CHAPTER 18

Chemical Equilibrium

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

The Nature of Chemical Equilibrium

SECTION 18-1

OBJECTIVES

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

In systems that are in equilibrium, opposing processes occur at the same time and at the same rate. For example, when an excess of sugar is placed in water, sugar molecules go into solution. At equilibrium, molecules of sugar are crystallizing at the same rate that molecules from the crystal are dissolving. The rate of evaporation of a liquid in a closed vessel can eventually be equaled by the rate of condensation of its vapor. The resulting equilibrium vapor pressure is a characteristic of the liquid at the prevailing temperature. Le Châtelier's principle, which you read about in Chapter 12, can help predict the outcome of changes made to these equilibrium systems. The preceding examples are physical equilibria. The concept of equilibrium and Le Châtelier's principle also apply to chemical processes.

Reversible Reactions

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

Mercury(II) oxide decomposes when heated.

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

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

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

Figure 18-1 shows both of these reactions taking place. Suppose mercury(II) oxide is heated in a closed container from which neither the mercury nor the oxygen can escape. Once decomposition has begun, the mercury and oxygen released can recombine to form mercury(II) oxide again. Thus, both reactions can proceed at the same time. Under these conditions, the rate of the composition reaction will eventually equal that of the decomposition reaction. At equilibrium, mercury and oxygen will

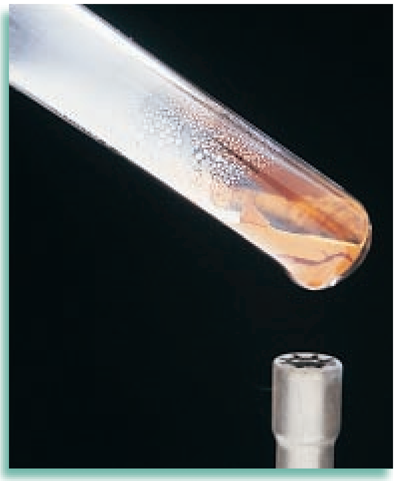

FIGURE 18-1 When heated, mercury(II) oxide decomposes into the elements from which it was formed. Liquid mercury reacts with oxygen to re-form mercury(II) oxide. Together these reactions represent a reversible chemical process.

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

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

Equilibrium, a Dynamic State

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Module 7: Equilibrium

Many chemical reactions are reversible under ordinary conditions of temperature and concentration. They will reach a state of equilibrium unless at least one of the substances involved escapes or is removed from the reaction system. In some cases, however, the forward reaction is nearly completed before the rate of the reverse reaction becomes high enough to establish equilibrium. Here, the products of the forward reaction are favored, meaning that at equilibrium there is a higher concentration of products than of reactants. The favored reaction that produces this situation is referred to as a reaction to the right because the convention for writing chemical reactions is that *left-to-right* is forward and *right-to-left* is reverse. An example of such a system is the dissociation of hydrobromic acid in aqueous solution.

$$HBr(aq) + H_2O(l) \overset{\longrightarrow}{\leftarrow} H_3O^+(aq) + Br^-(aq)$$

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

In other cases, the forward reaction is barely under way when the rate of the reverse reaction becomes equal to that of the forward reaction, and equilibrium is established. In these cases, the products of the reverse reaction are favored and the original reactants are formed. That is, at equilibrium there is a higher concentration of reactants than of products. The favored reaction that produces this situation is referred to as a reaction to the left. An example of such a system is the acid-base reaction between carbonic acid and water.

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

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

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

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

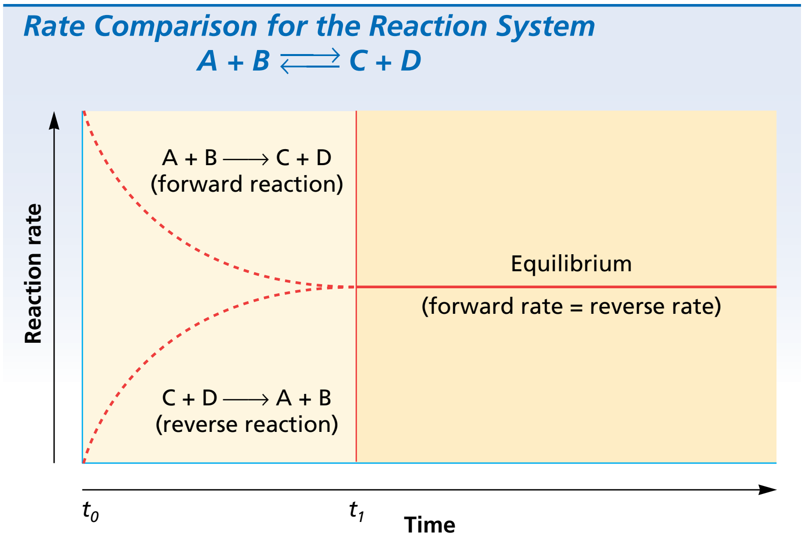
The Equilibrium Expression

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

$$n\mathrm{A} + m\mathrm{B} \rightleftharpoons x\mathrm{C} + y\mathrm{D}$$

Initially, the concentrations of C and D are zero and those of A and B are maximum. Figure 18-2 shows that over time the rate of the forward reaction decreases as A and B are used up. Meanwhile, the rate of the reverse reaction increases as C and D are formed. When these two reaction rates become equal, equilibrium is established. The individual concentrations of A, B, C, and D undergo no further change if conditions remain the same.

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



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

FIGURE 18-2 Shown are reaction rates for the hypothetical equilibrium reaction system $A + B \rightleftharpoons C + D$. From the time A and B are mixed together at t_0, the rate of the forward reaction declines and the rate of the reverse reaction increases until both forward and reverse reaction rates are equal at t_1, when the equilibrium condition begins.

remain constant. The ratio of the mathematical product $[C]^x \times [D]^y$ to the mathematical product $[A]^n \times [B]^m$ for this reaction has a definite value at a given temperature. It is the equilibrium constant of the reaction and is designated by the letter *K*. The following equation describes the equilibrium constant for the hypothetical equilibrium system. [C] indicates the concentration of C in moles per liter. The concentrations of the other substances are indicated similarly.

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

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

The Equilibrium Constant

The numerical value of *K* for a particular equilibrium system is obtained experimentally. The chemist must analyze the equilibrium mixture and determine the concentrations of all substances. The value of *K* for a given equilibrium reaction at a given temperature shows the extent to which the reactants are converted into the products of the reaction. If *K* is equal to 1, the products of the concentrations raised to the appropriate power in the numerator and denominator have the same value. Therefore, at equilibrium, there are roughly equal concentrations of reactants and products. If the value of *K* is low, the forward reaction occurs only very slightly before equilibrium is established, and the reactants are favored. A high value of *K* indicates an equilibrium in which the original reactants are largely converted to products. Only the concentrations of substances that can actually change are included in *K*. This means that *pure* solids and liquids are omitted because their concentrations cannot change.

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

The H_2, I_2, HI Equilibrium System

Consider the reaction between H_2 and I_2 vapor in a sealed flask at an elevated temperature. The rate of reaction can be followed by observing the rate at which the violet color of the iodine vapor diminishes, as shown in Figure 18-3. Suppose the hydrogen gas is present in excess and the reaction continues until all the iodine is used up. The color of the flask's contents, provided by the iodine gas, will gradually become less intense because the product, hydrogen iodide, HI, and the excess hydrogen are both colorless gases.

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

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

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

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

Chemists have carefully measured the concentrations of H_2, I_2, and HI in equilibrium mixtures at various temperatures. In some experiments, the flasks were filled with hydrogen iodide at known pressure. The flasks were held at fixed temperatures until equilibrium was established. In other experiments, hydrogen and iodine were the original substances. Experimental data, together with the calculated values for K, are listed in Table 18-1. Experiments 1 and 2 began with hydrogen iodide. Experiments 3 and 4 began with hydrogen and iodine. Note the close agreement obtained for the numerical values of the equilibrium constant in all cases.

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

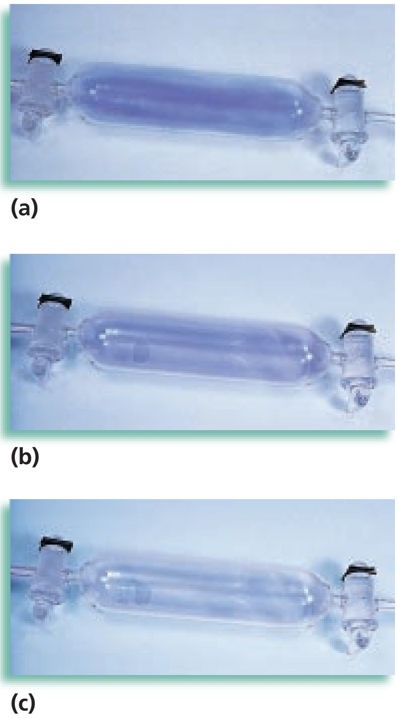


FIGURE 18-3 Hydrogen iodide gas is produced from gaseous hydrogen and iodine. The violet color of iodine gas (a) becomes fainter as the reaction consumes the iodine (b). The violet does not disappear but reaches a constant intensity when the reaction reaches equilibrium (c).

TABLE 18-1 *Typical Equilibrium Concentrations of H_2, I_2, and HI in mol/L at 425°C*

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

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

The balanced chemical equation for an equilibrium system helps establish the expression for the equilibrium constant. The data in Table 18-1 show that the validity of this expression is confirmed when the actual values of the equilibrium concentrations of reactants and products are determined experimentally. The values of K are calculated from these concentrations. No information concerning the kinetics of the reacting systems is required.

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

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

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

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

$$\begin{aligned}[HI] &= \sqrt{0.015 \times 0.015 \times 54.34} \\ &= 0.11 \text{ mol/L}\end{aligned}$$

SAMPLE PROBLEM 18-1

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

SOLUTION

1 ANALYZE

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

Unknown: K

2 PLAN

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

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

3 COMPUTE

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

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

4 EVALUATE The answer has the correct number of significant figures and is close to an estimated value of 8×10^{-6}, calculated as $\dfrac{1 \times 10^{-10}}{(6 \times 10^{-3})(2 \times 10^{-3})}$.

PRACTICE

1. At equilibrium a mixture of N_2, H_2, and NH_3 gas at 500°C is determined to consist of 0.602 mol/L of N_2, 0.420 mol/L of H_2, and 0.113 mol/L of NH_3. What is the equilibrium constant for the reaction $N_2(g) + 3H_2(g) \rightleftarrows 2NH_3(g)$ at this temperature? *Answer* 0.286
2. The reaction $AB_2C(g) \rightleftarrows B_2(g) + AC(g)$ reached equilibrium at 900 K in a 5.00 L vessel. At equilibrium 0.084 mol of AB_2C, 0.035 mol of B_2, and 0.059 mol of AC were detected. What is the equilibrium constant at this temperature for this system? *Answer* 4.9×10^{-3}
3. At equilibrium a 1.0 L vessel contains 20.0 mol of H_2, 18.0 mol of CO_2, 12.0 mol of H_2O, and 5.9 mol of CO at 427°C. What is the value of K at this temperature for the following reaction? *Answer* 0.20
$$CO_2(g) + H_2(g) \rightleftarrows CO(g) + H_2O(g)$$
4. A reaction between gaseous sulfur dioxide and oxygen gas to produce gaseous sulfur trioxide takes place at 600°C. At that temperature, the concentration of SO_2 is found to be 1.50 mol/L, the concentration of O_2 is 1.25 mol/L, and the concentration of SO_3 is 3.50 mol/L. Using the balanced chemical equation, calculate the equilibrium constant for this system. *Answer* 4.36

SECTION REVIEW

1. What is meant by *chemical equilibrium*?
2. What is an equilibrium constant?
3. How does the value of an equilibrium constant relate to the relative quantities of reactants and products at equilibrium?
4. What is meant by a *chemical-equilibrium expression*?
5. Hydrochloric acid, HCl, is a strong acid that dissociates completely in water to form H_3O^+ and Cl^-. Would you expect the value of K for the reaction $HCl(aq) + H_2O(l) \rightleftarrows H_3O^+(aq) + Cl^-(aq)$ to be 1×10^{-2}, 1×10^{-5}, or "very large"? Justify your answer.
6. Write the chemical-equilibrium expression for the reaction $4HCl(g) + O_2(g) \rightleftarrows 2Cl_2(g) + 2H_2O(g)$.
7. At equilibrium at 2500 K, $[HCl] = 0.0625$ mol/L and $[H_2] = [Cl_2] = 0.0045$ mol/L for the reaction $H_2(g) + Cl_2(g) \rightleftarrows 2HCl(g)$. Find the value of K.
8. An equilibrium mixture at 425°C is found to consist of 1.83×10^{-3} mol/L of H_2, 3.13×10^{-3} mol/L of I_2, and 1.77×10^{-2} mol/L of HI. Calculate the equilibrium constant, K, for the reaction $H_2(g) + I_2(g) \rightleftarrows 2HI(g)$.
9. For the reaction $H_2(g) + I_2(g) \rightleftarrows 2HI(g)$ at 425°C, calculate [HI], given $[H_2] = [I_2] = 4.79 \times 10^{-4}$ mol/L and $K = 54.3$.

GREAT DISCOVERIES

Fixing the Nitrogen Problem

HISTORICAL PERSPECTIVE

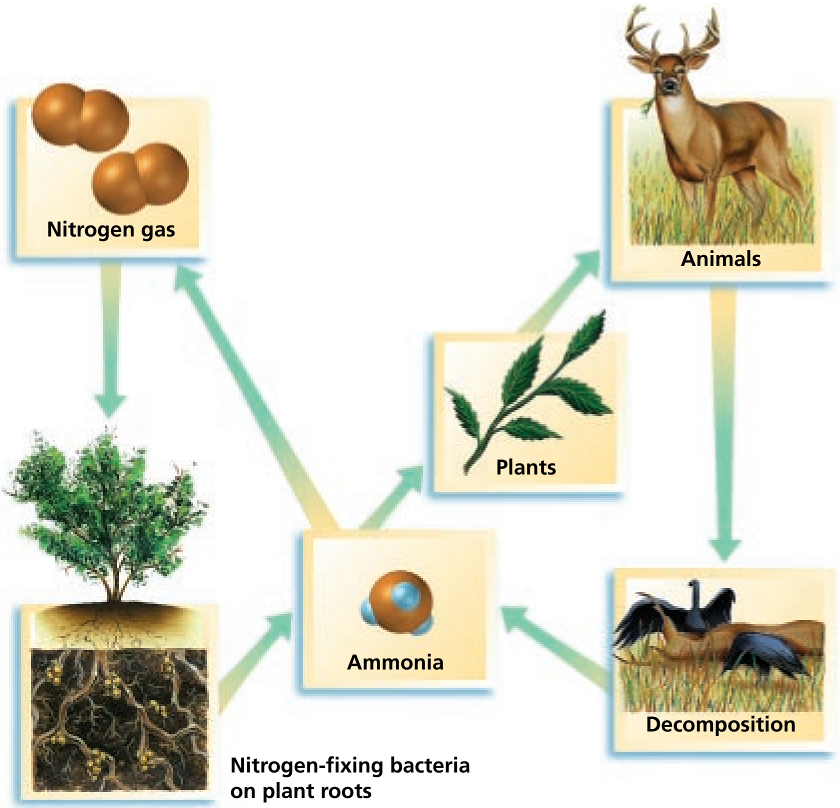
Each year, the chemical industry synthesizes tons of nitrogenous fertilizer, increasing agricultural production around the globe. But prior to 1915, humans had to rely solely on natural resources for fertilizer, and the dwindling supply of these materials caused widespread fear of world starvation. A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

The Malthusian Threat

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

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

But soil often lacks sufficient amounts of the organisms that fix nitrogen for plants, so fertilizers containing usable nitrogen compounds are added. In 1898, two-thirds of the world's supply of these compounds came from Chile, where beds of sodium nitrate, or Chilean saltpeter, were abundant.



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

But, as the chemist William Crookes emphasized in his speech to the British Association that year, these reserves were limited; it was up to his colleagues to discover alternatives and prevent Malthus's dire forecast from coming true:

> *It is the chemist who must come to the rescue of the threatened communities.*

The Haber-Nernst Controversy

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

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

> *From dull red heat . . . no catalyst can produce more than traces of ammonia . . . and even at . . . increased pressures the position of the equilibrium must remain very unfavorable.*

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

Haber was convinced that he was right. Applying Le Châtelier's principle, he ran the reaction at increased pressure to attain an amount of ammonia that could be measured more accurately.

Haber and his assistants confirmed their original findings, and Nernst later conceded a mathematical error. But more important, the new round of experiments indicated that a reasonable amount of ammonia might be attained at pressures of 200 atm (402 kPa) using a uranium or osmium catalyst.


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

Scaling Up

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

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

> *It is remarkable how matter . . . reveals new facets. Iron . . . studied a hundred times in the pure state, now works in the impure state.*

An Eerie Epilogue

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

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SECTION 18-2

Shifting Equilibrium

OBJECTIVES

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

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Module 7: Equilibrium

In systems that have attained chemical equilibrium, the forward and reverse reactions are proceeding at equal rates. Any change that alters the rates of these reactions disturbs the original equilibrium. The system then seeks a new equilibrium state. By shifting an equilibrium in the desired direction, chemists can often improve the yield of the product they are seeking.

Predicting the Direction of Shift

Le Châtelier's principle provides a means of predicting the influence of stress factors on equilibrium systems. As you may recall from Chapter 12, Le Châtelier's principle states that *if a system at equilibrium is subjected to a stress, the equilibrium is shifted in the direction that tends to relieve the stress.* This principle is true for all dynamic equilibria, chemical as well as physical. Changes in pressure, concentration, and temperature illustrate the application of Le Châtelier's principle to chemical equilibrium.

Changes in Pressure

A change in pressure affects only equilibrium systems in which gases are involved. For changes in pressure to affect the system, the total number of moles of gas on the left side of the equation must be different from the total number of moles on the right side of the equation. For example, the balanced chemical equation for the decomposition of solid $CaCO_3$ given on page 564 indicates that 0 mol reactant gases produce 1 mol of product gases. The change in moles is 1. Therefore, a high pressure favors the reverse reaction because fewer CO_2 molecules are produced. A similar argument can explain the increased production of CO_2 that accompanies a low system pressure.

Next let us consider the Haber process for the synthesis of ammonia.

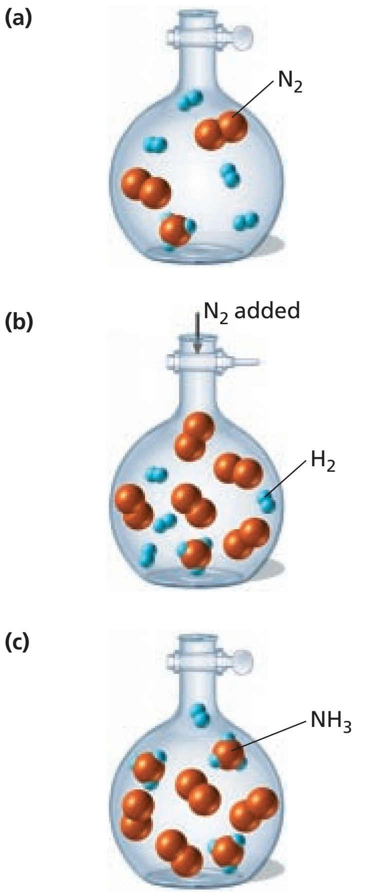
$$N_2(g) + 3H_2(g) \rightleftarrows 2NH_3(g)$$

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

An increase in pressure on confined gases causes an increase in the concentrations of these gases. So changes in pressure may shift the equilibrium position, but they do not affect the value of the equilibrium constant.

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

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



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

FIGURE 18-4 (a) H_2, N_2, and NH_3 are in equilibrium within a closed system. (b) Addition of more N_2 causes a stress on the initial equilibrium. (c) The new equilibrium position for this system. There is now a higher concentration of N_2, a lower concentration of H_2, and a higher concentration of NH_3.

Changes in Concentration

An increase in the concentration of a reactant is a stress on the equilibrium system. It causes an increase in collision frequency and, generally, an increase in reaction rate. Consider the following hypothetical reaction.

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

An increase in the concentration of A shifts the equilibrium to the right. Both A and B are used up faster, and more of C and D is formed. The equilibrium is reestablished with a lower concentration of B. The equilibrium has shifted to reduce the stress caused by the increase in concentration of A. Figure 18-4 illustrates the effect on a system in equilibrium produced by increasing the concentration of a reactant. Similarly, an increase in the concentration of B drives the reaction to the right. An increase in the concentration of either C or D increases the rate of the reverse reaction, and the equilibrium shifts to the left. A decrease in the concentration of C or D has the same effect on the position of the equilibrium as does an increase in the concentration of A or B; the equilibrium shifts to the right.

Changes in concentration have no effect on the value of the equilibrium constant. This is because such changes have an equal effect on the numerator and the denominator of the chemical equilibrium expression. Thus, all concentrations give the same value or numerical ratio for the equilibrium constant when equilibrium is reestablished.

Many chemical processes involve heterogeneous reactions in which the reactants and products are in different phases. The *concentrations* of pure substances in solid and liquid phases are not changed by adding or removing quantities of the substance. This is because concentration is density-dependent, and the density of these phases is constant, regardless of the total amounts present. *A pure substance in a condensed phase, solid or liquid, can be eliminated from the expression for the*

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equilibrium constant. The concentration of the pure solid or liquid is set equal to 1 in the equilibrium expression, signifying that the concentration is assumed to remain unchanged in the equilibrium system.

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

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

The products are a solid and a gas, leading to the following expression for the equilibrium constant.

$$K = \frac{[CaO][CO_2]}{[CaCO_3]} = \frac{[1][CO_2]}{[1]} = [CO_2]$$

Carbon dioxide is the only substance in the system subject to changes in concentration. Because it is a gas, the system is affected by pressure changes.

Changes in Temperature

Reversible reactions are exothermic in one direction and endothermic in the other. The effect of changing the temperature of an equilibrium mixture depends on which of the opposing reactions is endothermic and which is exothermic.

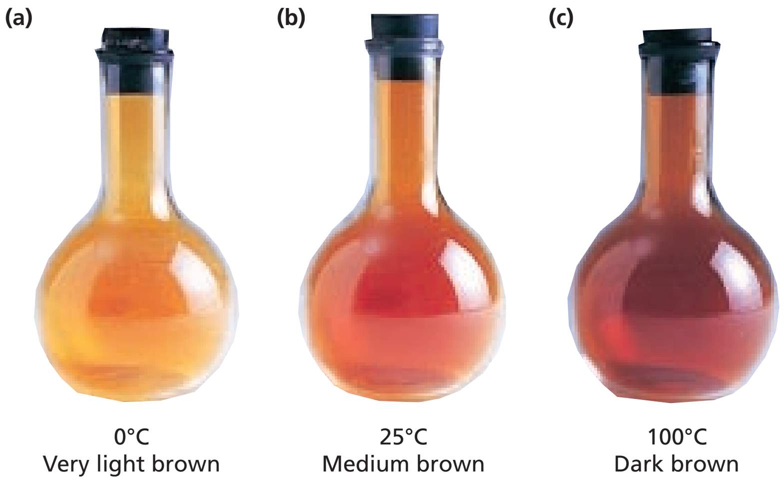
According to Le Châtelier's principle, the addition of heat shifts the equilibrium so that heat is absorbed. This favors the endothermic reaction. The removal of heat favors the exothermic reaction. A rise in temperature increases the rate of any reaction. In an equilibrium system, however, the rates of the opposing reactions are raised unequally. Thus, the value of the equilibrium constant for a given system is affected by the temperature.

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

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

A high temperature is not desirable because it favors the decomposition of ammonia, the endothermic reaction. At low temperatures, however, the forward reaction is too slow to be commercially useful. The temperature used represents a compromise between kinetic and equilibrium requirements. It is high enough that equilibrium is established rapidly but low enough that the equilibrium concentration of ammonia is significant. Moderate temperature (about 500°C) and very high pressure (700–1000 atm) produce a satisfactory yield of ammonia.

The production of colorless dinitrogen tetroxide gas, N_2O_4, from dark brown NO_2 gas is also an exothermic reaction. Figure 18-5 shows how temperature affects the equilibrium of this system. In this figure, all three flasks contain the same total mass of gas, a mixture of NO_2 and N_2O_4. In Figure 18-5(a) the temperature of the system is lowered to 0°C. This causes the equilibrium of the system to shift to the right, allowing more of the colorless N_2O_4 gas to form, which produces a light brown color.



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

FIGURE 18-5 Different temperatures can cause an equilibrium system to shift and seek a new equilibrium position.

The system is at equilibrium at 25°C in Figure 18-5(b). The system contains an equilibrium mixture of NO_2 and N_2O_4, producing a medium brown color. As the temperature is raised to 100°C, as shown in Figure 18-5(c), the equilibrium shifts to the left, causing more of the dark brown NO_2 gas to form.

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

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

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

The reactions of the system are also accelerated by a suitable catalyst. However, catalysts have no effect on relative equilibrium amounts. They only affect the rates at which equilibrium is reached. This is because catalysts increase the rates of forward and reverse reactions in a system by equal factors. Therefore, they do not affect K.

Reactions That Go to Completion

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

Formation of a Gas

Unstable substances formed as products of ionic reactions decompose spontaneously. An example is carbonic acid, H_2CO_3, the acid in carbonated water, such as club soda, which yields a gas as a decomposition product.

$$H_2CO_3(aq) \longrightarrow H_2O(l) + CO_2(g)$$

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

Formation of a Precipitate

When solutions of sodium chloride and silver nitrate are mixed, a white precipitate of silver chloride immediately forms, as shown in Figure 18-6. The overall ionic equation for this reaction follows.

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

If chemically equivalent amounts of the two solutes are used, only Na^+ ions and NO_3^- ions remain in solution in appreciable quantities. Almost all of the Ag^+ ions and Cl^- ions combine and separate from the solution as a precipitate of AgCl. This is because AgCl is only very sparingly soluble in water. It separates by precipitation from what turns out to be a saturated solution of its particles. The reaction thus effectively goes to completion because an essentially insoluble product is formed.

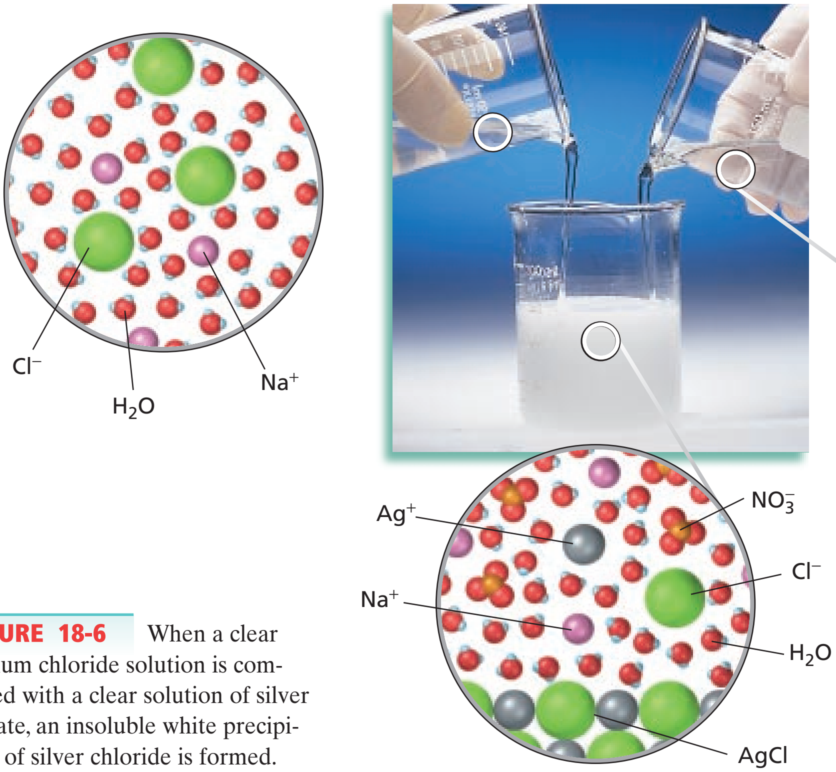


FIGURE 18-6 When a clear sodium chloride solution is combined with a clear solution of silver nitrate, an insoluble white precipitate of silver chloride is formed.

Formation of a Slightly Ionized Product

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

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

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

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

Because it is only slightly ionized, the water exists almost entirely as covalently bonded molecules. Thus, insofar as they are initially present in equal amounts, hydronium ions and hydroxide ions are almost entirely removed from the solution. The reaction effectively runs to completion because the product is only slightly ionized.

Common-Ion Effect

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

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

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

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

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

The common-ion effect is also observed when one ion species of a weak electrolyte is added in excess to a solution. Acetic acid, CH_3COOH, is such an electrolyte. A 0.1 M CH_3COOH solution is only about 1.4% ionized to produce hydronium ions and acetate ions, CH_3COO^-. The ionic equilibrium is shown by the following equation.

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

Small additions of sodium acetate, $NaCH_3COO$ (an ionic salt that is completely dissociated in water), to a solution containing acetic acid greatly increase the acetate-ion concentration. The equilibrium shifts in the direction that uses up some of the acetate ions in accordance with Le Châtelier's principle. More molecules of acetic acid are formed and the concentration of hydronium ions is reduced. In general, the addition of a salt with an ion common to the solution of a weak electrolyte reduces the ionization of the electrolyte. Figure 18-7 shows a 0.25 M CH_3COOH solution on the left that has a pH of about 2.7. Mixing that with the 0.10 M $NaCH_3COO$ solution in the center produces the solution on the right, which has a pH of about 4.5, indicating lower $[H_3O^+]$ and thus lowered acetic acid ionization. (The universal indicator used turns red in acidic solutions, green in weakly basic solutions, and yellow in neutral solutions.)

FIGURE 18-7 The solution of CH_3COOH on the left is combined with the solution of $NaCH_3COO$ in the center. Both contain the common ion, CH_3COO^-. They produce the solution on the right, which is only slightly acidic due to the decreased ionization of the acid. The colors of the solutions are due to the addition of acid-base indicators.

SECTION REVIEW

1. Name three ways the chemical equilibrium can be disturbed.
2. Describe three situations in which ionic reactions go to completion.
3. Describe the common-ion effect.
4. Identify the common ion in each of the following situations.
   a. 5 g of NaCl is added to a 2.0 M solution of HCl
   b. 50 mL of 1.0 M $NaCH_3COO$ is added to 1.0 M CH_3COOH
   c. 10 pellets of NaOH are added to 100 mL of water
5. Predict the effect that decreasing pressure would have on each of the following reaction systems at equilibrium.
   a. $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$
   b. $NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$
   c. $2H_2O_2(aq) \rightleftharpoons 2H_2O(l) + O_2(g)$
   d. $3O_2(g) \rightleftharpoons 2O_3(g)$
6. When solid carbon reacts with oxygen gas to form carbon dioxide, 393.51 kJ of heat are released. Does this reaction become more favorable or less favorable as the temperature decreases? Explain.

SECTION 18-3

Equilibria of Acids, Bases, and Salts

OBJECTIVES

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

Ionization Constant of a Weak Acid

About 1.4% of the solute molecules in a 0.1 M acetic acid solution are ionized at room temperature. The remaining 98.6% of the acetic acid molecules, CH_3COOH, remain nonionized. Thus, the solution contains three species of particles in equilibrium: CH_3COOH molecules, H_3O^+ ions, and acetate ions, CH_3COO^-. The equilibrium constant for this system expresses the equilibrium ratio of ions to molecules. From the equilibrium equation for the ionization of acetic acid, the equilibrium constant equation can be written.

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

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

At the 0.1 M concentration, water molecules greatly exceed the number of acetic acid molecules. Without introducing a measurable error, one can assume that the molar concentration of H_2O molecules remains constant in such a solution. Thus, because both K and $[H_2O]$ are constant, the product $K[H_2O]$ is constant.

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

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

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

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

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

TABLE 18-2 *Ionization of Acetic Acid*

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

CHEMISTRY INTERACTIVE TUTOR

Module 8: Strong and Weakly Ionized Species, pH, and Titrations

Ionization data and constants for some dilute acetic acid solutions at 25°C are given in Table 18-2. Notice that the numerical value of K_a is almost identical for each solution molarity shown. The numerical value of K_a for CH_3COOH at 25°C can be determined by substituting numerical values for concentration into the equilibrium equation.

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

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

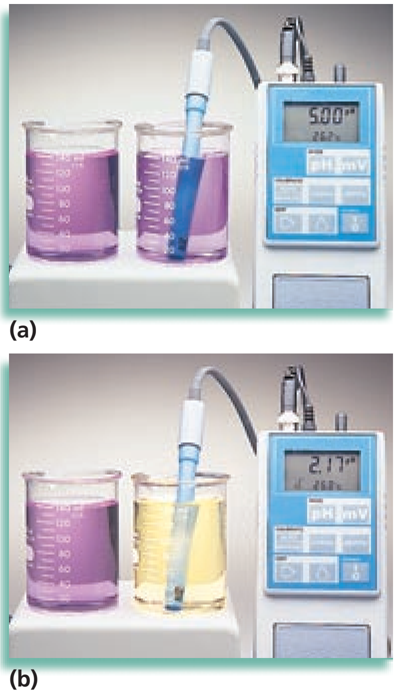


FIGURE 18-8 (a) The beaker on the left contains a buffered solution and an indicator with a pH of about 7. The beaker on the right contains mostly water with a trace amount of acid and an indicator. The pH meter shows a pH of 5.00 for this solution. (b) After 5 mL of 0.10 M HCl is added to both beakers, the beaker on the left does not change color, indicating no substantial change in its pH. However, the beaker on the right undergoes a definite color change, and the pH meter shows a pH of 2.17.

Buffers

The solution just described contains both a weak acid, CH_3COOH, and a salt of the weak acid, $NaCH_3COO$. The solution can react with either an acid or a base. When small amounts of acids or bases are added, the pH of the solution remains nearly constant. The weak acid and the common ion, CH_3COO^-, act as a "buffer" against significant changes in the pH of the solution. *Because it can resist changes in pH, this solution is a* **buffered solution.** Figure 18-8 shows how a buffered and a nonbuffered solution react to the addition of an acid.

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

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

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

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

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

The pH of the solution again remains practically unchanged.

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

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

If a small amount of an acid is added to the solution instead, hydroxide ions from the solution accept protons from the added hydronium ions to form nonionized water molecules. Ammonia molecules in the solution then ionize and restore the equilibrium concentration of hydronium ions and the pH of the solution.

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

Buffer action has many important applications in chemistry and physiology. Human blood is naturally buffered to maintain a pH of between 7.3 and 7.5. This is essential because large changes in pH would lead to serious disturbances of normal body functions. Figure 18-9 shows an example of one of the many medicines buffered to prevent large and potentially damaging changes in pH.

FIGURE 18-9 Many consumer products are buffered to protect the body from potentially harmful pH changes.

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Ionization Constant of Water

Recall from Chapter 16 that the self-ionization of water is an equilibrium reaction.

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

Equilibrium is established with a very low concentration of H_3O^+ and OH^- ions. The following expression for the equilibrium constant is derived from the balanced chemical equation.

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$$

Hydrolysis of Salts

Salts are formed during the neutralization reaction between a Brønsted acid and a Brønsted base. When a salt dissolves in water, it produces positive ions (cations) of the base from which it was formed and negative ions (anions) of the acid from which it was formed. Therefore, the solution might be expected to be neutral. The aqueous solutions of some salts, such as NaCl and KNO_3, are neutral, having a pH of 7. However, when sodium carbonate dissolves in water, the resulting solution turns red litmus paper blue, indicating a pH greater than 7. Ammonium chloride produces an aqueous solution that turns blue litmus paper red, indicating a pH less than 7. Salts formed from the combination of strong or weak acids and bases are shown in Figure 18-10.

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

Anion Hydrolysis

In the Brønsted sense, the anion of the salt is the conjugate base of the acid from which it was formed. It is also a proton acceptor. If the acid is weak, its conjugate base (the anion) will be strong enough to remove protons from some water molecules, proton donors, to form OH^- ions. An

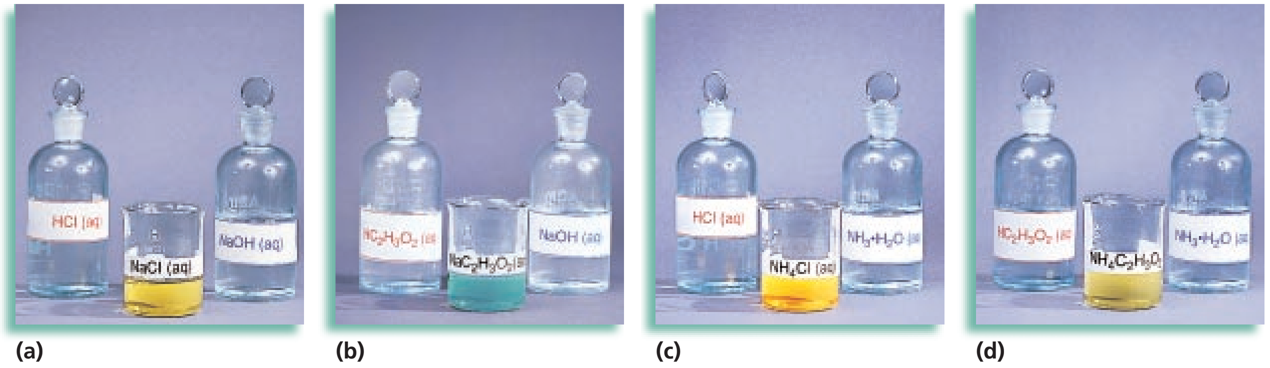

FIGURE 18-10 The universal indicator shows that the pH of salt solutions varies, depending on the strength of the acid and the base that formed the salt. (a) NaCl is formed from a strong acid and a strong base; the color of the indicator shows the pH is neutral. (b) The indicator shows the pH of the sodium acetate solution is basic. This was formed from a strong base and a weak acid. (c) The strong acid and weak base combination in ammonium chloride produces an acidic solution, as shown by the color of the indicator. (d) The weak acid and weak base that form ammonium acetate are of comparable strength. A solution of ammonium acetate is essentially neutral.

equilibrium is established in which the net effect of the anion hydrolysis is an increase in the hydroxide-ion concentration, $[OH^-]$, of the solution.

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

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

From this equation, the generalized expression for K_a can be written. Recall that the concentration of water in dilute aqueous solutions is essentially constant, so it is included in the equilibrium constant instead of in the concentration ratio.

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

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

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

In the forward reaction, the anion, A^-, acquires a proton from the water molecule to form the weak acid, HA, and hydroxide ion, OH^-. The extent of OH^- ion formation and the position of the equilibrium depends on the relative strength of the anion, A^-. The lower the K_a value of HA, the stronger the attraction for protons that A^- will have compared with OH^-, and the greater the production of OH^- ion will be. Therefore, as the relative strength of A^- increases, the equilibrium position lies farther to the right.

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

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

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

Cation Hydrolysis

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

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

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

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

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

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

In the forward reaction, the cation BH^+ donates a proton to the water molecule to form the hydronium ion and the weak base, B. The extent of H_3O^+ ion formation and the position of the equilibrium depend on the relative strength of the cation, BH^+. The lower the K_b value of B, the stronger the donation of protons that BH^+ will have compared with H_3O^+, and the greater the production of H_3O^+ ions will be. Therefore, as the relative strength of BH^+ increases, the equilibrium position lies farther to the right.

Ammonium chloride, NH_4Cl, dissociates in water to produce NH_4^+ ions, Cl^- ions, and an acidic solution. Chloride ions are the conjugate base of a strong acid, HCl, so they show no noticeable tendency to hydrolyze in aqueous solution. Ammonium ions, however, are the conjugate acid of a weak base, NH_3. Ammonium ions donate protons to water molecules. Equilibrium is established with an increased $[H_3O^+]$, so the pH is *lower* than 7.

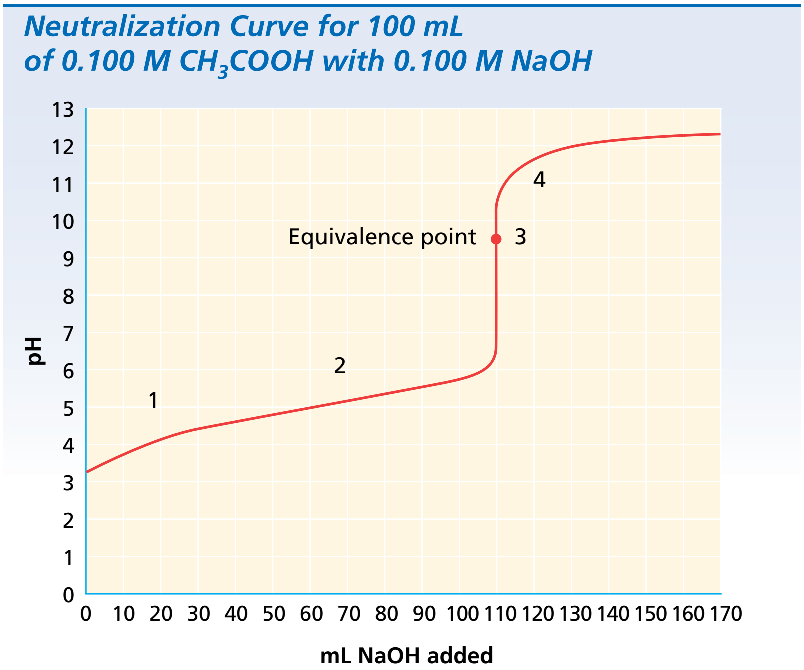

FIGURE 18-11 At point *1* on the titration curve, only acetic acid is present. The pH depends on the weak acid alone. At *2* there is a mixture of CH_3COOH and CH_3COO^-. Adding NaOH changes the pH slowly. At point *3* all acid has been converted to CH_3COO^-. This hydrolyzes to produce a slightly basic solution. At *4* the pH is due to the excess OH^- that has been added.

Hydrolysis in Acid-Base Reactions

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

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

The aqueous solutions of salts formed from reactions between weak acids and strong bases are basic, as Figure 18-11 shows. Anions of the dissolved salt are hydrolyzed in the water solvent, and the pH of the solution is raised, indicating that the hydroxide-ion concentration has increased. Aqueous solutions of sodium acetate, $NaCH_3COO$, are basic. The acetate ions, CH_3COO^-, undergo hydrolysis because they are the anions of the weak acid–acetic acid. The cations of the salt are the positive ions from a strong base, NaOH, and do not hydrolyze appreciably.

Figure 18-12 shows that salts of strong acids and weak bases produce acidic aqueous solutions. Cations of the dissolved salt are hydrolyzed in

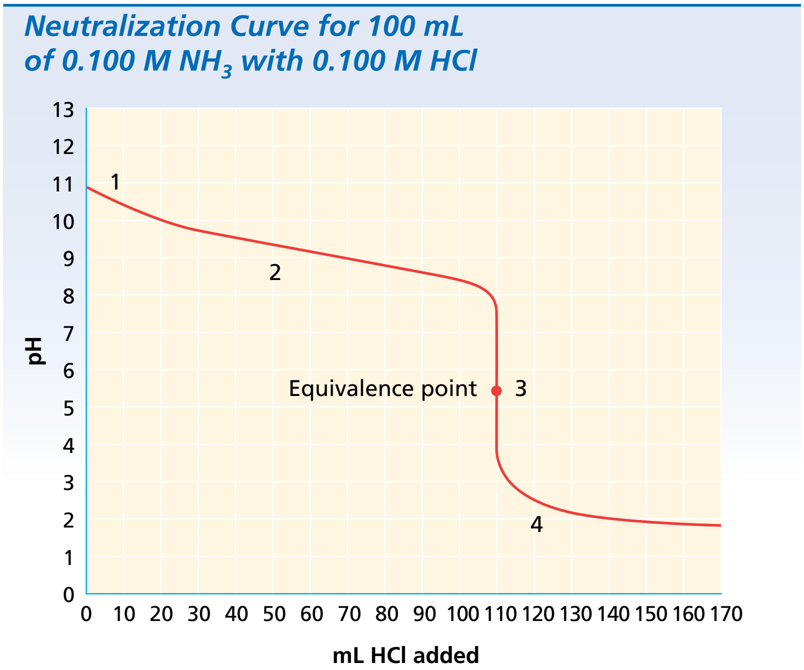

FIGURE 18-12 At point *1* on the titration curve, only aqueous ammonia is present. The pH is determined by the base alone. At *2* there is a mixture of NH_3 and NH_4^+. Adding HCl changes the pH slowly. At point *3* all aqueous ammonia has been converted to NH_4^+. At *4* the pH is determined by the excess H_3O^+ that is being added.

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

Salts of weak acids and weak bases can produce either acidic, neutral, or basic aqueous solutions, depending on the salt dissolved. This is because both ions of the dissolved salt are hydrolyzed extensively. If both ions are hydrolyzed equally, the solution remains neutral. The ions in ammonium acetate, NH_4CH_3COO, hydrolyze equally, producing a neutral solution, as shown in Figure 18-10(d) on page 572.

In cases in which both the acid and the base are very weak, the salt may undergo essentially complete decomposition to the products of hydrolysis. For example, when aluminum sulfide is placed in water, both a precipitate and a gas are formed. The reaction is symbolized by the following chemical equation.

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

Both products are sparingly soluble in water and are removed from solution.

SECTION REVIEW

1. What is meant by an *acid-ionization constant*?

2. How is an acid-ionization equilibrium expression written?

3. What is meant by the term *buffered solution*?

4. Which of the following combinations of solutions would form buffers when they are mixed?
a. 50 mL of 1.0 M HCl and 50 mL of 1.0 M NaCl
b. 25 mL of 0.5 M HNO_2 and 50 mL of 1.0 M $NaNO_2$
c. 25 mL of 1.0 M HNO_2 and 25 mL of 1.0 M NaCl

5. What is meant by the *ion-product constant* for water? What is the value of this constant?

6. For each of the following reactions, identify each conjugate acid-base pair.
a. $H_2CO_3 + H_2O \rightleftharpoons HCO_3^- + H_3O^+$
b. $H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$
c. $H_2S + NH_3 \rightleftharpoons HS^- + NH_4^+$
d. $H_2PO_4^- + H_2O \rightleftharpoons H_3PO_4 + OH^-$

7. What is hydrolysis? Compare cation and anion hydrolysis.

8. Which of the following ions hydrolyze in aqueous solution?

a. NO_3^-	d. K^+	g. CO_3^{2-}
b. F^-	e. CH_3COO^-	h. PO_4^{3-}
c. NH_4^+	f. SO_4^{2-}	

9. Identify the following solutions as acidic, basic, or neutral.

a. 0.5 M KI	c. 0.25 M NH_4NO_3
b. 0.10 M $Ba(OH)_2$	d. 0.05 M $BaCO_3$

10. Identify the acid and base from which each of the following salts was formed.

a. K_2CrO_4	c. CaF_2
b. $Ca(CH_3COO)_2$	d. $(NH_4)_2SO_4$

Solubility Equilibrium

SECTION 18-4

OBJECTIVES

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

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

Solubility Product

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

A general rule is often used to express solubilities qualitatively. By this rule, a substance is said to be *soluble* if the solubility is *greater than* 1 g per 100 g of water. It is said to be *insoluble* if the solubility is *less than* 0.1 g per 100 g of water. Substances whose solubilities fall between these limits are described as *slightly soluble.*

The equilibrium principles developed in this chapter apply to all saturated solutions of sparingly soluble salts. Silver chloride is so sparingly soluble in water that it is sometimes described as insoluble. Its solution reaches saturation at a very low concentration of its ions. All Ag^+ and Cl^- ions in excess of this concentration eventually precipitate as AgCl.

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

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

$$K = \frac{[\mathrm{Ag}^+][\mathrm{Cl}^-]}{[\mathrm{AgCl}]}$$

Because the concentration of a pure substance in the solid or liquid phase remains constant, adding more solid AgCl to this equilibrium system does not change the concentration of the undissolved AgCl present. Thus, [AgCl] does not appear in the final expression. Rearranging the equilibrium expression so that both constants are on the same side of the equation gives the solubility-product constant K_{sp}. *The* **solubility-product constant** *of a substance is the product of the molar concentrations of its ions in a saturated solution, each raised to the power that is the coefficient of that ion in the chemical equation.*

$$K[\text{AgCl}] = [\text{Ag}^+][\text{Cl}^-]$$
$$K_{sp} = [\text{Ag}^+][\text{Cl}^-]$$

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

Calcium fluoride is another sparingly soluble salt. The equilibrium in a saturated CaF_2 solution is described by the following equation.

$$\text{CaF}_2(s) \rightleftharpoons \text{Ca}^{2+}(aq) + 2\text{F}^-(aq)$$

The solubility-product constant has the following form.

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

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

The numerical value of K_{sp} can be determined from solubility data. Data listed in Appendix Table A-13 (page 901) indicate that a maximum of 8.9×10^{-5} g of AgCl can dissolve in 100. g of water at 10°C. One mole of AgCl has a mass of 143.32 g. The saturation concentration, or solubility, of AgCl can therefore be expressed in moles per liter of water, which is very nearly equal to moles per liter of solution.

$$\frac{8.9 \times 10^{-5}\ \text{g AgCl}}{100.\ \text{g H}_2\text{O}} \times \frac{1\ \text{g H}_2\text{O}}{\text{mL H}_2\text{O}} \times \frac{1000\ \text{mL}}{\text{L}} \times \frac{1\ \text{mol AgCl}}{143.32\ \text{g AgCl}}$$
$$= 6.2 \times 10^{-6}\ \text{mol/L}$$

Silver chloride dissociates in solution, contributing equal numbers of Ag^+ and Cl^- ions. The ion concentrations in the saturated solution are therefore 6.2×10^{-6} mol/L.

$$[\text{Ag}^+] = 6.2 \times 10^{-6}$$
$$[\text{Cl}^-] = 6.2 \times 10^{-6}$$

and

$$K_{sp} = [\text{Ag}^+][\text{Cl}^-]$$
$$K_{sp} = (6.2 \times 10^{-6})(6.2 \times 10^{-6})$$
$$K_{sp} = (6.2 \times 10^{-6})^2$$
$$K_{sp} = 3.8 \times 10^{-11}$$

This result is the solubility-product constant of AgCl at 10°C.

From Appendix Table A-13, the solubility of CaF_2 is 1.7×10^{-3} g/100 g of water at 26°C. Expressed in moles per liter, as before, this concentration becomes 2.2×10^{-4} mol/L. CaF_2 dissociates in solution to yield twice as many F^- ions as Ca^{2+} ions. The ion concentrations in the saturated solution are 2.2×10^{-4} for the calcium ion and $2(2.2 \times 10^{-4})$, or 4.4×10^{-4}, for the fluoride ion. Note that at equilibrium at 26°C, $[Ca^{2+}]$ equals the solubility of 2.2×10^{-4} mol/L but $[F^-]$ equals twice the solubility, or 4.4×10^{-4} mol/L. The number of moles of positive and negative ions per mole of compound must always be accounted for when using K_{sp} and solubilities.

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

$$K_{sp} = (2.2 \times 10^{-4})(4.4 \times 10^{-4})^2$$

$$K_{sp} = 4.3 \times 10^{-11}$$

Thus, the solubility-product constant of CaF_2 is 4.3×10^{-11} at 26°C.

It is difficult to measure very small concentrations of a solute with precision. For this reason, solubility data from different sources may report different values of K_{sp} for a substance. Thus, calculations of K_{sp} ordinarily should be limited to two significant figures. Representative values of K_{sp} at 25°C for some sparingly soluble compounds are listed in Table 18-3. Assume that all data used in K_{sp} calculations have been taken at 25°C unless otherwise specified.

At this point, you should note the difference between the solubility of a given solid and its solubility-product constant. Remember that the

TABLE 18-3 *Solubility-Product Constants, K_{sp}, at 25°C*

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

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

SAMPLE PROBLEM 18-2

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

SOLUTION

1 ANALYZE

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

Unknown: K_{sp}

2 PLAN

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

$$\frac{\text{g CuCl}}{100.\text{ g } H_2O} \times \frac{1 \text{ g } H_2O}{1 \text{ mL } H_2O} \times \frac{1000 \text{ mL}}{1 \text{ L}} \times \frac{1 \text{ mol CuCl}}{\text{g CuCl}} = \text{solubility in mol/L}$$

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

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

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

3 COMPUTE

The molar mass of CuCl is 99.0 g/mol.

$$\text{solubility} = \frac{1.08 \times 10^{-2} \cancel{\text{g CuCl}}}{100.\text{ g } \cancel{H_2O}} \times \frac{1 \cancel{\text{g } H_2O}}{1 \cancel{\text{mL}}} \times \frac{1000 \cancel{\text{mL}}}{\text{L}} \times \frac{1 \text{ mol CuCl}}{99.0 \cancel{\text{g CuCl}}} =$$

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

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

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

4 EVALUATE

The answer contains the proper number of significant figures and is close to the K_{sp} value given in Table 18-3.

PRACTICE

1. Calculate the solubility-product constant, K_{sp}, of lead(II) chloride, $PbCl_2$, which has a solubility of 1.0 g/100. g H_2O at a temperature other than 25°C.	*Answer* 1.9×10^{-4}
2. Five grams of Ag_2SO_4 will dissolve in 1 L of water. Calculate the solubility product constant for this salt.	*Answer* 2×10^{-5}

Calculating Solubilities

Once known, the solubility-product constant can be used to determine the solubility of a sparingly soluble salt. Suppose you wish to know how much barium carbonate, $BaCO_3$, can be dissolved in 1 L of water at 25°C. From Table 18-3, K_{sp} for $BaCO_3$ has the numerical value 5.1×10^{-9}. The equilibrium equation is written as follows.

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

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

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

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

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

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

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

The solubility of $BaCO_3$ is 7.14×10^{-5} mol/L.

Thus, the solution concentration is 7.14×10^{-5} M for Ba^{2+} ions and 7.14×10^{-5} M for CO_3^{2-} ions.

SAMPLE PROBLEM 18-3

Calculate the solubility of silver acetate, $AgCH_3COO$, in mol/L, given the K_{sp} value for this compound listed in Table 18-3.

SOLUTION

1 ANALYZE

Given: $K_{sp} = 1.9 \times 10^{-3}$

Unknown: solubility of $AgCH_3COO$

2 PLAN

$$AgCH_3COO \rightleftarrows Ag^{+}(aq) + CH_3COO^{-}(aq)$$

$$K_{sp} = [Ag^{+}][CH_3COO^{-}]$$

$[Ag^{+}] = [CH_3COO^{-}]$, so let $[Ag^{+}] = x$ and $[CH_3COO^{-}] = x$

3 COMPUTE

$$K_{sp} = [Ag^{+}][CH_3COO^{-}]$$

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

$$x^2 = 1.9 \times 10^{-3}$$

$$x = \sqrt{1.9 \times 10^{-3}}$$

Solubility of $AgCH_3COO = \sqrt{1.9 \times 10^{-3}} = 4.4 \times 10^{-2}$ mol/L

4 EVALUATE The answer has the proper number of significant figures and is close to an estimated value of 5.0×10^{-2} calculated as $\sqrt{2.5 \times 10^{-3}}$.

PRACTICE

1. Calculate the solubility of cadmium sulfide, CdS, in mol/L, given the K_{sp} value listed in Table 18-3.	*Answer* 8.9×10^{-14} mol/L
2. Determine the concentration of strontium ions in a saturated solution of strontium sulfate, $SrSO_4$, if the K_{sp} for $SrSO_4$ is 3.2×10^{-7}.	*Answer* 5.7×10^{-4} mol/L

Precipitation Calculations

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

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

Suppose that unequal quantities of $BaCl_2$ and Na_2CO_3 are dissolved in water and that the solutions are mixed. If the ion product $[Ba^{2+}][CO_3^{2-}]$ exceeds the K_{sp} of $BaCO_3$, a precipitate of $BaCO_3$ forms. Precipitation continues until the ion concentrations decrease to the point at which $[Ba^{2+}][CO_3^{2-}]$ equals the K_{sp}.

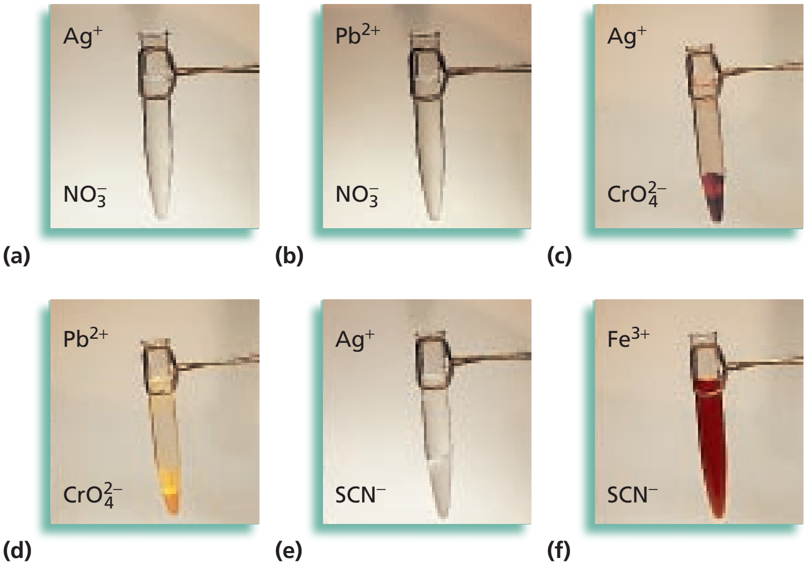

FIGURE 18-13 Nitrate salts of Ag^+ (a) and Pb^{2+} (b) are soluble. When chromate ions, CrO_4^{2-}, combine with Ag^+ (c) or Pb^{2+} (d), an insoluble salt forms. Thiocyanate ions, SCN^-, can form an insoluble salt with Ag^+ (e) or a soluble salt with Fe^{3+} (f).

Substances differ greatly in their tendencies to form precipitates when mixed in moderate concentrations. The photos in Figure 18-13 show the behavior of some negative ions in the presence of certain metallic ions. Note that some of the combinations have produced precipitates and some have not. The solubility product can be used to predict whether a precipitate forms when two solutions are mixed.

SAMPLE PROBLEM 18-4

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

SOLUTION

1 *ANALYZE*

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

Unknown: whether a precipitate forms

2 *PLAN*

The two possible new pairings of ions are NaCl and $BaSO_4$. Of these, $BaSO_4$ is a sparingly soluble salt. It will precipitate if the ion product $[Ba^{2+}][SO_4^{2-}]$ in the combined solution exceeds K_{sp} for $BaSO_4$. From the list of solubility products in Table 18-3, the K_{sp} is found to be 1.1×10^{-10}. The solubility-equilibrium equation follows.

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

The solubility-equilibrium expression is written as follows.

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

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

3 *COMPUTE*

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

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

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

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

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

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

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

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

Trial value of the ion product:

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

The ion product is much greater than the value of K_{sp}, so precipitation occurs.

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

PRACTICE

1. Does a precipitate form when 100. mL of 0.0025 M $AgNO_3$ and 150. mL of 0.0020 M NaBr solutions are mixed?	*Answer* AgBr precipitates.
2. Does a precipitate form when 20. mL of 0.038 M $Pb(NO_3)_2$ and 30. mL of 0.018 M KCl solutions are mixed?	*Answer* $PbCl_2$ does *not* precipitate.

Limitations on the Use of K_{sp}

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

SECTION REVIEW

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

CHAPTER 18 REVIEW

CHAPTER SUMMARY

18-1

- A reaction system in which the forward and reverse reactions occur simultaneously and at the same rate is said to be in *equilibrium.* Both reactions continue, but there is no net change in the composition of the system.
- At equilibrium, the ratio of the product of the mole concentrations of substances formed to the product of the mole concentrations of reactants, each raised to the appropriate power, has a definite numerical value, *K,* which is the equilibrium constant at a given temperature. For values of *K* greater than 1, the products of the forward reaction are favored. For values of *K* less than 1, the products of the reverse reaction are favored.

Vocabulary

chemical equilibrium (554)
chemical-equilibrium expression (556)
equilibrium constant (556)
reversible reaction (553)

18-2

- Any change that alters the rate of either the forward or reverse reaction disturbs the equilibrium of the system. According to Le Châtelier's principle, the equilibrium is shifted in the direction that relieves the stress.
- Catalysts increase the rates of forward and reverse reactions equally, and they do not shift an equilibrium or change the value of *K*.
- The common-ion effect is recognized when a solution containing ions like those of a reactant in an equilibrium system is added to the system. Le Châtelier's principle explains the response of the system to the stress.

Vocabulary

common-ion effect (567)

18-3

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

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

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

Vocabulary

acid-ionization constant (569)
buffered solution (570)
hydrolysis (572)

18-4

- Ions of salts that are very sparingly soluble form saturated aqueous solutions at low concentrations. The solubility-equilibrium expression for such salts yields a useful constant—the solubility-product constant, K_{sp}. The value of K_{sp} equals the product of the molar concentrations of solute ions in the saturated solution raised to a power equal to the coefficient in the balanced equation for the solution of one mole.

Vocabulary

solubility-product constant (578)

REVIEWING CONCEPTS

1. Describe and explain how the concentrations of A, B, C, and D change from the time when A and B are first combined to the point at which equilibrium is established for the reaction $A + B \rightleftharpoons C + D$. (18-1)

2. a. Write the general expression for an equilibrium constant based on the equation $nA + mB + \ldots \rightleftharpoons xC + yD + \ldots$
b. What information is provided by the value of K for a given equilibrium system at a specified temperature? (18-1)

3. In general, which reaction is favored (forward, reverse, or neither) if the value of K at a specified temperature is
a. equal to 1?
b. very small?
c. very large? (18-1)

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

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

a. increased pressure
b. decreased pressure (18-2)

5. In heterogeneous reaction systems, what types of substances do not appear in the equilibrium constant expression? Why? (18-2)

6. Explain the effect of a catalyst on an equilibrium system. (18-2)

7. Predict the effect of each of the following on the indicated equilibrium system in terms of which reaction will be favored (forward, reverse, or neither).

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

a. addition of Cl_2
b. removal of HCl
c. increased pressure
d. decreased temperature
e. removal of H_2
f. decreased pressure
g. addition of a catalyst
h. increased temperature
i. decreased system volume (18-2)

8. How would parts (a) through (i) of item 7 affect the new equilibrium concentration of HCl and the value of K at the new equilibrium? (18-2)

9. Changes in the concentrations of the reactants and products at equilibrium have no impact on the value of the equilibrium constant. Explain. (18-2)

10. What relative pressure (high or low) would result in the production of the maximum level of CO_2 according to the following? Explain. (18-2)

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

11. What relative conditions (reactant concentrations, pressure, and temperature) would favor a high equilibrium concentration of the underlined substance in each of the following equilibrium systems?
a. $2CO(g) + O_2(g) \rightleftharpoons \underline{2CO_2(g)} + 167\ \text{kJ}$
b. $Cu^{2+}(aq) + 4NH_3(aq) \rightleftharpoons \underline{Cu(NH_3)_4^{2+}(aq)} + 42\ \text{kJ}$
c. $2HI(g) + 12.6\ \text{kJ} \rightleftharpoons H_2(g) + \underline{I_2(g)}$
d. $4HCl(g) + O_2(g) \rightleftharpoons 2H_2O(g) + \underline{2Cl_2(g)} + 113\ \text{kJ}$
e. $H_2O(l) + 42\ \text{kJ} \rightleftharpoons \underline{H_2O(g)}$ (18-2)

12. A combustion reaction proceeding in air under standard pressure is transferred to an atmosphere of pure oxygen under the same pressure.
a. What effect would you observe?
b. How can you account for this effect? (18-2)

13. What two factors determine the extent to which reacting ions are removed from solution? (18-2)

14. Identify the three conditions under which ionic reactions can run to completion, and write an equation for each. (18-2)

15. a. Write the ion-product constant expression for water.
b. What is the value of this constant at 25°C? (18-3)

16. List and distinguish between the four general categories of salts, based on their hydrolysis properties, and give an example of each. (18-3)

17. The pH of a solution containing both acetic acid and sodium acetate is higher than that of a solution containing the same concentration of acetic acid alone. Explain. (18-3)

18. The ionization constant, K_a, for acetic acid is 1.8×10^{-5} at 25°C. Explain the significance of this value. (18-3)

19. a. From the development of K_a described in Section 18-3, show how you would express an ionization constant, K_b, for the weak base NH_3.
b. In this case, $K_b = 1.8 \times 10^{-5}$. What is the significance of this numerical value to equilibrium? (18-3)

20. A saturated solution is not necessarily a concentrated solution. Explain. (18-4)

21. What rule of thumb is used to distinguish between soluble, insoluble, and slightly soluble substances? (18-4)

22. What is the major solubility characteristic of those types of substances typically involved in solubility-equilibrium systems? (18-4)

23. What is the relationship between K_{sp} and the product of the ion concentrations in terms of determining whether a solution of those ions is saturated? (18-4)

PROBLEMS

Equilibrium Constant

24. Determine the value of the equilibrium constant for each reaction given, assuming that the equilibrium concentrations are found to be those specified. (Concentrations are in mol/L.) (Hint: See Sample Problem 18-1.)
a. $A + B \rightleftharpoons C$; $[A] = 2.0$; $[B] = 3.0$; $[C] = 4.0$
b. $D + 2E \rightleftharpoons F + 3G$; $[D] = 1.5$; $[E] = 2.0$; $[F] = 1.8$; $[G] = 1.2$
c. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$; $[N_2] = 0.45$; $[H_2] = 0.14$; $[NH_3] = 0.62$

25. An equilibrium mixture at a specific temperature is found to consist of 1.2×10^{-3} mol/L HCl, 3.8×10^{-4} mol/L O_2, 5.8×10^{-2} mol/L H_2O, and 5.8×10^{-2} mol/L Cl_2 according to the following: $4HCl(g) + O_2(g) \rightleftharpoons 2H_2O(g) + 2Cl_2(g)$. Determine the value of the equilibrium constant for this system.

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

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

27. The value of the equilibrium constant for the reaction below is 40.0 at a specified temperature. What would be the value of that constant for the reverse reaction under the same conditions? $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

Solubility-Product Constant

28. The ionic substance EJ dissociates to form E^{2+} and J^{2-} ions. The solubility of EJ is 8.45×10^{-6} mol/L. What is the value of the solubility-product constant? (Hint: See Sample Problem 18-2.)

29. Calculate the solubility-product constant K_{sp} for each of the following, based on the solubility information provided:
a. $BaSO_4 = 2.4 \times 10^{-4}$ g/100. g H_2O at 20°C
b. $Ca(OH)_2 = 0.173$ g/100. g H_2O at 20°C

30. Calculate the solubility of a substance MN that ionizes to form M^{2+} and N^{2-} ions, given that $K_{sp} = 8.1 \times 10^{-6}$. (Hint: See Sample Problem 18-3.)

31. Use the K_{sp} values given in Table 18-3 to evaluate the solubility of each of the following in moles per liter.
a. AgBr
b. CoS

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

33. The ionic substance T_3U_2 ionizes to form T^{2+} and U^{3-} ions. The solubility of T_3U_2 is 3.77×10^{-20} mol/L. What is the value of the solubility-product constant?

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

35. Calculate whether a precipitate will form if 0.35 L of 0.0044 M $Ca(NO_3)_2$ and 0.17 L of 0.000 39 M NaOH are mixed at 25°C. (See Table 18-3 for K_{sp} values.) (Hint: See Sample Problem 18-4.)

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

37. If 2.50 g of solid $Fe(NO_3)_3$ is added to 100. mL of a 1.0×10^{-20} M NaOH solution, will a precipitate form?

MIXED REVIEW

38. Calcium carbonate is only slightly soluble in water.

a. Write the equilibrium equation for calcium carbonate in solution.

b. Write the equilibrium-constant expression, K, and the solubility-product constant expression, K_{sp}, for the equilibrium in a saturated solution of $CaCO_3$.

39. Calculate the concentration of Hg^{2+} ions in a saturated solution of $HgS(s)$. What volume of solution contains one Hg^{2+} ion?

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

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

The components were analyzed and it was found that $[H_2] = 0.61$ mol/L, $[CO_2] = 1.6$ mol/L, $[H_2O] = 1.1$ mol/L, and $[CO] = 1.4$ mol/L.

41. A solution in equilibrium with solid barium phosphate is found to have a barium ion concentration of 5×10^{-4} M and a K_{sp} of 3.4×10^{-23}. Calculate the concentration of phosphate ion.

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

$$N_2O(g) + \tfrac{1}{2}O_2(g) \rightleftharpoons 2NO(g)$$

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

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

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

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

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

CRITICAL THINKING

46. Predicting Outcomes When gasoline burns in an automobile engine, nitric oxide is formed from oxygen and nitrogen. Nitric oxide is a major air pollutant. High temperatures like those found in a combustion engine are needed for the reaction. The reaction follows.

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

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

TECHNOLOGY & LEARNING

47. Graphing Calculator Calculating the Equilibrium Constant, K, for a System

The graphing calculator can run a program that calculates K for a system, given the concentrations of the products and the concentrations of the reactants.

Given the balanced chemical equation

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

and the equilibrium mixture at 425°C, you can calculate the equilibrium constant for the system. Then you can use the program to make calculations.

Go to Appendix C. If you are using a TI 83 Plus, you can download the program and data and run the application as directed. If you are using another calculator, your teacher will provide you with keystrokes and data sets to use. Remember that you will need to name the program and check the display, as explained in Appendix C. You will then be ready to run the program. After you have graphed the data, answer these questions.

a. What is the equilibrium constant given the following equilibrium concentrations? 0.012840 mol/L of H_2, 0.006437 mol/L of I_2, and 0.066807 mol/L of HI

b. What is the equilibrium constant given the following equilibrium concentrations? 0.000105 mol/L of H_2, 0.000107 mol/L of I_2, and 0.000779 mol/L of HI

c. What is the equilibrium constant given the following equilibrium concentrations? 0.000527 mol/L of H_2, 0.000496 mol/L of I_2, and 0.003757 mol/L of HI

HANDBOOK SEARCH

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

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

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

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

49. The reactions used to confirm the presence of transition metal ions often involve the formation of precipitates. Review the analytical tests for the transition metals in the *Elements Handbook*. Use that information and Table 18-3 to determine the minimum concentration of Zn^{2+} needed to produce a precipitate that confirms the presence of Zn. Assume enough sulfide ion reagent is added to the unknown solution in the test tube to produce a sulfide ion concentration of 1.4×10^{-20} M.

RESEARCH & WRITING

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

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

ALTERNATIVE ASSESSMENT

52. **Performance** Fill a drinking glass with water and add sugar by the teaspoonful, stirring after each addition. Continue adding the sugar until some of the sugar remains undissolved, even after vigorous stirring. Now heat the sugar-water solution. How are you using Le Châtelier's principle to shift the equilibrium of the system?