_3COOCH_2CH_3 + H_2O$$

Why does the removal of water result in the production of more ethyl acetate?

76. How would these equilibria be affected by decreasing the temperature?

a. $2O_3(g) \rightleftharpoons 3O_2(g) + \text{heat}$

b. $\text{heat} + H_2(g) + F_2(g) \rightleftharpoons 2HF(g)$

77. How would simultaneously increasing the temperature and volume of the system affect these equilibria?

a. $2O_3(g) \rightleftharpoons 3O_2(g) + \text{heat}$

b. $\text{heat} + N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

78. The solubility product constant for lead(II) arsenate ($Pb_3(AsO_4)_2$) is 4.0×10^{-36} at 298 K. Calculate the molar solubility of the compound at this temperature.

79. Evaluate this statement: A low value for K_{eq} means that both the forward and reverse reactions are occurring slowly.

80. Food Flavoring Benzaldehyde, known as artificial almond oil, is used in food flavorings. What is the molar concentration of benzaldehyde (C_7H_6O) at 298 K, when its density is 1.043 g/mL?

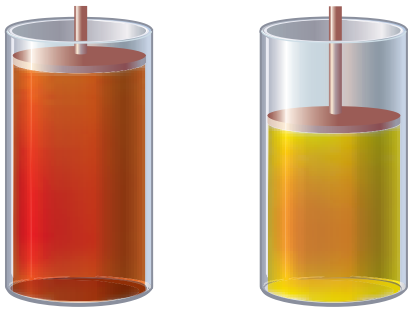


Figure 17.24

81. In the equilibrium system $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, N_2O_4 is colorless and NO_2 is reddish-brown. Explain the different colors of the equilibrium system as shown in **Figure 17.24.**

82. Describe the process by which adding potassium hydroxide to a saturated aluminum hydroxide solution reduces the concentration of aluminum ions. Write the solubility equilibrium equation and solubility product constant expression for a saturated aqueous solution of aluminum hydroxide.

83. At 298 K, K_{sp} for cadmium iodate ($Cd(IO_3)_2$) equals 2.3×10^{-8}. What are the molar concentrations of cadmium ions and iodate ions in a saturated solution at 298 K?

Think Critically

84. Analyze Suppose that an equilibrium system at a given temperature has a K_{eq} equal to 1.000. Evaluate the possibility that such a system is made up of 50% reactants and 50% products. Explain your answer.

85. Evaluate Imagine that you are a chemical engineer designing a production facility for a particular process. The process will utilize a reversible reaction that reaches a state of equilibrium. Analyze the merits of a continuous-flow process or a batch process for such a reaction and determine which is preferable. As a reaction proceeds in a continuous-flow process, reactants are continuously introduced into the reaction chamber and products are continuously removed from the chamber. In a batch process, the reaction chamber is charged with reactants, the reaction is allowed to occur, and the chamber is later emptied of all materials.

86. Interpret Data What compound would precipitate first if a 0.500*M* sodium fluoride solution were added gradually to a solution already containing 0.500*M* concentrations of both barium ions and magnesium ions? Use the data in **Table 17.6.** Write the solubility equilibrium equations and solubility product constant expressions for both compounds. Explain your answer.

Table 17.6 Data for Two Compounds

Compound	Molar Mass (g/mol)	Solubility at 25°C (g/L)
BaF_2	175.33	1.1
MgF_2	62.30	0.13

87. Apply Smelling salts, sometimes used to revive a person who is unconscious, are made of ammonium carbonate. The equation for the endothermic decomposition of ammonium carbonate is as follows.

$$(NH_4)_2CO_3(s) \rightleftharpoons 2NH_3(g) + CO_2(g) + H_2O(g)$$

Would you expect smelling salts to work as well on a cold winter day as on a warm summer day? Explain your answer.

88. Recognize Cause and Effect Suppose you have 12.56 g of a mixture made up of sodium chloride and barium chloride. Explain how you could use a precipitation reaction to determine how much of each compound the mixture contains.

89. Compare and Contrast Which of the two solids, calcium phosphate or iron(III) phosphate, has the greater molar solubility? K_{sp} ($Ca_3(PO_4)_2$) $= 1.2 \times 10^{-29}$; K_{sp} ($FePO_4$) $= 1.0 \times 10^{-22}$. Which compound has the greater solubility, expressed in grams per liter?

Challenge Problem

90. Synthesis of Phosgene Phosgene ($COCl_2$) is a toxic gas that is used in the manufacture of certain dyes, pharmaceuticals, and pesticides. Phosgene can be produced by the reaction between carbon monoxide and chlorine described by the equation $CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$. Initially 1.0000 mol CO and 1.0000 mol Cl_2 are introduced into a 10.00-L reaction vessel. When equilibrium is established, both of their molar concentrations are found to be 0.0086 mol/L. What is the molar concentration of phosgene at equilibrium? What is K_{eq} for the system?

Cumulative Review

91. Explain the general trend in ionization energy as you go from left to right along Periods 1–5 of the periodic table. *(Chapter 6)*

92. How are the lengths of covalent bonds related to their strength? *(Chapter 8)*

93. How are the chemical bonds in H_2, O_2, and N_2 different? *(Chapter 8)*

94. How can you tell if a chemical equation is balanced? *(Chapter 9)*

95. What mass of carbon must burn to produce 4.56 L CO_2 gas at STP? *(Chapter 11)*

$$C(s) + O_2(g) \rightarrow CO_2(g)$$

96. Describe a hydrogen bond. What conditions must exist for a hydrogen bond to form? *(Chapter 12)*

■ **Figure 17.25**

97. What gas law is exemplified in **Figure 17.25?** State the law. *(Chapter 13)*

98. When you reverse a thermochemical equation, why must you change the sign of ΔH? *(Chapter 15)*

99. What is the sign of the free energy change, $\Delta G°_{system}$, for a spontaneous reaction? *(Chapter 15)*

Additional Assessment

WRITING in Chemistry

100. A New Compound Imagine that you are a scientist who has created a unique new liquid. You have named the liquid *yollane*, abbreviated *yo*. Yollane is nontoxic, inexpensive to make, and can dissolve huge volumes of gaseous carbon dioxide in the equilibrium $CO_2(g) \rightleftharpoons CO_2(yo)$, $K_{eq} = 3.4 \times 10^6$. Write a newspaper or magazine article that explains the merits of yollane in combating global warming.

101. Kidney Stones Research the role that solubility plays in the formation of kidney stones. Find out what compounds are found in kidney stones and their K_{sp} values. Summarize your findings in a health information flyer.

102. Hard Water The presence of magnesium and calcium ions in water makes the water "hard." Explain in terms of solubility why the presence of these ions is often undesirable. Find out what measures can be taken to eliminate them.

DBQ Document-Based Question

Reducing Pollution *Automobile exhausts contain the dangerous pollutants nitrogen monoxide (NO) and carbon monoxide (CO). An alloy catalyst offers a promising way to reduce the amounts of these gases in the atmosphere. When NO and CO are passed over this catalyst, the following equilibrium is established.*

$$2NO(g) + 2CO(g) \rightleftharpoons N_2(g) + 2CO_2(g)$$

The equilibrium constant is found to vary with temperature as shown in **Table 17.7.**

Data obtained from: Worz, et al. 2003. Cluster size-dependent mechanisms of the CO + NO reaction on small Pdn (N < or = 30) clusters on oxide surfaces. *J Am Chem Soc. 125(26): 7964–70.*

Table 17.7 K_{eq} v. Temperature

700 K	800 K	900 K	1000 K
9.10×10^{97}	1.04×10^{66}	4.66×10^{54}	3.27×10^{45}

103. Write the equilibrium constant expression for this equilibrium.

104. Examine the relationship between K_{eq} and temperature. Use Le Châtelier's principle to deduce whether the forward reaction is exothermic or endothermic.

105. Explain how automobile radiators plated with the alloy might help reduce the atmospheric concentrations of NO and CO.

Cumulative

Standardized Test Practice

Multiple Choice

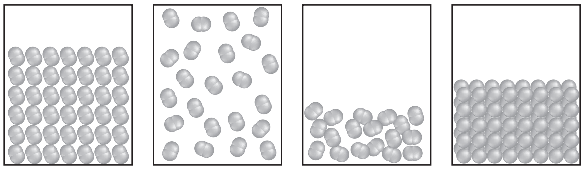
1. Which describes a system that has reached chemical equilibrium?
A. No new product is formed by the forward reaction.
B. The reverse reaction no longer occurs in the system.
C. The concentration of reactants in the system is equal to the concentration of products.
D. The rate at which the forward reaction occurs equals the rate of the reverse reaction.

2. The reaction between persulfate ($S_2O_8^{2-}$) and iodide (I^-) ions is often studied in student laboratories because it occurs slowly enough for its rate to be measured:

$$S_2O_8^{2-}(aq) + 2I^-(aq) \longrightarrow 2SO_4^{2-}(aq) + I^2(aq)$$

This reaction has been experimentally determined to be first order in $S_2O_8^{2-}$ and first order in I^-. Therefore, what is the overall rate law for this reaction?
A. rate = $k[S_2O_8^{2-}]^2[I^-]$
B. rate = $k[S_2O_8^{2-}][I^-]$
C. rate = $k[S_2O_8^{2-}][I^-]^2$
D. rate = $k[S_2O_8^{2-}]^2[I^-]^2$

Use the diagrams below to answer Question 3.



A B C D

3. Which diagram shows the substance that has the weakest intermolecular forces?
A. A
B. B
C. C
D. D

4. Which type of intermolecular force results from a temporary imbalance in the electron density around the nucleus of an atom?
A. ionic bonds
B. London dispersion forces
C. dipole-dipole forces
D. hydrogen bonds

Use the table below to answer Questions 5 to 7.

Concentration Data for the Equilibrium System $MnCO_3(s) \longrightarrow Mn^{2+}(aq) + CO_3^{2-}(aq)$ at 298 K				
Trial	$[Mn^{2+}]_0$ (M)	$[CO_3^{2-}]_0$ (M)	$[Mn^{2+}]_{eq}$ (M)	$[CO_3^{2-}]_{eq}$ (M)
1	0.0000	0.00400	5.60×10^{-9}	4.00×10^{-3}
2	0.0100	0.0000	1.00×10^{-2}	2.24×10^{-9}
3	0.0000	0.0200	1.12×10^{-9}	2.00×10^{-2}

5. What is the K_{sp} for $MnCO_3$ at 298 K?
A. 2.24×10^{-11}
B. 4.00×10^{-11}
C. 1.12×10^{-9}
D. 5.60×10^{-9}

6. What is the molar solubility of $MnCO_3$ at 298 K?
A. $4.73 \times 10^{-6}M$
B. $6.32 \times 10^{-2}M$
C. $7.48 \times 10^{-5}M$
D. $3.35 \times 10^{-5}M$

7. A 50.0-mL volume of $3.00 \times 10^{-6}M$ K_2CO_3 is mixed with 50.0 mL of $MnCl_2$. A precipitate of $MnCO_3$ will form only when the concentration of the $MnCl_2$ solution is greater than which of the following?
A. $7.47 \times 10^{-6}M$
B. $1.49 \times 10^{-5}M$
C. $2.99 \times 10^{-5}M$
D. $1.02 \times 10^{-5}M$

8. The kinetic-molecular theory describes the microscopic behavior of gases. One main point of the theory is that within a sample of gas, the frequency of collisions between individual gas particles and between the particles and the walls of their container increases if the sample is compressed. Which gas law states this relationship in mathematical terms?
A. Gay-Lussac's law
B. Charles's law
C. Boyle's law
D. Avogadro's law

9. $AB(s) + C_2(l) \longrightarrow AC(g) + BC(g)$
Which cannot be predicted about this reaction?
A. The entropy of the system decreases.
B. The entropy of the products is higher than that of the reactants.
C. The change in entropy for this reaction, ΔS_{rxn}, is positive.
D. The disorder of the system increases.

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Short Answer

Use the equation below to answer Questions 10 to 12.

$$PCl_5 + H_2O \longrightarrow HCl + H_3PO_4$$

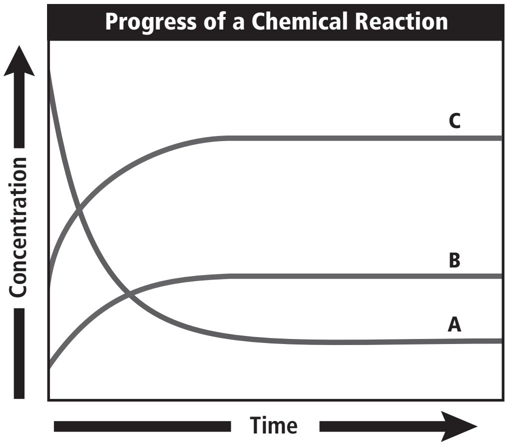
10. Balance this equation, using the smallest whole-number coefficients.

11. Identify the mole ratio of water to phosphoric acid.

12. Use your balanced chemical equation to show the setup for determining the amount of hydrogen chloride produced when 25.0 g of phosphorus pentachloride is completely consumed.

Extended Response

Use the graph below to answer Questions 13 to 15.



13. Describe the shape of the graph when equilibrium has been established.

14. Explain why the concentration of reactants is not zero at the end of this reaction.

15. Classify the type of chemical reaction that is represented in this graph. How do the data support your conclusion?

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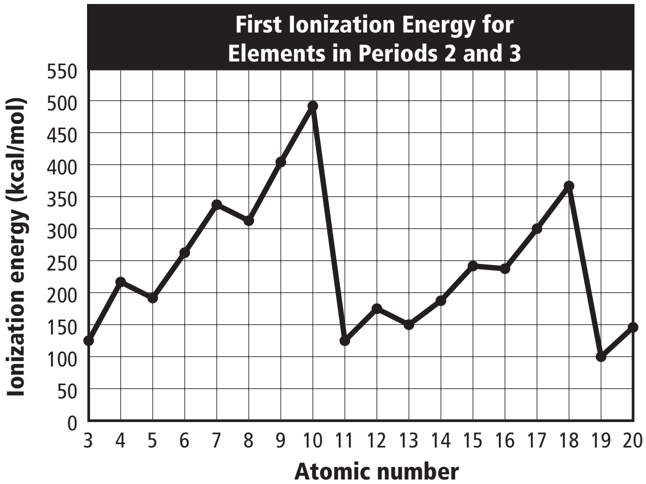
16. The formation of perchloryl fluoride (ClO_3F) has an equilibrium constant of 3.42×10^{-9} at 298 K.

$$Cl_2(g) + 3O_2(g) + F_2(g) \longrightarrow 2ClO_3F(g)$$

At equilibrium, $[Cl_2] = 0.563M$, $[O_2] = 1.01M$, and $[ClO_3F] = 1.47 \times 10^{-5}M$. What is $[F_2]$?

A. $9.18 \times 10^{-2}M$
B. $3.73 \times 10^{-10}M$
C. $1.09 \times 10^{-1}M$
D. $6.32 \times 10^{-2}M$
E. $6.32 \times 10^{-7}M$

Use the graph below to answer Questions 17 and 18.



17. Which family of elements tends to have the lowest ionization energy in its period?

A. representative elements
B. transition elements
C. alkali elements
D. alkaline earth elements
E. halogens

18. Using the graph, what is the approximate ionization energy of the element with atomic number 7?

A. 300 kcal/mol
B. 310 kcal/mol
C. 325 kcal/mol
D. 340 kcal/mol
E. 390 kcal/mol

NEED EXTRA HELP?																		
If You Missed Question . . .	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Review Section . . .	17.1	16.3	12.2	12.2	17.3	17.3	17.3	13.1	15.5	9.1	11.1	11.2	17.4	17.1	9.2	17.3	6.3	6.3