Trial value of the ion product:

$$[\text{Ba}^{2+}][\text{SO}_4^{2-}] = (5.0 \times 10^{-3})(2.5 \times 10^{-3}) = 1.2 \times 10^{-5}$$

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

**4 EVALUATE**

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

**PRACTICE**

1. Does a precipitate form when 100 mL of 0.0025 M AgNO$_3$ and 150 mL of 0.0020 M NaBr solutions are mixed?
   - **Answer** AgBr precipitates.

2. Does a precipitate form when 20 mL of 0.038 M Pb(NO$_3$)$_2$ and 30 mL of 0.018 M KCl solutions are mixed?
   - **Answer** PbCl$_2$ does not precipitate.

**Limitations on the Use of $K_{sp}$**

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

**SECTION REVIEW**

1. What is a solubility-product constant? How are such constants determined?
2. How are solubility-product constants used to calculate solubilities?
3. What is an ion product?
4. How are calculations to predict possible precipitation carried out?
5. What is the value of $K_{sp}$ for Ag$_2$SO$_4$ 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 \times 10^{-3} M AgNO$_3$ is mixed with 20.0 mL of 2.00 \times 10^{-3} M NaCl at 25°C.

**CHAPTER SUMMARY**

18.1. A reaction system in which the forward and reverse reactions occur simultaneously and at the same rate is said to be in equilibrium. Both reactions continue, but there is no net change in the composition of the system. At equilibrium, the ratio of the product of the mole concentrations of substances formed to the corresponding product of the molal concentrations of reactants is constant. The equilibrium constant is given by:

$$K_{eq} = \frac{[\text{products}]}{[\text{reactants}]}$$

18.2. Any change that alters the rate of either the forward or reverse reaction disturbs the equilibrium of the system. According to Le Chatelier’s principle, the equilibrium is shifted in the direction that relieves the stress. Catalysts increase the rates of forward and reverse reactions equally, and they do not shift the equilibrium.

**18.3**

- The equilibrium expression for the ionization constant of the weak acid HA follows:
  $$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

- 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.

**18.4**

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

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

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

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

4. Predict whether each of the following pressure changes would favor the forward or reverse reaction.
   \( 2NO(g) + O_2(g) \rightarrow 2NO_2(g) \)
   a. increased pressure b. decreased pressure (18-2)

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

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

7. Predict the effect of each of the following on the indicated equilibrium system in terms of which reaction will be favored (forward, reverse, or neither).
   \( H_2(g) + Cl_2(g) \rightarrow 2HCl(g) + 184 kJ \)
   a. addition of \( Cl_2 \) b. removal of \( H_2 \) c. increased pressure d. decreased temperature e. removal of \( H_2 \) f. decreased pressure g. addition of a catalyst h. increased temperature i. decreased system volume (18-2)

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

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

10. What relative pressure (high or low) would result in the production of the maximum level of \( CO_2 \) according to the following? Explain.
    \[ 2CO(g) + O_2(g) \rightarrow 2CO_2(g) \] (18-2)

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

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

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

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

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

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

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

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

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

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

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

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

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

PROBLEMS

Equilibrium Constant

24. Determine the value of the equilibrium constant for each reaction given, assuming that the equilibrium concentrations are found to be those specified. (Concentrations are in mol/L.) (Hint: See Sample Problem 18-1.)
   a. \( A + B \rightarrow C \); [A] = 2.0; [B] = 3.0; [C] = 4.0
   b. \( D + 2E \rightarrow F + 3G \); [D] = 1.5; [E] = 2.0; [F] = 1.8; [G] = 1.2
   c. \( (NH_4)^+ + 8H_2O(g) \rightarrow 2NH_3(g) + J_2 \); [J] = 0.45; [H_2O] = 0.14\[NH_3] = 0.62

25. An equilibrium mixture at a specific temperature is found to consist of \( 1.2 \times 10^{-3} \) mol/L \( HCl \), \( 3.8 \times 10^{-4} \) mol/L \( O_2 \), \( 5.8 \times 10^{-2} \) mol/L \( H_2O \), and \( 5.8 \times 10^{-3} \) mol/L \( Cl_2 \); according to the following:
   \( 4HCl(g) + O_2(g) \rightarrow 2H_2O(g) + 2Cl_2(g) \)
   Determine the value of the equilibrium constant for this system. (18-3)

26. At 450°C the value of the equilibrium constant for the following system is \( 6.59 \times 10^3 \). If \( [NH_3] = 1.25 \times 10^{-4} \) M and \( H_2 = 2.75 \times 10^{-5} \) M, determine the concentration of \( N_2 \) at that point. (18-3)
   \[ N_2(g) + 3H_2(g) \rightarrow 2NH_3(g) \]

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

Solubility-Product Constant

28. The ionic substance \( E \) dissociates to form \( E^{2+} \) and \( I^{-} \) ions. The solubility of \( E \) is \( 4.85 \times 10^{-6} \) mol/L. What is the value of the solubility-product constant? (Hint: See Sample Problem 18-2.)

29. Calculate the solubility-product constant \( K_{sp} \) for each of the following, based on the solubility information provided:
   a. \( Na_2SO_4 \); 2.4 \times 10^{-5} g/100 mL H_2O at 20°C
   b. \( Ca(OH)_2 \); 0.173 g/100 mL H_2O at 20°C

30. Calculate the solubility of a substance MN that ionizes to form \( MN^{2+} \) and \( N^{2-} \) ions, given that \( K_{sp} = 8.1 \times 10^{-9} \). (Hint: See Sample Problem 18-3.)

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

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

33. The ionic substance \( T_2U_3 \) ionizes to form \( T^{2+} \) and \( U^{-} \) ions. The solubility of \( T_2U_3 \) is \( 3.77 \times 10^{-20} \) mol/L. What is the value of the solubility-product constant?
34. A solution of AgCl contains 2.7 x 10^{-3} mol/L Ag⁺. What is the maximum chlorine concentration that can exist in this solution?

35. Calculate whether a precipitate will form if 0.35 L of 0.0044 M Ca(NO₃)₂ and 0.17 L of 0.0002 M NaOH are mixed at 25°C. (See Table 18-3 for K_{sp} values.) (Hint: See Sample Problem 18-4.)

36. Determine whether a precipitate will form if 1.70 g of solid AgNO₃ and 14.5 g of solid NaCl are dissolved in 200 mL of water to form a solution at 25°C.

37. If 2.50 g of solid Fe(NO₃)₂ is added to 100 mL of a 1.0 x 10^{-3} M NaOH solution, will a precipitate form?

**MIXED REVIEW**

38. Calcium carbonate is only slightly soluble in water.
   a. Write the equilibrium equation for calcium carbonate in solution.
   b. Write the equilibrium-constant expression, K, and the solubility-product constant expression, K_{sp}, for the equilibrium in a saturated solution of CaCO₃.

39. Calculate the concentration of Hg²⁺ ions in a saturated solution of Hg₂Cl₂. What volume of solution contains one Hg²⁺ ion?

40. Calculate the equilibrium constant, K, for the following reaction at 900°C:
    2H₂(g) + O₂(g) ⇌ 2H₂O(g) + CO(g)
    The components were analyzed and it was found that [H₂] = 0.61 mol/L, [CO] = 1.6 mol/L, [H₂O] = 1.1 mol/L, and [CO] = 1.4 mol/L.

41. A solution in equilibrium with solid barium phosphate is found to have a barium ion concentration of 5 x 10^{-4} M and a K_{sp} of 3.4 x 10^{-15}. Calculate the concentration of phosphate ion.

42. At 25°C, the value of K is 1.7 x 10^{-15} for the following reaction:
    N₂O₅(g) + O₃(g) ⇌ 2NO₂(g)
    It is determined that [N₂O₅] = 0.0035 mol/L and [O₃] = 0.0027 mol/L. Using this information, what is the concentration of NO₂(g) at equilibrium?

43. Tooth enamel is composed of the mineral hydroxyapatite, Ca₅(PO₄)₃OH, which has a K_{sp} of 6.8 x 10^{-31}. The molar solubility of hydroxyapatite is 2.7 x 10^{-9} mol/L. When hydroxyapatite is reacted with fluoride, the OH⁻ is replaced with the F⁻ ion on the mineral, forming fluorapatite, Ca₅(PO₄)₃F. The latter is harder and less susceptible to caries. The K_{sp} of fluorapatite is 1 x 10^{-40}. Calculate the solubility of fluorapatite in water. Given your calculations, can you support the fluoridation of drinking water?

44. Determine if a precipitate will form when 0.96 g Na₂CO₃ is combined with 0.20 g BaBr₂ in a 10 L solution (K_{sp} = 2.8 x 10^{-5}).

45. For the formation of ammonia, the equilibrium constant is calculated to be 5.2 x 10^{-3} at 25°C. After analysis, it is determined that [N₂] = 2.0 M and [H₂] = 0.80 M. How many grams of ammonia are in the 10 L reaction vessel at equilibrium? Use the following equilibrium equation.

N₂(g) + 3H₂(g) ⇌ 2NH₃(g)

**CRITICAL THINKING**

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

N₂(g) + O₂(g) ⇌ 2NO(g)

K for the reaction is 0.01 at 2000°F. If 4.0 mol of N₂, 0.1 mol of O₂, and 0.06 mol of NO are placed in a 1.0 L vessel at 2000°F, which reaction will be favored?

47. Graphing Calculator Calculating the Equilibrium Constant, K, for a System The graphing calculator can run a program that calculates K for a system, given the concentrations of the products and the concentrations of the reactants.

48. **HANDBOOK SEARCH**

An equilibrium system helps maintain the pH of the blood. Review the material on the carbon dioxidebicarbonate ion equilibrium system in Group 14 of the Elements Handbook and answer the following.

a. Write the equation for the equilibrium system that responds to changes in H₂O⁺ concentration.

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

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

49. The reactions used to confirm the presence of transition metal ions often involve the formation of precipitates. Review the analytical tests for the transition metals in the Elements Handbook. Use that information and Table 18-3 to determine the minimum concentration of Zn²⁺ 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 x 10^{-5} M.

**RESEARCH & WRITING**

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

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

**ALTERNATIVE ASSESSMENT**

52. **TECHNOLOGY & LEARNING**

Fill a drinking glass with water and add sugar by the teaspoonful, stirring after each addition. Continue adding the sugar until some of the sugar remains undissolved, even after vigorous stirring. How does this situation differ from the usual process of dissolving sugar in water?