CHAPTER 18
Chemical Equilibrium

BIG IDEA
A reaction system is at equilibrium when forward and reverse reactions occur simultaneously and at the same rate. Several factors can influence equilibrium.

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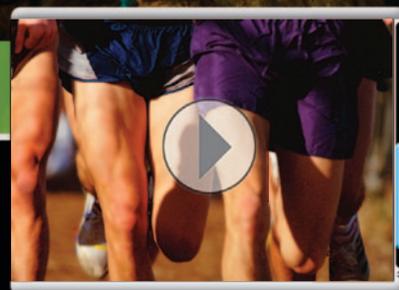
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Acids and Bases

The Nature of Chemical Equilibrium

Key Terms

reversible reaction   equilibrium constant
chemical equilibrium   chemical equilibrium expression

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

MAIN IDEA

All reactions are reversible under certain conditions.

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

Mercury(II) oxide decomposes when heated.

$$2HgO(s) \xrightarrow{\Delta} 2Hg(l) + O_2(g)$$
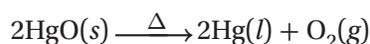
Mercury and oxygen combine to form mercury(II) oxide when heated gently.

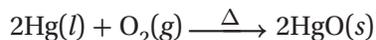$$2Hg(l) + O_2(g) \xrightarrow{\Delta} 2HgO(s)$$

Figure 1.1 shows both of these reactions taking place. Suppose mercury(II) oxide is heated in a closed container from which neither the mercury nor the oxygen can escape. Once decomposition has begun, the mercury and oxygen released can recombine to form mercury(II) oxide again. Thus, both reactions can proceed at the same time. Under these conditions, the rate of the synthesis reaction will eventually equal that of the decomposition reaction. At equilibrium, mercury and oxygen will 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: a state of dynamic equilibrium has been reached.

FIGURE 1.1

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

CRITICAL THINKING

Relate What is the relationship between reversible reactions and photosynthesis? Explain the importance of this connection.


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In such a state of dynamic equilibrium, 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.

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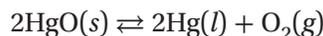
■ MAIN IDEA

Some reactions favor products, and others reactants.

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

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$
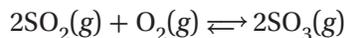
Notice that the equation is written showing an inequality of the two arrow lengths. The forward reaction is represented by the longer arrow to imply that the product is favored in this reaction.

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

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq)$$
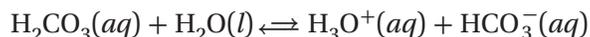
In still other cases, both forward and reverse reactions occur to nearly the same extent before chemical equilibrium is established. Neither reaction is favored, and considerable concentrations of both reactants and products are present at equilibrium. An example is the dissociation of sulfurous acid in water.

$$H_2SO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HSO_3^-(aq)$$
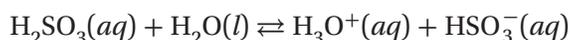
Chemical reactions ordinarily are used to convert available reactants into more desirable products. Chemists try to convert as much of these reactants as possible into products. The extent to which reactants are converted to products is indicated by the numerical value of the equilibrium constant, which will be described in the next section.

✓ CHECK FOR UNDERSTANDING

Explain The two terms *dynamic* and *equilibrium* seem to contradict each other at first. *Dynamic* means that changes are occurring, but *equilibrium* means that no overall change is happening. Given this, explain why the combination of the two, *dynamic equilibrium*, is correct.

MAIN IDEA

At equilibrium, the concentrations of reactants and products remain constant.

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.

$$n\text{A} + m\text{B} \rightleftharpoons x\text{C} + y\text{D}$$
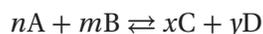
Initially, the concentrations of C and D are zero, and those of A and B are maximum. **Figure 1.2** shows that, over time, the rate of the forward reaction decreases as A and B are used up. Meanwhile, the rate of the reverse reaction increases as C and D are formed. When these two reaction rates become equal, equilibrium is established. The individual concentrations of A, B, C, and D undergo no further change if conditions remain the same.
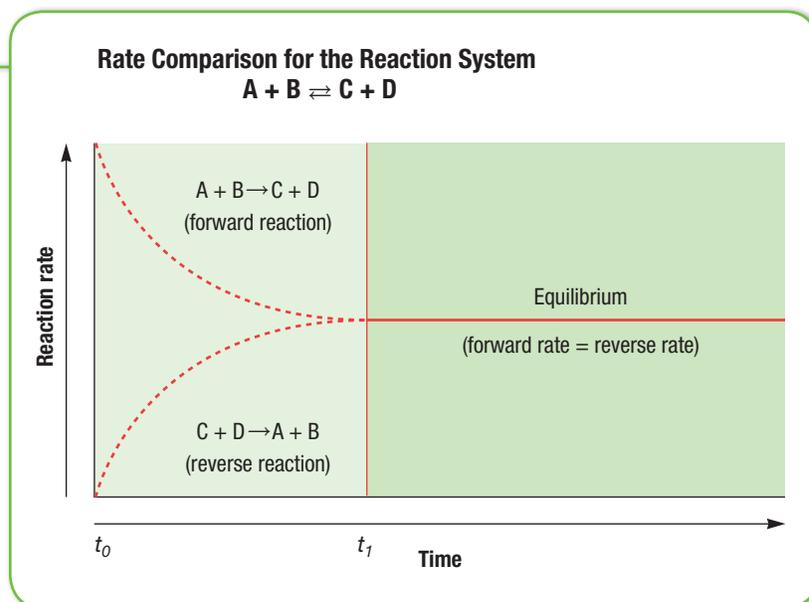
Once equilibrium is attained, the concentrations of products and reactants remain constant, so a ratio of their concentrations should also remain constant. The ratio of the mathematical product $[\text{C}]^x \times [\text{D}]^y$ to the mathematical product $[\text{A}]^n \times [\text{B}]^m$ for this reaction has a definite value at a given temperature. It is the equilibrium constant of the reaction and is designated by the letter K. The following equation describes the equilibrium constant for the hypothetical equilibrium system. The brackets ([ ]) indicate the concentration of each substance as expressed in mol/L. The superscripts are the coefficients of each substance in the balanced chemical equation.

Equilibrium Constant $\qquad K = \dfrac{[\text{C}]^x[\text{D}]^y}{[\text{A}]^n[\text{B}]^m}$

FIGURE 1.2

Equilibrium Reaction Systems 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.

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

A + B→C + D
(forward reaction)

Equilibrium
(forward rate = reverse rate)

C + D→A + B
(reverse reaction)

Reaction rate

t_0 t_1 **Time**

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

The Equilibrium Constant

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

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

The H_2, I_2, HI Equilibrium System

An excellent example of an equilibrium system occurs with the reaction between H_2 and I_2 vapor in a sealed flask at an elevated temperature. A typical look at this reaction can be seen in **Figure 1.3.** If the reaction were observed, its rate could be followed by making note of how quickly the violet color of the iodine vapor diminished. If colorless H_2 gas is present in excess, we might expect that the reaction would continue until all of the I_2 is used up. The violet color of the flask would decrease in intensity until all of the iodine reacts. At that time, the beaker would be colorless, because both HI and the excess H_2 are colorless gases.

In actuality, the color fades to a constant intensity but does not disappear completely, because the reaction is reversible. Once the reaction between H_2 and I_2 reaches a certain point, hydrogen iodide decomposes to re-form hydrogen and iodine. The rate of this reverse reaction increases as the concentration of hydrogen iodide increases.

FIGURE 1.3

H_2, I_2, HI Equilibrium System The violet color of the reactant iodine gas, I_2, gives an indication of the progress of the reaction between hydrogen and iodine. Both H_2 (reactant) and HI (product) are colorless gases. The darker the purple color in the flask, the less I_2 gas reacted, so the more reactants remain.

The rate of the forward reaction decreases accordingly. The concentrations of hydrogen and iodine decrease as they react. As the rates of the opposing reactions become equal, equilibrium is established. The constant color achieved indicates that equilibrium exists among hydrogen, iodine, and hydrogen iodide. The net chemical equation for the reaction system at equilibrium follows.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$
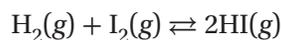
From this chemical equation, the following chemical equilibrium expression can be written. The concentration of HI is raised to the power of 2, because the coefficient of HI in the balanced chemical equation is 2.

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

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 **Figure 1.4.** Experiments 1 and 2 began with hydrogen iodide. Experiments 3 and 4 began with hydrogen and iodine. Note the close agreement obtained for the numerical values of the equilibrium constant in all cases.

At 425°C, the equilibrium constant for this equilibrium reaction system has the average value of 54.34. This value for K is constant for any system of H_2, I_2, and HI at equilibrium at this temperature. If the calculation for K yields a different result, there must be a reason. Either the H_2, I_2, and HI system has not reached equilibrium, or the system is not at 425°C.

The balanced chemical equation for an equilibrium system is necessary to write the expression for the equilibrium constant. The data in **Figure 1.4** 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.

FIGURE 1.4

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

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

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

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

Using the known K value and the given concentrations for H_2 and I_2, if you solve the equation for [HI], you will observe the following result:

$$[HI] = \sqrt{0.015 \times 0.015 \times 54.34}$$

$$[HI] = 0.11 \text{ mol/L}$$

When calculating concentrations at equilibrium, always be sure to note the temperature at which the reaction is taking place. Values for K do change with changing temperature.

Equilibrium Constant

Sample Problem A 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?

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

PLAN

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

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

SOLVE

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

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

Continued

Equilibrium Constant (continued)

CHECK YOUR WORK

The value of K is small, which is consistent with more N_2 and O_2 being present at equilibrium than NO. The answer has the correct number of significant figures and is close to an estimated value of 8×10^{-6}, calculated as:

$$\frac{(1 \times 10^{-5})^2}{(6 \times 10^{-3})(2 \times 10^{-3})}$$

Practice Answers in Appendix E

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

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

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

SECTION 1 FORMATIVE ASSESSMENT

Reviewing Main Ideas

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^-. Should the value of K for the reaction $HCl(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Cl^-(aq)$ be 1×10^{-2}, 1×10^{-5}, or "very large"? Justify your answer.

6. Write the chemical equilibrium expression for the following reaction:
$4HCl(g) + O_2(g) \rightleftharpoons 2Cl_2(g) + 2H_2O(g)$

7. At equilibrium at 2500 K, $[HCl] = 0.0625$ mol/L and $[H_2] = [Cl_2] = 0.00450$ mol/L for the reaction $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$. Find the value of K.

8. An equilibrium mixture at 425°C is found to consist of 1.83×10^{-3} mol/L of H_2, 3.13×10^{-3} mol/L of I_2, and 1.77×10^{-2} mol/L of HI. Calculate the equilibrium constant, K, for the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$.

9. For the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ at 425°C, calculate [HI], given $[H_2] = [I_2] = 4.79 \times 10^{-4}$ mol/L and $K = 54.3$.

Critical Thinking

10. **INFERRING RELATIONSHIPS** Use the data from Experiment 1 in **Figure 1.4** to calculate the value of K for the following reaction:

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$
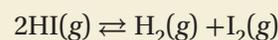
Do you see a relationship between the value you obtained and the value in the table?

Fixing the Nitrogen Problem

Historical Perspective

Each year, the chemical industry synthesizes tons of nitrogenous fertilizers, increasing agricultural production around the globe. But prior to 1915, people 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 organisms can utilize the gas that forms 78% of the atmosphere; they need nitrogen that has been combined with other elements, or "fixed," to survive.

But soils often lack enough of the microorganisms that fix nitrogen for plants, so fertilizers containing usable nitrogen compounds are added. In 1898, two-thirds of the world's supply of these compounds came from Chile, where beds of sodium nitrate, or Chile saltpeter, were abundant. But, as the chemist William Crookes emphasized in his speech to the British Association that year, these reserves were limited; it was up to his colleagues to discover alternatives and prevent Malthus's dire forecast from coming true.

Nitrogen gas

Nitrogen-fixing bacteria on plant roots

Ammonia

Plants

Animals

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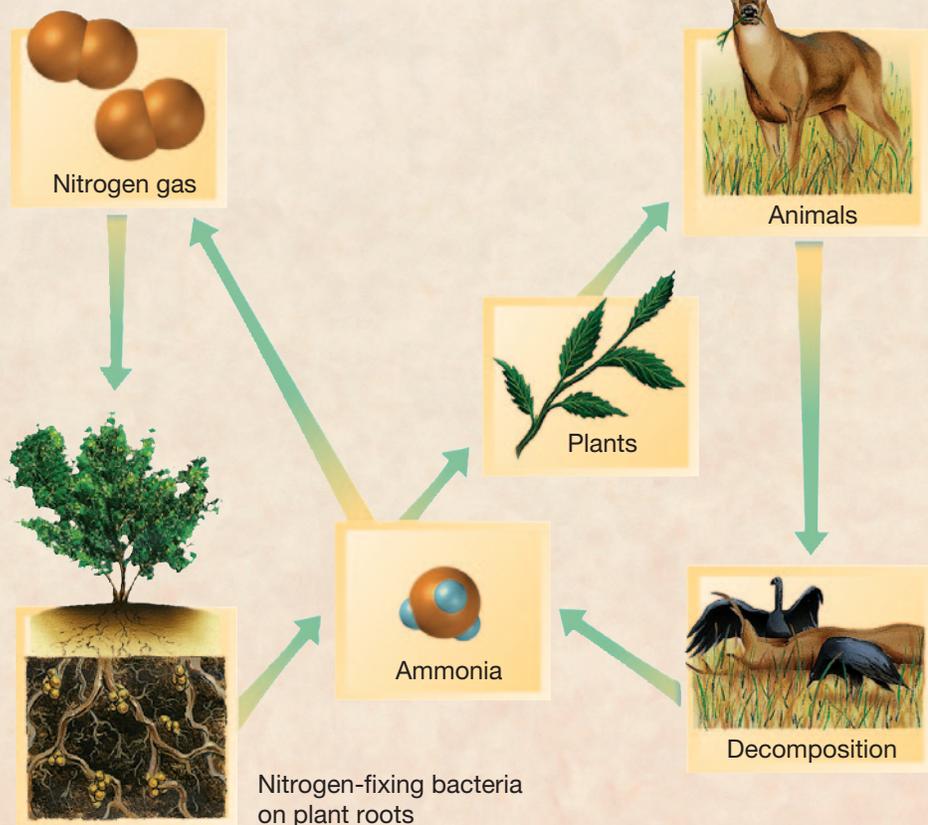
Nitrogen is released when living organisms die. It is also released from animal wastes and plant material. Some bacteria are able to break the bond holding the nitrogen molecule together, freeing the nitrogen atoms to combine with hydrogen to form ammonia. Plants can absorb the nitrogen in this form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

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 up to 1020°C using pure iron as well as other metals as a catalyst. He found that the amount of ammonia was a mere 0.005% to 0.012% at equilibrium.

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

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

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

Scaling Up

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

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

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.

An Eerie Epilogue

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

Questions

1. What is the major use for ammonia?

2. What did Haber find when he tried to synthesize ammonia at increased pressure?

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Shifting Equilibrium

Key Term
common-ion effect

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

▶ **MAIN IDEA**
Equilibrium shifts to relieve stress on the system.

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

Changes in Pressure

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

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

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$
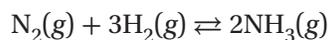
First, consider an increase in pressure as the applied stress. Can the system shift in a way that reduces the stress? Yes. An increase in pressure causes increases in the concentrations of all species. The system can reduce the number of molecules, and hence the total pressure, by shifting the equilibrium to the right. For each four molecules of reactants, nitrogen and hydrogen, there are two molecules of product, ammonia. By producing more NH_3, and using up N_2 and H_2, the system can reduce the total number of molecules. This leads to a decrease in pressure. Although the new equilibrium pressure is still higher than before, it is not as high as the pressure caused by the initial stress. Even though changes in pressure may shift the equilibrium position, they do not affect the value of the equilibrium constant.

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

Changes in Concentration

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

$$A + B \rightleftarrows C + D$$
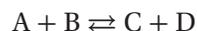
An increase in the concentration of A creates a stress. To relieve the stress, some of the added A reacts with B to form products C and D. The equilibrium is reestablished with a higher concentration of A than before the addition but with a lower concentration of B. Similarly, an increase in the concentration of B drives the reaction to the right. An increase in the concentration of either C or D shifts the equilibrium to the left. A decrease in the concentration of C or D has the same effect on the position of the equilibrium as does an increase in the concentration of A or B; the equilibrium shifts to the right. **Figure 2.1** gives an example of such an instance by showing what effects an increase of N_2 has on the equilibrium in the Haber process.

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

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

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

$$2H_2O(l) \rightleftarrows H_3O^+(aq) + OH^-(aq)$$
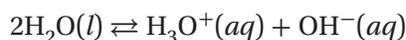
and the equation for K_w is $K_w = [H_3O^+][OH^-]$.

The following equation describes the equilibrium system established by the decomposition of solid calcium carbonate.
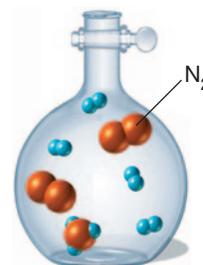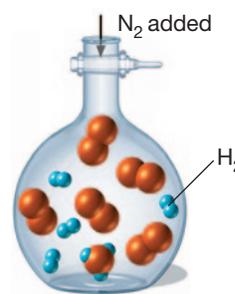
$$CaCO_3(s) \rightleftarrows CaO(s) + CO_2(g)$$
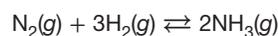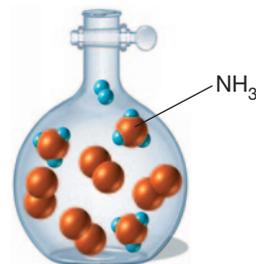
FIGURE 2.1

Concentration's Effect on Equilibrium

(a) N_2, H_2, and NH_3 are in equilibrium within a closed system.

(b) Addition of more N_2 causes a stress on the initial equilibrium.

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

(c) The new equilibrium position for this system has a higher concentration of N_2, a lower concentration of H_2, and a higher concentration of NH_3 than initially.

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

$$K = [CO_2]$$

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

Changes in Temperature

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

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

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

$$N_2(g) + 3H_2(g) \rightleftarrows 2NH_3(g) + 92 \text{ kJ}$$
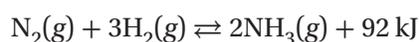
A high temperature favors the decomposition of ammonia, the endothermic reaction. But at low temperatures, the forward reaction is too slow to be commercially useful. The temperature used represents a compromise between kinetic and equilibrium requirements. It is high enough that equilibrium is established rapidly but low enough that the equilibrium concentration of ammonia is still significant. Moderate temperature (about 500°C) and very high pressure (700–1000 atm) produce a satisfactory yield of ammonia.

The production of colorless dinitrogen tetroxide gas, N_2O_4, from dark red-brown NO_2 gas is also an exothermic reaction. **Figure 2.2** shows how temperature affects the equilibrium of this system. **Figure 2.2b** shows the NO_2/N_2O_4 equilibrium mixture at 25°C. When the temperature of the system is lowered to 0°C, the system experiences a stress (removal of energy as heat). To counteract this stress, the system shifts to the right, in the direction of the exothermic reaction. This increases the amount of colorless N_2O_4 gas and decreases the amount of brown NO_2 gas; see **Figure 2.2a.** Because more N_2O_4 and less NO_2 are present, K is increased.

FIGURE 2.2

Temperature Effects on Equilibrium Different temperatures can cause an equilibrium system to shift and seek a new equilibrium position.

(a) When energy as heat is taken away from the system, the exothermic reaction is favored, so more N_2O_4 is produced. N_2O_4 is colorless, so the bottle appears lighter.

0°C

(b) At increasing temperatures, more of the endothermic reaction can occur, so more of the brown NO_2 forms.

25°C

(c) At even higher temperatures, still more of the brown NO_2 forms, and the color in the bottle appears even darker.

100°C

$$2NO_2(g) \rightleftarrows N_2O_4(g) + \text{energy as heat}$$
(brown)   (colorless)
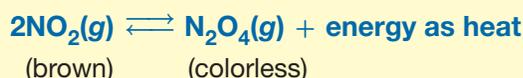
When the system is heated to 100°C, the added energy is the stress, and the equilibrium shifts to the left, or in the direction of the endothermic reaction. This shift decreases the amount of colorless N_2O_4 gas and increases the amount of brown NO_2 gas, see **Figure 2.2c.** Because less N_2O_4 gas and more NO_2 are present, K is decreased. The change in temperature changes the value of K. For a system in which the forward reaction is an exothermic reaction, increasing temperature decreases the value of K.

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

$$556 \text{ kJ} + CaCO_3(s) \rightleftarrows CaO(s) + CO_2(g)$$
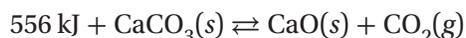
An increase in temperature caused by adding energy to the system causes the value of K to increase and the equilibrium to shift to the right.

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

▶ **MAIN IDEA**

Some ionic reactions seem to 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 forms a weak electrolyte effectively removes from solution virtually all of the reacting ions that compose it.

Formation of a Gas

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

$$H_3O^+ + HCO_3^- \rightarrow 2H_2O(l) + CO_2(g)$$
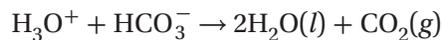
This reaction goes practically to completion because one of the products, CO_2, escapes as a gas if the container is open to the air and the other, water, is a weak electrolyte.

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 2.3.** The full ionic equation for this reaction follows.

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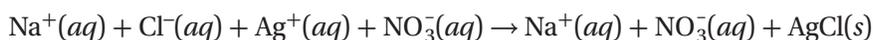
If chemically equivalent amounts of the two solutes are mixed, only Na^+ ions and NO_3^- ions remain in solution in appreciable quantities. Almost all of the Ag^+ ions and Cl^- ions combine and precipitate from the solution as AgCl, because AgCl is only very slightly soluble in water. The solution is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

FIGURE 2.3

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

Cl⁻
H₂O
Na⁺
Sodium chloride solution

NO₃⁻
Ag⁺
H₂O
Silver nitrate solution

Ag⁺
NO₃⁻
Na⁺
Cl⁻
H₂O
Silver chloride (AgCl) precipitate
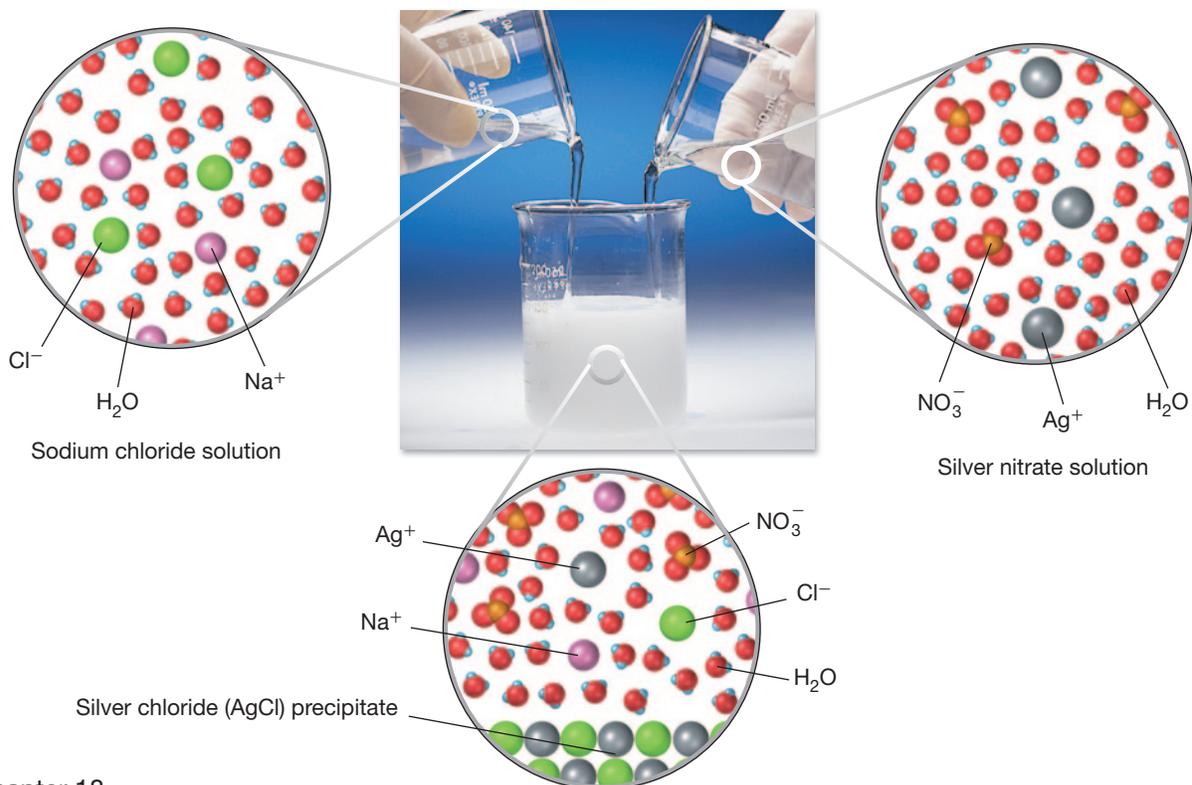
Formation of a Weak Electrolyte

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:

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

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

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

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

▶ MAIN IDEA
Common ions often produce precipitates.

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

$$HCl(g) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$$
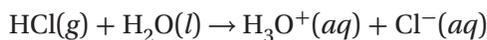
The equilibrium for a saturated solution of sodium chloride is described by the following equation.

$$NaCl(s) \rightleftharpoons Na^+(aq) + Cl^-(aq)$$
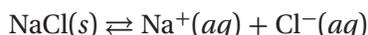
As the hydrogen chloride dissolves in sufficient quantity, it increases the concentration of Cl^- ions in the solution, which is a stress on the equilibrium system. The system can compensate, according to Le Châtelier's principle, by combining some of the added Cl^- ions with an equivalent amount of 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 the formation of a weak electrolyte, is an example of the common-ion effect.**

The common-ion effect is also observed when one ion species of a weak electrolyte is added in excess to a solution. Acetic acid, CH_3COOH, is such an electrolyte. A 0.1 M CH_3COOH solution is only about 1.3% ionized as hydronium ions and acetate ions, CH_3COO^-. The ionic equilibrium is shown by the following equation:
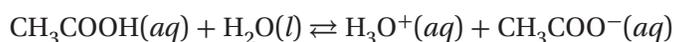
$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$

FIGURE 2.4

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

Addition of sodium acetate, $NaCH_3COO$ (an ionic salt soluble in water), to a solution containing acetic acid increases the acetate ion concentration. The equilibrium then shifts in the direction that uses up some of the added acetate ions in accordance with Le Châtelier's principle. More molecules of acetic acid are formed, and the concentration of hydronium ions is reduced. In general, the addition of a salt with an ion in common with the weak electrolyte reduces the ionization of the electrolyte. **Figure 2.4** 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.

✔ SECTION 2 **FORMATIVE ASSESSMENT**

▶ Reviewing Main Ideas

1. Name three ways the chemical equilibrium can be disturbed.

2. Describe three situations in which ionic reactions go to completion.

3. Describe the common-ion effect.

4. Identify the common ion in each of the following situations.

   a. 5 g of NaCl is added to a 2.0 M solution of HCl

   b. 50 mL of 1.0 M $NaCH_3COO$ is added to 1.0 M CH_3COOH

   c. 1 g of NH_4Cl is added to 100 mL of aqueous NH_3

5. Predict the effect that decreasing pressure would have on each of the following reaction systems at equilibrium.

   a. $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$

   b. $NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$

   c. $2H_2O_2(aq) \rightleftharpoons 2H_2O(l) + O_2(g)$

   d. $3O_2(g) \rightleftharpoons 2O_3(g)$

✔ Critical Thinking

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

Equilibria of Acids, Bases, and Salts

Key Terms

acid ionization constant
buffered solution
hydrolysis

▶ **MAIN IDEA**

The ionization constant is a measure of acid and base strength in solution.

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

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

$$K = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH][H_2O]}$$
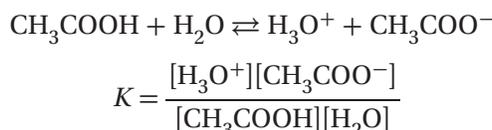
By convention, the concentration of water is not included in the equilibrium expression. Water is the solvent, and water molecules greatly exceed the number of acetic acid molecules. We can assume that the molar concentration of H_2O molecules remains constant in such a solution without introducing a measurable error. 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 is small since the concentration of ions is small. 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.

FIGURE 3.1

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}

FIGURE 3.2

Buffered Solution

(a) The beaker on the left contains a buffered solution and an indicator and has a pH of about 5. The beaker on the right contains mostly water with a trace amount of acid and an indicator. The pH meter shows a pH of 5.00 for this solution.

(b) After 5 mL of 0.10 M HCl is added to both beakers, the beaker on the left does not change color, indicating no substantial change in its pH. However, the beaker on the right undergoes a definite color change, and the pH meter shows a pH of 2.17.

Ionization data and constants for some dilute acetic acid solutions at 25°C are given in **Figure 3.1**. Notice that the numerical value of K_a is almost identical for each solution molarity shown. The numerical value of K_a for CH_3COOH at 25°C can be determined by substituting numerical values for concentration into the equilibrium equation.

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

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

▶ **MAIN IDEA**

Buffers resist changes in pH.

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 3.2** shows how a buffered and an unbuffered 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.

$$CH_3COO^-(aq) + H_3O^+(aq) \rightarrow CH_3COOH(aq) + H_2O(l)$$
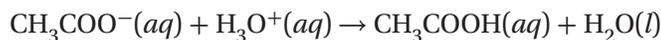
The hydronium ion concentration and the pH of the solution remain practically unchanged.

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

$$CH_3COOH(aq) + H_2O(l) \rightarrow H_3O^+(aq) + CH_3COO^-(aq)$$
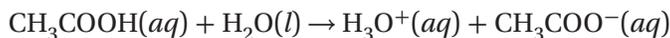
The pH of the solution again remains practically unchanged.

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.

$$NH_4^+(aq) + OH^-(aq) \rightarrow NH_3(aq) + H_2O(l)$$
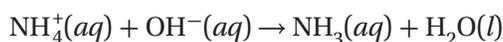
If a small amount of an acid is added to the solution instead, hydroxide ions from the solution accept protons from the added hydronium ions to form nonionized water molecules. Ammonia molecules in the solution then ionize and mostly replace the hydroxide ions neutralized by added H$_3$O$^+$.

$$NH_3(aq) + H_2O(l) \rightarrow NH_4^+(aq) + OH^-(aq)$$
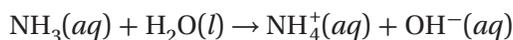
Buffer action has many important applications in chemistry and physiology. Human blood is naturally buffered to maintain a pH of between 7.3 and 7.5. This is essential, because large changes in pH would lead to serious disturbances of normal body functions. **Figure 3.3** shows an example of one of the many medicines buffered to prevent large and potentially damaging changes in pH.

✔ CRITICAL THINKING

Infer Aspirin, pictured here, is acidic. What would be the most obvious side effect on a person taking it in an unbuffered form?

▶ **MAIN IDEA**
Water is a weak electrolyte.

In the chapter "Acid-Base Titration and pH," you learned that the self-ionization of water is an equilibrium reaction.

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$
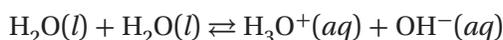
Equilibrium is established with a very low concentration of H$_3$O$^+$ and OH$^-$ ions. The expression for the equilibrium constant, $K_w = [H_3O^+][OH^-]$, is derived from the balanced chemical equation. The numerical value of K_w, obtained experimentally, is 1.0×10^{-14} at 25°C.

The self-ionization of water may seem inconsequential at first, since the percent of ionization is very low and the resulting product neutral; however, it has a major impact on the equilibrium achieved in the aqueous solutions of salts. Because salts dissociate into their constituent ions when dissolved, these ions can, and often do, interact with the ions produced by water's self-ionization. The result is a solution that can be acidic, basic, or neutral depending on the salt that forms.

Hydrolysis of anions and cations can produce non-neutral solutions.

Salts are formed during neutralization reactions between acids and bases. When a salt dissolves in water, it produces positive ions (cations) of the base from which it was formed and negative ions (anions) of the acid from which it was formed. Therefore, the solution might be expected to be neutral. The aqueous solutions of some salts, such as NaCl and KNO_3, are neutral, having a pH of 7. However, when sodium carbonate dissolves in water, the resulting solution turns red litmus paper blue, indicating a pH greater than 7. Ammonium chloride produces an aqueous solution that turns blue litmus paper red, indicating a pH less than 7. Salts formed from combining strong or weak acids and bases are shown in **Figure 3.4.**

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

FIGURE 3.4

Hydrolysis The universal indicator shows that the pH of salt solutions varies, depending on the strength of the acid and the base that formed the salt.

(a) NaCl is formed from a strong acid and a strong base; the color of the indicator shows the pH is neutral.

(b) The indicator shows the pH of the sodium acetate solution is basic. This was formed from a strong base and a weak acid.

(c) The strong acid and weak base combination in ammonium chloride produces an acidic solution, as shown by the reddish tint of the indicator.

(d) The weak acid and weak base that form ammonium acetate are of comparable strength. A solution of ammonium acetate is essentially neutral.

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

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

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$
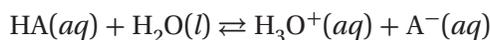
From this equation, the generalized expression for K_a can be written. Note that as before, water does not appear in the general equilibrium equation.

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

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

$$A^-(aq) + H_2O(l) \rightleftharpoons HA(aq) + OH^-(aq)$$
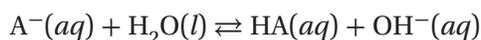
Neutral water has equal concentrations of H$_3$O$^+$ and OH$^-$. Since HA is a weak acid, the anion A$^-$ has a strong attraction for protons. Adding A$^-$ to water in effect attracts (removes) H$_3$O$^+$ in water to form HA. This causes OH$^-$ to increase relative to H$_3$O$^+$ as represented in the equation above. The lower the value of K_a, the stronger the attraction A$^-$ will have for protons and the larger the concentration of OH$^-$. In other words, the weaker the acid, HA, the stronger its conjugate base, A$^-$.

Aqueous solutions of sodium carbonate are strongly basic. The sodium ions, Na$^+$, in sodium carbonate do not undergo hydrolysis in aqueous solution, but the carbonate ions, CO$_3^{2-}$, react as a Brønsted base. A CO$_3^{2-}$ anion acquires a proton from a water molecule to form the weak Brønsted acid HCO$_3^-$ and the OH$^-$ ion.

$$CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$$
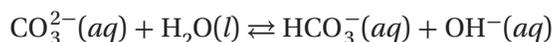
The OH$^-$ ion concentration increases until equilibrium is established. Consequently, the H$_3$O$^+$ ion concentration decreases so that the product [H$_3$O$^+$][OH$^-$] remains equal to the ionization constant, K_w, of water at the temperature of the solution. Thus, the pH is *higher* than 7, and the 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$_3$O$^+$ ions. An equilibrium is established in which the net effect of the cation hydrolysis is an increase in the hydronium ion concentration, [H$_3$O$^+$], of the solution.

✓ **CHECK FOR UNDERSTANDING**

Explain In the Cross-Disciplinary Connection feature "Blood Buffers" above, *hypo*ventilation is described as the opposite of *hyper*ventilation. Based on information in the feature, explain why one treatment for hyperventilation is breathing with a paper bag placed over the mouth and nose.

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 between water and the cation, BH^+, from the dissociation of the weak base, B, is shown by the general equilibrium equation:

$$BH^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + B(aq)$$
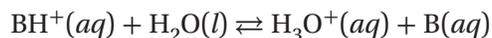
In the forward reaction, the cation BH^+ donates a proton to the water molecule to form the hydronium ion. Because H_3O^+ ions are formed, the solution must become more acidic, as shown in the equation above. The extent of H_3O^+ ion formation depends on the relative strength of the base B. The weaker the base, the greater the concentration of H_3O^+ ions will be. Therefore, the weaker the base, the stronger its conjugate acid.

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

Hydrolysis in Acid-Base Reactions

Many assume that a neutralization reaction between an acid and a base always results in a neutral solution. However, this is not necessarily the case. Hydrolysis can help explain why the end point of a neutralization reaction can occur at a pH other than 7.

FIGURE 3.5

Titration Curve of a Weak Acid and Strong Base At point 1, 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.

Titration Curve for 100 mL of 0.100 M CH_3COOH Titrated with 0.100 M NaOH
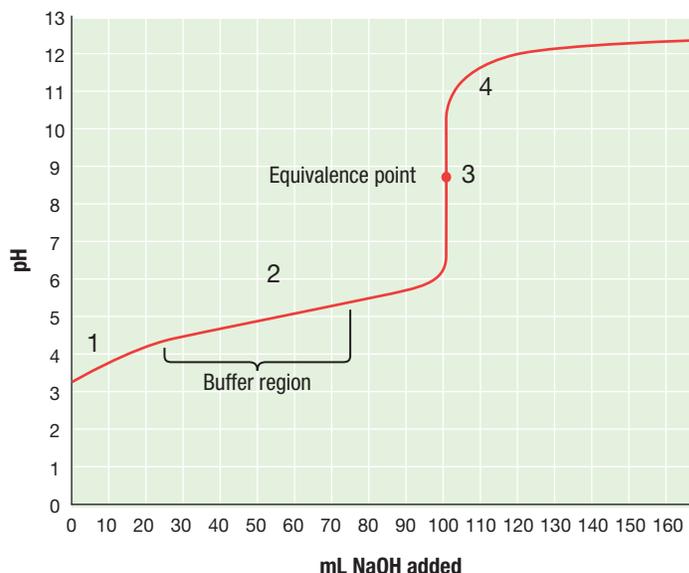
The hydrolysis properties of salts are determined by the relative strengths of the acids and bases from which the salts form. We can place these salts into four general categories: strong acid–strong base, strong acid–weak base, weak acid–strong base, and weak acid–weak base.

Salts of strong acids and strong bases produce neutral solutions because neither the cation of a strong base nor the anion of a strong acid hydrolyzes appreciably in aqueous solutions. An example of this is the reaction between HCl(aq), which is a strong acid, and NaOH(aq), which 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. KNO_3 is the salt of the strong acid HNO_3 and the strong base KOH and, in solution, also has a pH of 7.

Aqueous solutions of salts formed from weak acids and strong bases are basic at the equivalence point (see **Figure 3.5**). Anions of the dissolved salt are hydrolyzed by the water molecules, and the pH of the solution is raised, indicating that the hydroxide-ion concentration has increased. Aqueous solutions of sodium acetate, $NaCH_3COO$, are basic. The acetate ions, CH_3COO^-, undergo hydrolysis because they are the anions of the weak acid acetic acid. The cations of the salt are from a strong base, NaOH, and do not hydrolyze, because NaOH is 100% dissociated.

Figure 3.6 shows that salts of strong acids and weak bases are acidic at the equivalence point. Cations of the dissolved salt are hydrolyzed in 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.

Titration Curve of a Strong Acid and a Weak Base 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.

Titration Curve for 100 mL of 0.100 M NH_3 Titrated with 0.100 M HCl
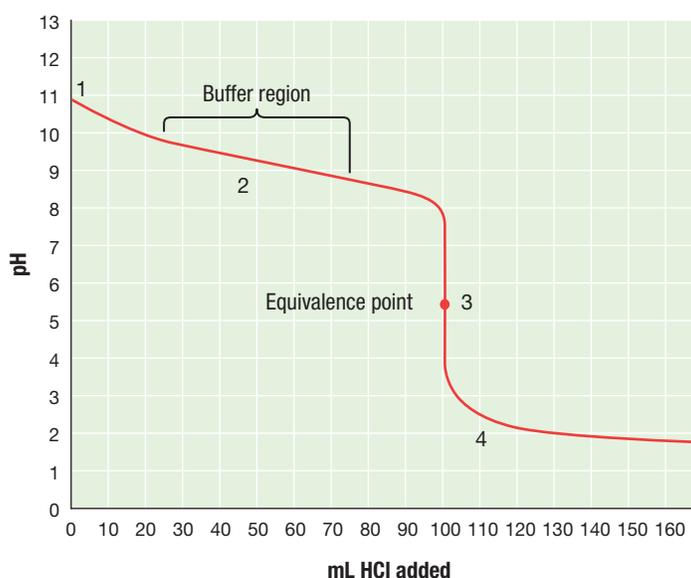
Salts of weak acids and weak bases can produce either acidic, neutral, or basic aqueous solutions, depending on the salt dissolved. This is because both ions of the dissolved salt are hydrolyzed extensively. If both ions are hydrolyzed equally, the solution remains neutral. The ions in ammonium acetate, NH_4CH_3COO, hydrolyze equally, producing a neutral solution (see **Figure 3.4d** in this section).
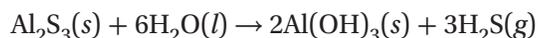
In salts formed from a weak acid and weak base, the cation and anion both undergo hydrolysis. For example, when aluminum sulfide is placed in water, Al^{3+} reacts with OH^-, forming $Al(OH)_3$, and S^{2-} reacts with H^+, forming H_2S. The reaction is shown by the following chemical equation.

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

Since $Al(OH)_3$ is a precipitate and H_2S is a gas, both leave the solution.

As you can see, there are several variations on neutralization reactions, each based on whether the reactants are strong or weak acids and bases. It is good practice to start your determination of the pH of one of these solutions by looking closely at the balanced equation for the reaction. By taking this first step and determining the strength or weakness of the reactants, you can make a generalized prediction of what the pH of the product solution will be at the equivalence point.

✔ SECTION 3 FORMATIVE ASSESSMENT

▶ Reviewing Main Ideas

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 its value at 25°C?

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

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

8. Which of the following ions hydrolyze in aqueous solution?
   a. NO_3^-
   b. F^-
   c. NH_4^+
   d. K^+
   e. CH_3COO^-
   f. SO_4^{2-}
   g. CO_3^{2-}
   h. PO_4^{3-}

9. Identify the following solutions as acidic, basic, or neutral.
   a. 0.5 M KI
   b. 0.10 M $Ba(OH)_2$
   c. 0.25 M NH_4NO_3
   d. 0.05 M K_2CO_3

10. Identify the acid and base from which each of the following salts was formed.
   a. K_2CrO_4
   b. $Ca(CH_3COO)_2$
   c. CaF_2
   d. $(NH_4)_2SO_4$

✔ Critical Thinking

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

Solubility Equilibrium

Key Term

solubility product constant

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.

▶ **MAIN IDEA**

The equilibrium product constant (K_{sp}) describes how soluble a substance is.

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 can be low, if the solubility of the solute is low.

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

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

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

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$
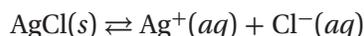
This is a heterogeneous reaction. Recall that the convention is to write its equilibrium expression without the solid species, AgCl. The resulting equilibrium expression is known as the solubility product constant, K_{sp}.

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

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 balanced chemical equation.

Like all such equilibrium expressions, the solubility product constant is expressing an equilibrium and, in the case of AgCl, is equal to the product of the concentrations of its ions in solution. It depends on the form of the equilibrium expression.

For example, calcium fluoride is another slightly soluble salt. The equilibrium in a saturated CaF_2 solution is described by the equation

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$$
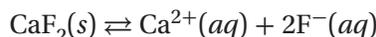
The solubility product constant has the following form.

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

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

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

$$\frac{1.9 \times 10^{-4} \text{ g AgCl}}{100. \text{ g H}_2\text{O}} \times \frac{1 \text{ g H}_2\text{O}}{1 \text{ mL H}_2\text{O}} \times \frac{1000 \text{ mL}}{1 \text{ L}} \times \frac{1 \text{ mol AgCl}}{143.32 \text{ g AgCl}}$$

$$= 1.3 \times 10^{-5} \text{ mol/L}$$

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

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

and

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

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

The solubility of CaF_2 is 1.6×10^{-3} g/100 g of water at 25°C. Expressed in moles per liter, as before, this concentration is 2.05×10^{-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 2.05×10^{-4} for the calcium ion and $2(2.05 \times 10^{-4})$, or 4.1×10^{-4}, for the fluoride ion. Note that at equilibrium at 25°C, $[Ca^{2+}]$ equals the solubility of 2.05×10^{-4} mol/L, but $[F^-]$ equals twice the solubility, or 4.1×10^{-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.

$$K_{sp} = [Ca^{2+}][F^-]^2$$
$$K_{sp} = (2.05 \times 10^{-4})(4.1 \times 10^{-4})^2$$
$$K_{sp} = 3.45 \times 10^{-11}$$

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

Comparing Solubility and K_{sp}

It is difficult to measure very small concentrations of a solute with precision. For this reason, solubility data from different sources may report different values of K_{sp} for a substance. Thus, calculations of K_{sp} ordinarily should be limited to two significant figures. Representative values of K_{sp} at 25°C for some slightly soluble compounds are listed in **Figure 4.1.** Assume that all data used in K_{sp} calculations have been taken at 25°C unless otherwise specified.

At this point, you should note the difference between the solubility of a given solid and its solubility product constant. Remember that the *solubility product constant* is an equilibrium constant representing the product of the molar concentrations of its ions, raised to the power of their coefficients in the solubility equilibrium expression, in a saturated solution. The solubility represents the maximum mass of solute that can dissolve in a given volume at a given temperature. Solubilities are often expressed in grams of solute per 100 g of water.

FIGURE 4.1

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}	$Fe(OH)_3$	$[Fe^{3+}][OH^-]^3$	4.0×10^{-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}

On the other hand, the *solubility* of a substance is a value and not a product of values. Solubility 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. Another way to distinguish the two is that solubility speaks of the substance as a whole, while the solubility product constant deals with its constituent parts.

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Solubility Product Constant

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

① ANALYZE

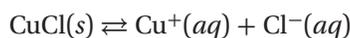**Given:** solubility of CuCl = 1.08×10^{-2} g CuCl/100. g H_2O

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 SOLVE

The molar mass of CuCl is 99.00 g/mol.

$$\text{solubility in mol/L} = \frac{1.08 \times 10^{-2} \text{ g CuCl}}{100. \text{ g } H_2O} \times \frac{1 \text{ g } H_2O}{1 \text{ mL}} \times \frac{1000 \text{ mL}}{1 \text{ L}} \times \frac{1 \text{ mol CuCl}}{99.00 \text{ g CuCl}} =$$

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

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

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

④ CHECK YOUR WORK

The answer contains the proper number of significant figures and is close to the K_{sp} value given in **Figure 4.1.**

Practice   Answers in Appendix E

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

Solubility of a slightly soluble salt is found using the solubility product constant.

Once known, the solubility product constant can be used to determine the solubility of a slightly soluble salt. Suppose you wish to know how many moles of barium carbonate, $BaCO_3$, can be dissolved in 1 L of water at 25°C. From **Figure 4.1**, K_{sp} for $BaCO_3$ has the numerical value 5.1×10^{-9}. The equilibrium equation is written as follows:

$$BaCO_3(s) \rightleftharpoons Ba^{2+}(aq) + CO_3^{2-}(aq)$$
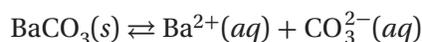
Given the value for K_{sp}, we can write the solubility equilibrium expression as follows:

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

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

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

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

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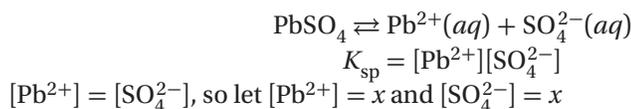
Calculating Solubility

Sample Problem C Calculate the solubility of lead sulfate, $PbSO_4$, in mol/L, using the K_{sp} value for this compound listed in **Figure 4.1**.

① ANALYZE

Given: $K_{sp} = 1.6 \times 10^{-8}$

Unknown: solubility of $PbSO_4$

② PLAN

$$PbSO_4 \rightleftharpoons Pb^{2+}(aq) + SO_4^{2-}(aq)$$
$$K_{sp} = [Pb^{2+}][SO_4^{2-}]$$
$$[Pb^{2+}] = [SO_4^{2-}], \text{ so let } [Pb^{2+}] = x \text{ and } [SO_4^{2-}] = x$$

③ SOLVE

$$PbSO_4 \rightleftharpoons Pb^{2+}(aq) + SO_4^{2-}(aq)$$
$$K_{sp} = x^2$$
$$x^2 = 1.6 \times 10^{-8}$$
$$x = \sqrt{1.6 \times 10^{-8}}$$
$$\text{Solubility of } PbSO_4 = \sqrt{1.6 \times 10^{-8}} = 1.3 \times 10^{-4} \text{ mol/L}$$
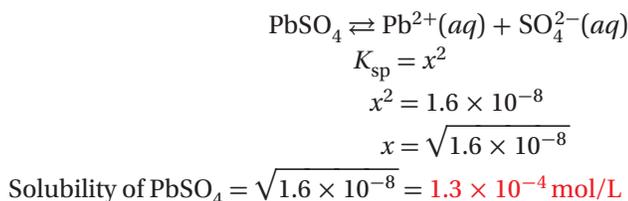
④ CHECK YOUR WORK

The answer has the proper number of significant figures and is of the expected order of magnitude.

Continued

1. Calculate the solubility of ferrous hydroxide, $Fe(OH)_2$, in mol/L, given the K_{sp} value listed in **Figure 4.1**.
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}.

▶ **MAIN IDEA**

Solubility constants predict precipitate formation.

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 the solutions are then mixed. If the ion product $[Ba^{2+}][CO_3^{2-}]$ exceeds the K_{sp} of $BaCO_3$, a precipitate of $BaCO_3$ forms. After precipitation, the ion concentrations are such that $[Ba^{2+}][CO_3^{2-}]$ equals the K_{sp}.

FIGURE 4.2

Precipitation Reactions

(a) Silver nitrate, $AgNO_3$, produces Ag^+ and NO_3^- ions in solution, so no precipitate forms.

(b) Adding silver nitrate to a solution of potassium bromide causes a precipitation of silver bromide, KBr.

(c) While potassium iodide, KI, and lead(II) nitrate, $Pb(NO_3)_2$ ions are soluble, when they mix, lead iodide, PbI_2, precipitates.

(d) While potassium chromate is an exception to the rule that chromates are insoluble, when it is added to silver nitrate, a silver chromate precipitate will form.

(e) While sulfates are generally very soluble, barium sulfate, $BaSO_4$, is an exception to the rule. So adding a barium-containing compound is often a test for the presence of sulfate ions.

(f) All hydroxides, except for a few, are insoluble, as seen when nickel(II) hydroxide, $Ni(OH)_2$, forms from mixing solutions containing nickel(II) chloride, $NiCl_2$, and sodium hydroxide, NaOH.

Substances differ greatly in their tendencies to form precipitates when mixed in moderate concentrations. The photos in **Figure 4.2** show the behavior of some anions in the presence of certain cations. Note that not all the combinations have produced precipitates. The solubility product can be used to predict whether a precipitate forms when two solutions are mixed.

Precipitation Calculations

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

1 ANALYZE

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

Unknown: whether a precipitate forms

2 PLAN

The two possible new pairings of ions are NaCl and $BaSO_4$. Of these, only $BaSO_4$ is a slightly soluble salt. It will precipitate if the ion product $[Ba^{2+}][SO_4^{2-}]$ in the mixed solution exceeds K_{sp} for $BaSO_4$. From the list of solubility products in **Figure 4.2**, the K_{sp} is found to be 1.1×10^{-10}. The solubility equilibrium equation follows:

$$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$$
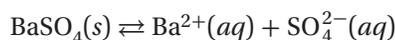
The solubility equilibrium expression is written as follows:

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

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

3 SOLVE

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

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

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

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

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

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

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

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

Calculate the ion product.

$$[Ba^{2+}][SO_4^{2-}] = (5.0 \times 10^{-3})(2.5 \times 10^{-3})$$
$$= 1.25 \times 10^{-5}$$

The ion product, which rounds to 1.3×10^{-5}, is greater than the value of K_{sp}, 1.1×10^{-10}, so precipitation occurs.

Continued

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

Practice   Answers in Appendix E

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

▶ **MAIN IDEA**

K_{sp} cannot be used for solutions of soluble compounds.

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

✓ SECTION 4 FORMATIVE ASSESSMENT

▶ **Reviewing Main Ideas**

1. What is a solubility product constant? How are such constants determined?

2. How are solubility product constants used to calculate solubilities?

3. What is an ion product?

4. How are calculations to predict possible precipitation carried out?

5. What is the value of K_{sp} for Ag_2SO_4 if 5.40 g is soluble in 1.00 L of water?

6. Determine whether a precipitate will form if 20.0 mL of 1.00×10^{-7} M $AgNO_3$ is mixed with 20.0 mL of 2.00×10^{-9} M NaCl at 25°C.

✓ **Critical Thinking**

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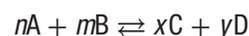
$$CaF_2 = 3.9 \times 10^{-11}$$
$$CrF_3 = 6.6 \times 10^{-11}$$
$$LaF_3 = 4.0 \times 10^{-17}$$

The equilibrium constant expression is derived from the balanced equilibrium equation. The equation defines an equilibrium constant, K, as a function of the concentrations of products and reactants at equilibrium.

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

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

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

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

Problem-Solving TIPS

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

Sample Problem

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

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

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

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

Practice

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

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

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

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

BIG IDEA A reaction system is at equilibrium when forward and reverse reactions occur simultaneously and at the same rate. Several factors can influence equilibrium.

SECTION 1 **The Nature of Chemical Equilibrium**

KEY TERMS

- A reaction system in which the forward and reverse reactions occur simultaneously and at the same rate is said to be at *equilibrium*. Both reactions continue, but there is no net change in the composition of the system.

- At equilibrium, the ratio of the product of the molar concentrations of substances formed to the product of the molar concentrations of reactants, each raised to the appropriate power, has a definite numerical value, *K*, which is the equilibrium constant at a given temperature.

reversible reaction

chemical equilibrium

equilibrium constant

chemical equilibrium expression

SECTION 2 **Shifting Equilibrium**

KEY TERM

- According to Le Châtelier's principle, when a stress (a change in concentration, pressure, or temperature) is applied to a system at equilibrium, the equilibrium is shifted in the direction that relieves the stress.

- The common-ion effect occurs when a solution containing ions in common with those in an equilibrium system involving ions as reactants or products is added to the system. Le Châtelier's principle explains the response of the system to the stress.

common-ion effect

SECTION 3 **Equilibria of Acids, Bases, and Salts**

KEY TERMS

- 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 strengths of the weak acid and weak base.

acid ionization constant

buffered solution

hydrolysis

SECTION 4 **Solubility Equilibrium**

KEY TERM

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

solubility product constant

SECTION 1
The Nature of Chemical Equilibrium

▶ **REVIEWING MAIN IDEAS**

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 $A + B \rightleftarrows C + D$.

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

3. In general, which reaction is favored (forward or reverse) if the value of K at a specified temperature is
   **a.** very small?
   b. very large?

PRACTICE PROBLEMS

4. Determine the value of the equilibrium constant for each reaction from the equilibrium concentrations given. (Concentrations are in mol/L.) (Hint: See Sample Problem A.)
   a. $A + B \rightleftarrows C$; $[A] = 2.0$; $[B] = 3.0$; $[C] = 4.0$
   b. $D + 2E \rightleftarrows F + 3G$; $[D] = 1.5$; $[E] = 2.0$; $[F] = 1.8$; $[G] = 1.2$
   c. $N_2(g) + 3H_2(g) \rightleftarrows 2NH_3(g)$; $[N_2] = 0.45$; $[H_2] = 0.14$; $[NH_3] = 0.62$

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

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

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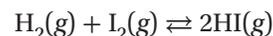
SECTION 2
Shifting Equilibrium

▶ **REVIEWING MAIN IDEAS**

8. Predict whether each of the following pressure changes would favor the forward or reverse reaction.
 $$2NO(g) + O_2(g) \rightleftarrows 2NO_2(g)$$
   a. increased pressure
   b. decreased pressure

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

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

11. Predict the effect of each of the following on the indicated equilibrium system in terms of the direction of equilibrium shift (forward, reverse, or neither).
    $$H_2(g) + Cl_2(g) \rightleftarrows 2HCl(g) + 184 \text{ kJ}$$
    a. addition of Cl_2
    b. removal of HCl
    c. increased pressure
    d. decreased temperature
    e. removal of H_2
    f. decreased pressure
    g. addition of a catalyst
    h. increased temperature
    i. decreased system volume

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

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

14. What relative pressure (high or low) would result in the production of the maximum level of CO_2 according to the following equation? Why?
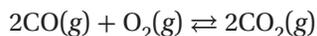
$$2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g)$$

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

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

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

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

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

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

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

$$Hb(aq) + O_2(g) \rightleftharpoons HbO_2(aq)$$
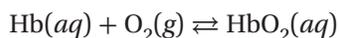
What will happen to the concentration of oxygenated hemoglobin, HbO_2, at high altitude, where the pressure of oxygen is 0.1 atm instead of 0.2 atm, as it is at sea level?

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

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

SECTION 3
Equilibria of Acids, Bases, and Salts

▶ **REVIEWING MAIN IDEAS**

19. a. Write the ion product constant expression for water.
b. What is the value of this constant at 25°C?

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

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

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

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

SECTION 4
Solubility Equilibrium

▶ **REVIEWING MAIN IDEAS**

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

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

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

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

PRACTICE PROBLEMS

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

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

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

31. Use the K_{sp} values given in **Figure 4.2** to evaluate the solubility of each of the following in moles per liter.
   a. AgBr
   b. CoS

32. A 25.0 mL sample of 0.0500 M $Pb(NO_3)_2$ is combined with 25.0 mL of 0.0400 M Na_2SO_4 at 25°C.
   a. Write the solubility equilibrium equation at 25°C.
   b. Write the solubility equilibrium expression for the net reaction.

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

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

35. Calculate whether a precipitate will form if 0.35 L of 0.0044 M $Ca(NO_3)_2$ and 0.17 L of 0.000 39 M NaOH are mixed at 25°C. (See **Figure 4.2** for K_{sp} values.) (Hint: See Sample Problem D.)

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

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

Mixed Review

▶ REVIEWING MAIN IDEAS

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

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

40. Calculate the equilibrium constant, K, for the following reaction at 900°C.
$$H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$$
The components were analyzed, and it was found that $[H_2] = 0.061$ mol/L, $[CO_2] = 0.16$ mol/L, $[H_2O] = 0.11$ mol/L, and $[CO] = 0.14$ mol/L.

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

42. At 25°C, the value of K is 1.7×10^{-13} for the following reaction.
$$2N_2O(g) + O_2(g) \rightleftharpoons 4NO(g)$$
It is determined that $[N_2O] = 0.0035$ mol/L and $[O_2] = 0.0027$ mol/L. Using this information, what is the concentration of NO(g) at equilibrium?

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

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

45. For the formation of ammonia, the equilibrium constant is calculated to be 5.2×10^{-5} at 25°C. After analysis, it is determined that $[N_2] = 2.00$ M and $[H_2] = 0.80$ M. How many grams of ammonia are in the 10. L reaction vessel at equilibrium? Use the following equilibrium equation.
$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

CRITICAL THINKING

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

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

$$N_2(g) + O_2(g) \rightleftarrows 2NO(g)$$
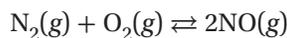
K for the reaction is 0.01 at 2000°C. If 4.0 mol of N_2, 0.1 mol of O_2, and 0.08 mol of NO are placed in a 1.0-L vessel at 2000°C, predict which reaction will be favored.

USING THE HANDBOOK

48. An equilibrium system helps maintain the pH of the blood. Review the material on the carbon dioxide–bicarbonate ion equilibrium system in Group 14 of the *Elements Handbook* (Appendix A), 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* (Appendix A). Use that information and **Figure 4.2** 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 AND 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-Bosch process.

ALTERNATIVE ASSESSMENT

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

Standards-Based Assessment

Record your answers on a separate piece of paper.

MULTIPLE CHOICE

1 A chemical reaction is in equilibrium when —

A forward and reverse reactions have ceased
B the equilibrium constant equals 1
C forward and reverse reaction rates are equal
D no reactants remain

2 Which change can cause the value of the equilibrium constant to change?

A temperature
B concentration of a reactant
C concentration of a product
D none of the above

3 Consider the following reaction:

$$2C(s) + O_2(g) \rightleftarrows 2CO(g)$$
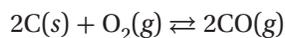
The equilibrium constant expression for this reaction is —

A $\dfrac{[CO]^2}{[O_2]}$

B $\dfrac{[CO]^2}{[O_2][C]^2}$

C $\dfrac{2[CO]}{[O_2][2C]}$

D $\dfrac{[CO]}{[O_2]^2}$

4 If an exothermic reaction has reached equilibrium, then increasing the temperature will —

A favor the forward reaction
B favor the reverse reaction
C favor both the forward and reverse reactions
D have no effect on the equilibrium

5 Le Châtelier's principle states that —

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

6 The graph below shows the neutralization curve for 100 mL of 0.100 M acid with 0.100 M base. Which letter represents the equivalence point?
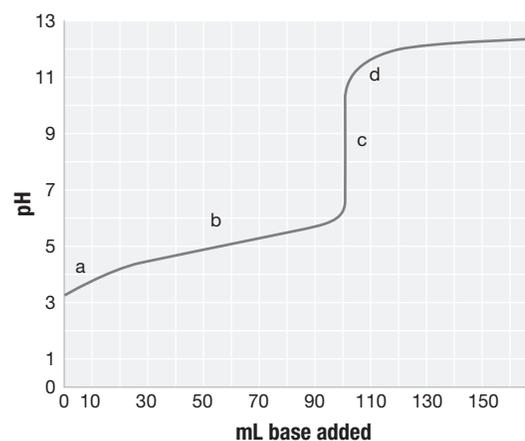
A a
B b
C c
D d

GRIDDED RESPONSE

7 The solubility product of calcium chromate, $CaCrO_4$, is 7.1×10^{-4}. What is the solubility of this compound in mol/L? (Give your answer to two significant figures.)