

CHAPTER
17

ADDITIONAL ASPECTS OF AQUEOUS EQUILIBRIA



CANARY SPRING, which is part of Mammoth Hot Springs in Yellowstone National Park.

WHAT'S AHEAD

17.1 The Common-Ion Effect

We begin by considering a specific example of Le Châtelier's principle known as the *common-ion effect*.

17.2 Buffered Solutions

We then consider the composition of *buffered solutions*, or *buffers*, and learn how they resist pH change upon the addition of small amounts of a strong acid or a strong base.

17.3 Acid-Base Titrations

We continue by examining acid-base titration in detail, and we explore how to determine pH at any point in an acid-base titration.

17.4 Solubility Equilibria

Next, we learn how to use equilibrium constants known as *solubility-product constants* to determine to what extent a sparingly soluble salt will dissolve in water.

17.5 Factors That Affect Solubility

We investigate some of the factors that affect solubility, including the common-ion effect and the effect of acids.

17.6 Precipitation and Separation of Ions

Continuing the discussion of solubility equilibria, we learn how to precipitate ions selectively.

17.7 Qualitative Analysis for Metallic Elements

We conclude the chapter with an explanation of how the principles of solubility and complexation equilibria can be used to identify ions qualitatively in solution.

WATER IS THE MOST COMMON AND MOST IMPORTANT SOLVENT ON EARTH. In a sense, it is the solvent of life. It is difficult to imagine how living matter in all its complexity could exist with any liquid other than water as the solvent. Water occupies its position of importance because of its abundance

and its exceptional ability to dissolve a wide variety of substances. For example, the chapter-opening photograph shows a hot spring; this water contains a high concentration of ions (especially Mg^{2+} , Ca^{2+} , Fe^{2+} , CO_3^{2-} , and SO_4^{2-}). The ions are dissolved as the hot water, initially underground, passes through various rocks on its way to the surface and dissolves minerals in the rocks. When the solution reaches the surface and cools, the minerals deposit and make the terracelike formations seen in the photograph.

The various aqueous solutions encountered in nature typically contain many solutes. For example, the aqueous solutions in hot springs and oceans, as well as those in biological fluids, contain a variety of dissolved ions and molecules. Consequently, many equilibria can occur simultaneously in these solutions.

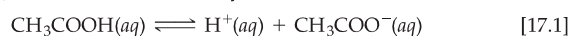
In this chapter we take a step toward understanding such complex solutions by looking first at further applications of acid–base equilibria. The idea is to consider not only solutions in which there is a single solute but also those containing a mixture of solutes. We then broaden our discussion to include two additional types of aqueous equilibria: those involving slightly soluble salts and those involving the formation of metal complexes in solution. For the most part, the discussions and calculations in this chapter are an extension of those in Chapters 15 and 16.

17.1 THE COMMON-ION EFFECT

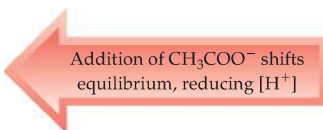
In Chapter 16 we examined the equilibrium concentrations of ions in solutions containing a weak acid or a weak base. We now consider solutions that contain a weak acid, such as acetic acid (CH_3COOH), and a soluble salt of that acid, such as sodium acetate (CH_3COONa). Notice that these solutions contain two substances that share a *common ion* CH_3COO^- . It is instructive to view these solutions from the perspective of Le Châtelier's principle. ∞ (Section 15.7) Sodium acetate is a soluble ionic compound and is therefore a strong electrolyte. ∞ (Section 4.1) Consequently, it dissociates completely in aqueous solution to form Na^+ and CH_3COO^- ions:



In contrast, CH_3COOH is a weak electrolyte that ionizes as follows:



The CH_3COO^- from CH_3COONa causes this equilibrium to shift to the left, thereby decreasing the equilibrium concentration of $\text{H}^+(aq)$.



In other words, the presence of the added acetate ion causes the acetic acid to ionize less than it normally would.

Whenever a weak electrolyte and a strong electrolyte contain a common ion, the weak electrolyte ionizes less than it would if it were alone in solution. We call this observation the **common-ion effect**. Sample Exercises 17.1 and 17.2 illustrate how equilibrium concentrations may be calculated when a solution contains a mixture of a weak electrolyte and a strong electrolyte that have a common ion. The procedures are similar to those encountered for weak acids and weak bases in Chapter 16.

SAMPLE EXERCISE 17.1 | Calculating the pH When a Common Ion Is Involved

What is the pH of a solution made by adding 0.30 mol of acetic acid and 0.30 mol of sodium acetate to enough water to make 1.0 L of solution?

SOLUTION

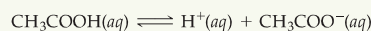
Analyze: We are asked to determine the pH of a solution of a weak electrolyte (CH_3COOH) and a strong electrolyte (CH_3COONa) that share a common ion, CH_3COO^- .

Plan: In any problem in which we must determine the pH of a solution containing a mixture of solutes, it is helpful to proceed by a series of logical steps:

1. Consider which solutes are strong electrolytes and which are weak electrolytes, and identify the major species in solution.
2. Identify the important equilibrium that is the source of H^+ and therefore determines pH.
3. Tabulate the concentrations of ions involved in the equilibrium.
4. Use the equilibrium-constant expression to calculate $[\text{H}^+]$ and then pH.

Solve: First, because CH_3COOH is a weak electrolyte and CH_3COONa is a strong electrolyte, the major species in the solution are CH_3COOH (a weak acid), Na^+ (which is neither acidic nor basic and is therefore a spectator in the acid–base chemistry), and CH_3COO^- (which is the conjugate base of CH_3COOH).

Second, $[\text{H}^+]$ and, therefore, the pH are controlled by the dissociation equilibrium of CH_3COOH :



(We have written the equilibrium using $\text{H}^+(aq)$ rather than $\text{H}_3\text{O}^+(aq)$ but both representations of the hydrated hydrogen ion are equally valid.)

Third, we tabulate the initial and equilibrium concentrations as we did in solving other equilibrium problems in Chapters 15 and 16:

	$\text{CH}_3\text{COOH}(aq)$	\rightleftharpoons	$\text{H}^+(aq)$	$+$	$\text{CH}_3\text{COO}^-(aq)$
Initial	0.30 M		0		0.30 M
Change	$-x$ M		$+x$ M		$+x$ M
Equilibrium	$(0.30 - x)$ M		x M		$(0.30 + x)$ M

The equilibrium concentration of CH_3COO^- (the common ion) is the initial concentration that is due to CH_3COONa (0.30 M) plus the change in concentration (x) that is due to the ionization of CH_3COOH .

Now we can use the equilibrium-constant expression:

$$K_a = 1.8 \times 10^{-5} = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

(The dissociation constant for CH_3COOH at 25 °C is from Appendix D; addition of CH_3COONa does not change the value of this constant.)

Substituting the equilibrium-constant concentrations from our table into the equilibrium expression gives

$$K_a = 1.8 \times 10^{-5} = \frac{x(0.30 + x)}{0.30 - x}$$

Because K_a is small, we assume that x is small compared to the original concentrations of CH_3COOH and CH_3COO^- (0.30 M each). Thus, we can ignore the very small x relative to 0.30 M, giving

$$K_a = 1.8 \times 10^{-5} = \frac{x(0.30)}{0.30}$$

$$x = 1.8 \times 10^{-5} \text{ M} = [\text{H}^+]$$

The resulting value of x is indeed small relative to 0.30, justifying the approximation made in simplifying the problem.

$$\text{pH} = -\log(1.8 \times 10^{-5}) = 4.74$$

Finally, we calculate the pH from the equilibrium concentration of $\text{H}^+(aq)$:

Comment: In Section 16.6 we calculated that a 0.30 M solution of CH_3COOH has a pH of 2.64, corresponding to $[\text{H}^+] = 2.3 \times 10^{-3}$ M. Thus, the addition of CH_3COONa has substantially decreased $[\text{H}^+]$, as we would expect from Le Châtelier's principle.

■ PRACTICE EXERCISE

Calculate the pH of a solution containing 0.085 M nitrous acid (HNO_2 ; $K_a = 4.5 \times 10^{-4}$) and 0.10 M potassium nitrite (KNO_2).
Answer: 3.42

SAMPLE EXERCISE 17.2 | Calculating Ion Concentrations When a Common Ion Is Involved

Calculate the fluoride ion concentration and pH of a solution that is 0.20 M in HF and 0.10 M in HCl.

SOLUTION

Analyze: We are asked to determine the concentration of F^- and the pH in a solution containing the weak acid HF and the strong acid HCl. In this case the common ion is H^+ .

Plan: We can again use the four steps outlined in Sample Exercise 17.1.

Solve: Because HF is a weak acid and HCl is a strong acid, the major species in solution are HF, H^+ , and Cl^- . The Cl^- , which is the conjugate base of a strong acid, is merely a spectator ion in any acid–base chemistry. The problem asks for $[F^-]$, which is formed by ionization of HF. Thus, the important equilibrium is



The common ion in this problem is the hydrogen (or hydronium) ion. Now we can tabulate the initial and equilibrium concentrations of each species involved in this equilibrium:

	HF(aq)	$H^+(aq)$	$F^-(aq)$
Initial	0.20 M	0.10 M	0
Change	$-x$ M	$+x$ M	$+x$ M
Equilibrium	$(0.20 - x)$ M	$(0.10 + x)$ M	x M

The equilibrium constant for the ionization of HF, from Appendix D, is 6.8×10^{-4} . Substituting the equilibrium-constant concentrations into the equilibrium expression gives

$$K_a = 6.8 \times 10^{-4} = \frac{[H^+][F^-]}{[HF]} = \frac{(0.10 + x)(x)}{0.20 - x}$$

If we assume that x is small relative to 0.10 or 0.20 M, this expression simplifies to

$$\frac{(0.10)(x)}{0.20} = 6.8 \times 10^{-4}$$

$$x = \frac{0.20}{0.10} (6.8 \times 10^{-4}) = 1.4 \times 10^{-3} M = [F^-]$$

This F^- concentration is substantially smaller than it would be in a 0.20 M solution of HF with no added HCl. The common ion, H^+ , suppresses the ionization of HF. The concentration of $H^+(aq)$ is

$$[H^+] = (0.10 + x) M \approx 0.10 M$$

Thus,

$$pH = 1.00$$

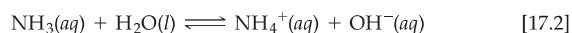
Comment: Notice that for all practical purposes, $[H^+]$ is due entirely to the HCl; the HF makes a negligible contribution by comparison.

PRACTICE EXERCISE

Calculate the formate ion concentration and pH of a solution that is 0.050 M in formic acid ($HCOOH$; $K_a = 1.8 \times 10^{-4}$) and 0.10 M in HNO_3 .

Answer: $[HCOO^-] = 9.0 \times 10^{-5}$; $pH = 1.00$

Sample Exercises 17.1 and 17.2 both involve weak acids. The ionization of a weak base is also decreased by the addition of a common ion. For example, the addition of NH_4^+ (as from the strong electrolyte NH_4Cl) causes the base-dissociation equilibrium of NH_3 to shift to the left, decreasing the equilibrium concentration of OH^- and lowering the pH:



Addition of NH_4^+ shifts equilibrium, reducing $[OH^-]$

GIVE IT SOME THOUGHT

A mixture of 0.10 mol of NH_4Cl and 0.12 mol of NH_3 is added to enough water to make 1.0 L of solution. (a) What are the initial concentrations of the major species in the solution? (b) Which of the ions in this solution is a spectator ion in any acid–base chemistry occurring in the solution? (c) What equilibrium reaction determines $[\text{OH}^-]$ and therefore the pH of the solution?

17.2 BUFFERED SOLUTIONS

Solutions such as those discussed in Section 17.1, which contain a weak conjugate acid–base pair, can resist drastic changes in pH upon the addition of small amounts of strong acid or strong base. These solutions are called **buffered solutions** (or merely **buffers**). Human blood, for example, is a complex aqueous mixture with a pH buffered at about 7.4 (see the “Chemistry and Life” box near the end of this section). Much of the chemical behavior of seawater is determined by its pH, buffered at about 8.1 to 8.3 near the surface. Buffered solutions find many important applications in the laboratory and in medicine (Figure 17.1 ▶).

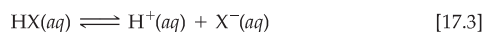
Composition and Action of Buffered Solutions

A buffer resists changes in pH because it contains both an acid to neutralize OH^- ions and a base to neutralize H^+ ions. The acid and base that make up the buffer, however, must not consume each other through a neutralization reaction. These requirements are fulfilled by a weak acid–base conjugate pair such as $\text{CH}_3\text{COOH}-\text{CH}_3\text{COO}^-$ or $\text{NH}_4^+-\text{NH}_3$. Thus, buffers are often prepared by mixing a weak acid or a weak base with a salt of that acid or base. The $\text{CH}_3\text{COOH}-\text{CH}_3\text{COO}^-$ buffer can be prepared, for example, by adding CH_3COONa to a solution of CH_3COOH . The $\text{NH}_4^+-\text{NH}_3$ buffer can be prepared by adding NH_4Cl to a solution of NH_3 . By choosing appropriate components and adjusting their relative concentrations, we can buffer a solution at virtually any pH.

GIVE IT SOME THOUGHT

Which of the following conjugate acid–base pairs will *not* function as a buffer: $\text{C}_2\text{H}_5\text{COOH}$ and $\text{C}_2\text{H}_5\text{COO}^-$; HCO_3^- and CO_3^{2-} ; HNO_3 and NO_3^- ? Explain.

To understand better how a buffer works, let’s consider a buffer composed of a weak acid (HX) and one of its salts (MX, where M^+ could be Na^+ , K^+ , or another cation). The acid-dissociation equilibrium in this buffered solution involves both the acid and its conjugate base:



The corresponding acid-dissociation-constant expression is

$$K_a = \frac{[\text{H}^+][\text{X}^-]}{[\text{HX}]} \quad [17.4]$$

Solving this expression for $[\text{H}^+]$, we have

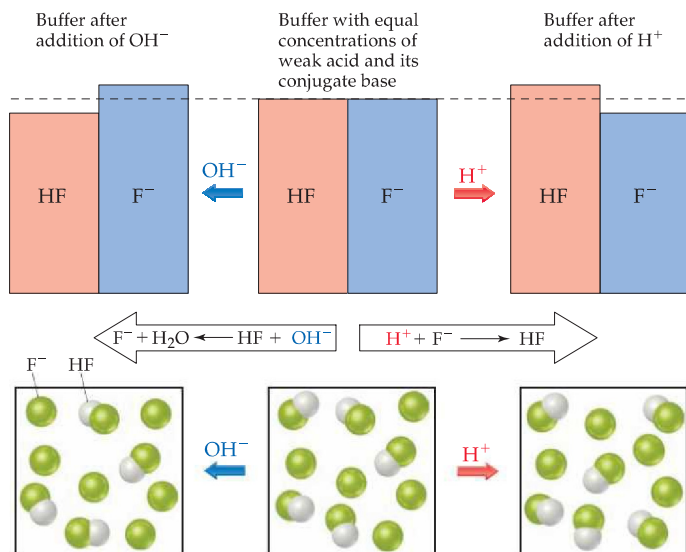
$$[\text{H}^+] = K_a \frac{[\text{HX}]}{[\text{X}^-]} \quad [17.5]$$

We see from this expression that $[\text{H}^+]$, and thus the pH, is determined by two factors: the value of K_a for the weak-acid component of the buffer and the ratio of the concentrations of the conjugate acid–base pair, $[\text{HX}]/[\text{X}^-]$.

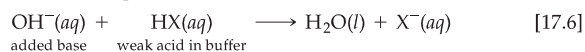


▲ **Figure 17.1** Buffer solutions. Prepackaged buffer solutions and ingredients for making up buffer solutions of predetermined pH can be purchased.

► **Figure 17.2 Buffer action.** When a small portion of OH^- is added to a buffer consisting of a mixture of the weak acid HF and its conjugate base (left), the OH^- reacts with the HF, decreasing $[\text{HF}]$ and increasing $[\text{F}^-]$ in the buffer. Conversely, when a small portion of H^+ is added to the buffer (right), the H^+ reacts with the F^- , decreasing $[\text{F}^-]$ and increasing $[\text{HF}]$ in the buffer. Because pH depends on the ratio of F^- to HF, the resulting pH change is small.

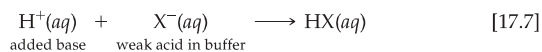


If OH^- ions are added to the buffered solution, they react with the acid component of the buffer to produce water and X^- :

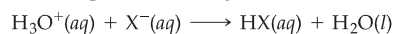


This reaction causes $[\text{HX}]$ to decrease and $[\text{X}^-]$ to increase. As long as the amounts of HX and X^- in the buffer are large compared to the amount of OH^- added, however, the ratio $[\text{HX}]/[\text{X}^-]$ does not change much, and thus the change in pH is small. A specific example of such a buffer, the HF/ F^- buffer, is shown in Figure 17.2▲.

If H^+ ions are added, they react with the base component of the buffer:



This reaction can also be represented using H_3O^+ :



Using either equation, we see that the reaction causes $[\text{X}^-]$ to decrease and $[\text{HX}]$ to increase. As long as the change in the ratio $[\text{HX}]/[\text{X}^-]$ is small, the change in pH will be small.

Figure 17.2 shows a buffer consisting of equal concentrations of hydrofluoric acid and fluoride ion (center). The addition of OH^- (left) reduces $[\text{HF}]$ and increases $[\text{F}^-]$. The addition of H^+ (right) reduces $[\text{F}^-]$ and increases $[\text{HF}]$.

GIVE IT SOME THOUGHT

- (a) What happens when NaOH is added to a buffer composed of CH_3COOH and CH_3COO^- ? (b) What happens when HCl is added to this buffer?

Calculating the pH of a Buffer

Because conjugate acid–base pairs share a common ion, we can use the same procedures to calculate the pH of a buffer that we used to treat the common-ion effect (see Sample Exercise 17.1). However, we can sometimes take an alternate approach that is based on an equation derived from Equation 17.5.

Taking the negative log of both sides of Equation 17.5, we have

$$-\log[\text{H}^+] = -\log\left(K_a \frac{[\text{HX}]}{[\text{X}^-]}\right) = -\log K_a - \log \frac{[\text{HX}]}{[\text{X}^-]}$$

Because $-\log[\text{H}^+] = \text{pH}$ and $-\log K_a = \text{p}K_a$, we have

$$\text{pH} = \text{p}K_a - \log \frac{[\text{HX}]}{[\text{X}^-]} = \text{p}K_a + \log \frac{[\text{X}^-]}{[\text{HX}]} \quad [17.8]$$

In general,

$$\text{pH} = \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]} \quad [17.9]$$

where [acid] and [base] refer to the equilibrium concentrations of the *conjugate acid–base pair*. Note that when [base] = [acid], $\text{pH} = \text{p}K_a$.

Equation 17.9 is known as the **Henderson–Hasselbalch equation**. Biologists, biochemists, and others who work frequently with buffers often use this equation to calculate the pH of buffers. In doing equilibrium calculations, we have seen that we can normally neglect the amounts of the acid and base of the buffer that ionize. Therefore, we can usually use the starting concentrations of the acid and base components of the buffer directly in Equation 17.9.

SAMPLE EXERCISE 17.3 | Calculating the pH of a Buffer

What is the pH of a buffer that is 0.12 M in lactic acid [$\text{CH}_3\text{CH}(\text{OH})\text{COOH}$, or $\text{HC}_3\text{H}_5\text{O}_3$] and 0.10 M in sodium lactate [$\text{CH}_3\text{CH}(\text{OH})\text{COONa}$ or $\text{NaC}_3\text{H}_5\text{O}_3$]? For lactic acid, $K_a = 1.4 \times 10^{-4}$.

SOLUTION

Analyze: We are asked to calculate the pH of a buffer containing lactic acid $\text{HC}_3\text{H}_5\text{O}_3$ and its conjugate base, the lactate ion ($\text{C}_3\text{H}_5\text{O}_3^-$).

Plan: We will first determine the pH using the method described in Section 17.1. Because $\text{HC}_3\text{H}_5\text{O}_3$ is a weak electrolyte and $\text{NaC}_3\text{H}_5\text{O}_3$ is a strong electrolyte, the major species in solution are $\text{HC}_3\text{H}_5\text{O}_3$, Na^+ , and $\text{C}_3\text{H}_5\text{O}_3^-$. The Na^+ ion is a spectator ion. The $\text{HC}_3\text{H}_5\text{O}_3\text{–C}_3\text{H}_5\text{O}_3^-$ conjugate acid–base pair determines $[\text{H}^+]$ and thus pH; $[\text{H}^+]$ can be determined using the acid–dissociation equilibrium of lactic acid.

Solve: The initial and equilibrium concentrations of the species involved in this equilibrium are

$$\text{HC}_3\text{H}_5\text{O}_3(aq) \rightleftharpoons \text{H}^+(aq) + \text{C}_3\text{H}_5\text{O}_3^-(aq)$$

Initial	0.12 M	0	0.10 M
Change	$-x$ M	$+x$ M	$+x$ M
Equilibrium	$(0.12 - x)$ M	x M	$(0.10 + x)$ M

The equilibrium concentrations are governed by the equilibrium expression:

$$K_a = 1.4 \times 10^{-4} = \frac{[\text{H}^+][\text{C}_3\text{H}_5\text{O}_3^-]}{[\text{HC}_3\text{H}_5\text{O}_3]} = \frac{x(0.10 + x)}{(0.12 - x)}$$

Because K_a is small and a common ion is present, we expect x to be small relative to either 0.12 or 0.10 M. Thus, our equation can be simplified to give

$$K_a = 1.4 \times 10^{-4} = \frac{x(0.10)}{0.12}$$

Solving for x gives a value that justifies our approximation:

$$[\text{H}^+] = x = \left(\frac{0.12}{0.10}\right)(1.4 \times 10^{-4}) = 1.7 \times 10^{-4} \text{ M}$$

$$\text{pH} = -\log(1.7 \times 10^{-4}) = 3.77$$

Alternatively, we could have used the Henderson–Hasselbalch equation to calculate pH directly:

$$\begin{aligned} \text{pH} &= \text{p}K_a + \log\left(\frac{[\text{base}]}{[\text{acid}]}\right) = 3.85 + \log\left(\frac{0.10}{0.12}\right) \\ &= 3.85 + (-0.08) = 3.77 \end{aligned}$$

PRACTICE EXERCISE

Calculate the pH of a buffer composed of 0.12 M benzoic acid and 0.20 M sodium benzoate. (Refer to Appendix D.)

Answer: 4.42

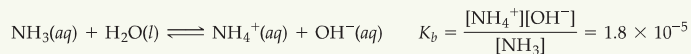
SAMPLE EXERCISE 17.4 | Preparing a Buffer

How many moles of NH_4Cl must be added to 2.0 L of 0.10 M NH_3 to form a buffer whose pH is 9.00? (Assume that the addition of NH_4Cl does not change the volume of the solution.)

SOLUTION

Analyze: Here we are asked to determine the amount of NH_4^+ ion required to prepare a buffer of a specific pH.

Plan: The major species in the solution will be NH_4^+ , Cl^- , and NH_3 . Of these, the Cl^- ion is a spectator (it is the conjugate base of a strong acid). Thus, the NH_4^+ – NH_3 conjugate acid–base pair will determine the pH of the buffer solution. The equilibrium relationship between NH_4^+ and NH_3 is given by the base-dissociation constant for NH_3 :



The key to this exercise is to use this K_b expression to calculate $[\text{NH}_4^+]$.

Solve: We obtain $[\text{OH}^-]$ from the given pH:

$$\text{pOH} = 14.00 - \text{pH} = 14.00 - 9.00 = 5.00$$

and so

$$[\text{OH}^-] = 1.0 \times 10^{-5} \text{ M}$$

Because K_b is small and the common ion NH_4^+ is present, the equilibrium concentration of NH_3 will essentially equal its initial concentration:

$$[\text{NH}_3] = 0.10 \text{ M}$$

We now use the expression for K_b to calculate $[\text{NH}_4^+]$:

$$[\text{NH}_4^+] = K_b \frac{[\text{NH}_3]}{[\text{OH}^-]} = (1.8 \times 10^{-5}) \frac{(0.10 \text{ M})}{(1.0 \times 10^{-5} \text{ M})} = 0.18 \text{ M}$$

Thus, for the solution to have pH = 9.00, $[\text{NH}_4^+]$ must equal 0.18 M. The number of moles of NH_4Cl needed to produce this concentration is given by the product of the volume of the solution and its molarity:

$$(2.0 \text{ L})(0.18 \text{ mol NH}_4\text{Cl/L}) = 0.36 \text{ mol NH}_4\text{Cl}$$

Comment: Because NH_4^+ and NH_3 are a conjugate acid–base pair, we could use the Henderson–Hasselbalch equation (Equation 17.9) to solve this problem. To do so requires first using Equation 16.41 to calculate $\text{p}K_a$ for NH_4^+ from the value of $\text{p}K_b$ for NH_3 . We suggest you try this approach to convince yourself that you can use the Henderson–Hasselbalch equation for buffers for which you are given K_b for the conjugate base rather than K_a for the conjugate acid.

PRACTICE EXERCISE

Calculate the concentration of sodium benzoate that must be present in a 0.20 M solution of benzoic acid ($\text{C}_6\text{H}_5\text{COOH}$) to produce a pH of 4.00.

Answer: 0.13 M

Buffer Capacity and pH Range

Two important characteristics of a buffer are its capacity and its effective pH range. **Buffer capacity** is the amount of acid or base the buffer can neutralize before the pH begins to change to an appreciable degree. The buffer capacity depends on the amount of acid and base from which the buffer is made. The pH of the buffer depends on the K_a for the acid and on the relative concentrations of the acid and base that comprise the buffer. According to Equation 17.5, for example, $[\text{H}^+]$ for a 1-L solution that is 1 M in CH_3COOH and 1 M in CH_3COONa will be the same as for a 1-L solution that is 0.1 M in CH_3COOH and 0.1 M in CH_3COONa . The first solution has a greater buffering capacity, however, because it contains more CH_3COOH and CH_3COO^- . The greater the amounts of the conjugate acid–base pair, the more resistant is the ratio of their concentrations, and hence the pH, is to change.

The **pH range** of any buffer is the pH range over which the buffer acts effectively. Buffers most effectively resist a change in pH in *either* direction when the concentrations of weak acid and conjugate base are about the same. From Equation 17.9 we see that when the concentrations of weak acid and conjugate base are equal, $\text{pH} = \text{p}K_a$. This relationship gives the optimal pH of any buffer. Thus, we usually try to select a buffer whose acid form has a $\text{p}K_a$ close to the desired pH. In practice, we find that if the concentration of one component of the buffer is more than 10 times the concentration of the other component, the buffering action is poor. Because $\log 10 = 1$, *buffers usually have a usable range within ± 1 pH unit of $\text{p}K_a$* (that is, a range of $\text{pH} = \text{p}K_a \pm 1$).

GIVE IT SOME THOUGHT

What is the optimal pH buffered by a solution containing CH_3COOH and CH_3COONa ? (K_a for CH_3COOH is 1.8×10^{-5} .)

Addition of Strong Acids or Bases to Buffers

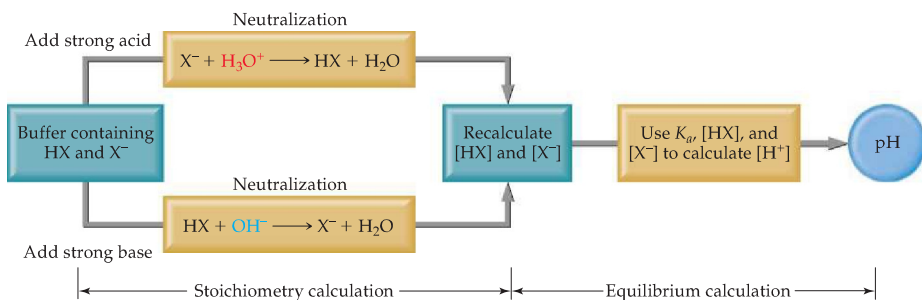
Let's now consider in a more quantitative way the response of a buffered solution to the addition of a strong acid or base. In solving these problems, it is important to understand that reactions between strong acids and weak bases proceed essentially to completion, as do those between strong bases and weak acids. Thus, as long as we do not exceed the buffering capacity of the buffer, we can assume that the strong acid or strong base is completely consumed by reaction with the buffer.

Consider a buffer that contains a weak acid HX and its conjugate base X^- . When a strong acid is added to this buffer, the added H^+ is consumed by X^- to produce HX; thus, $[\text{HX}]$ increases and $[X^-]$ decreases. (See Equation 17.7.) When a strong base is added to the buffer, the added OH^- is consumed by HX to produce X^- ; in this case $[\text{HX}]$ decreases and $[X^-]$ increases. (See Equation 17.6.) These two situations are summarized in Figure 17.2.

To calculate how the pH of the buffer responds to the addition of a strong acid or a strong base, we follow the strategy outlined in Figure 17.3 ▼:

1. Consider the acid–base neutralization reaction, and determine its effect on $[\text{HX}]$ and $[X^-]$. This step of the procedure is a *stoichiometry calculation*.
2. Use K_a and the new concentrations of $[\text{HX}]$ and $[X^-]$ from step 1 to calculate $[\text{H}^+]$. This second step of the procedure is a standard *equilibrium calculation* and is most easily done using the Henderson–Hasselbalch equation.

The complete procedure is illustrated in Sample Exercise 17.5.



▲ **Figure 17.3 Calculation of the pH of a buffer after the addition of acid or base.** First consider how the neutralization reaction between the added strong acid or strong base and the buffer affects the composition of the buffer (stoichiometry calculation). Then calculate the pH of the remaining buffer (equilibrium calculation). As long as the amount of added acid or base does not exceed the buffer capacity, the Henderson–Hasselbalch equation, Equation 17.9, can be used for the equilibrium calculation.

SAMPLE EXERCISE 17.5 | Calculating pH Changes in Buffers

A buffer is made by adding 0.300 mol CH_3COOH and 0.300 mol CH_3COONa to enough water to make 1.00 L of solution. The pH of the buffer is 4.74 (Sample Exercise 17.1). (a) Calculate the pH of this solution after 0.020 mol of NaOH is added. (b) For comparison, calculate the pH that would result if 0.020 mol of NaOH were added to 1.00 L of pure water (neglect any volume changes).

SOLUTION

Analyze: We are asked to determine the pH of a buffer after addition of a small amount of strong base and to compare the pH change to the pH that would result if we were to add the same amount of strong base to pure water.

Plan: (a) Solving this problem involves the two steps outlined in Figure 17.3. Thus, we must first do a stoichiometry calculation to determine how the added OH^- reacts with the buffer and affects its composition. Then we can use the resultant composition of the buffer and either the Henderson–Hasselbalch equation or the equilibrium-constant expression for the buffer to determine the pH.

Solve: *Stoichiometry Calculation:* The OH^- provided by NaOH reacts with CH_3COOH , the weak acid component of the buffer. Prior to this neutralization reaction, there are 0.300 mol each of CH_3COOH and CH_3COO^- . Neutralizing the 0.020 mol OH^- requires 0.020 mol of CH_3COOH . Consequently, the amount of CH_3COOH decreases by 0.020 mol, and the amount of the product of the neutralization, CH_3COO^- , increases by 0.020 mol. We can create a table to see how the composition of the buffer changes as a result of its reaction with OH^- :



Buffer before addition	0.300 mol	0	—	0.300 mol
Addition	—	0.020 mol	—	—
Buffer after addition	0.280 mol	0	—	0.320 mol

Equilibrium Calculation: We now turn our attention to the equilibrium that will determine the pH of the buffer, namely the ionization of acetic acid.



Using the quantities of CH_3COOH and CH_3COO^- remaining in the buffer, we can determine the pH using the Henderson–Hasselbalch equation.

$$\text{pH} = 4.74 + \log \frac{0.320 \text{ mol}/1.00 \text{ L}}{0.280 \text{ mol}/1.00 \text{ L}} = 4.80$$

Comment Notice that we could have used mole amounts in place of concentrations in the Henderson–Hasselbalch equation and gotten the same result. The volumes of the acid and base are equal and cancel.

If 0.020 mol of H^+ was added to the buffer, we would proceed in a similar way to calculate the resulting pH of the buffer. In this case the pH decreases by 0.06 units, giving $\text{pH} = 4.68$, as shown in the figure in the margin.

(b) To determine the pH of a solution made by adding 0.020 mol of NaOH to 1.00 L of pure water, we can first determine pOH using Equation 16.18 and subtracting from 14.

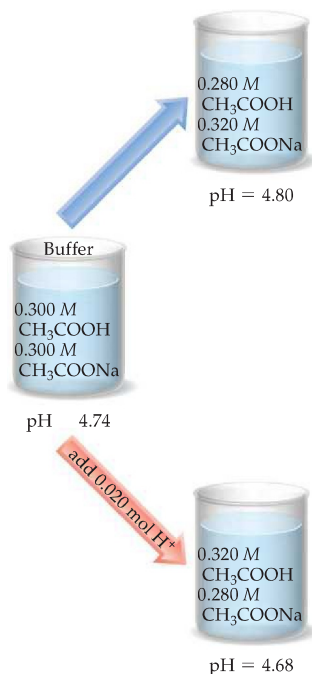
$$\text{pH} = 14 - (-\log 0.020) = 12.30$$

Note that although the small amount of NaOH changes the pH of water significantly, the pH of the buffer changes very little.

PRACTICE EXERCISE

Determine (a) the pH of the original buffer described in Sample Exercise 17.5 after the addition of 0.020 mol HCl and (b) the pH of the solution that would result from the addition of 0.020 mol HCl to 1.00 L of pure water.

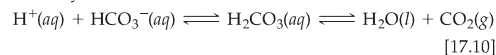
Answers: (a) 4.68, (b) 1.70



Many of the chemical reactions that occur in living systems are extremely sensitive to pH. Many of the enzymes that catalyze important biochemical reactions, for example, are effective only within a narrow pH range. For this reason the human body maintains a remarkably intricate system of buffers, both within tissue cells and in the fluids that transport cells. Blood, the fluid that transports oxygen to all parts of the body (Figure 17.4), is one of the most prominent examples of the importance of buffers in living beings.

Human blood is slightly basic with a normal pH of 7.35 to 7.45. Any deviation from this normal pH range can have extremely disruptive effects on the stability of cell membranes, the structures of proteins, and the activities of enzymes. Death may result if the blood pH falls below 6.8 or rises above 7.8. When the pH falls below 7.35, the condition is called *acidosis*; when it rises above 7.45, the condition is called *alkalosis*. Acidosis is the more common tendency because ordinary metabolism generates several acids within the body.

The major buffer system that is used to control the pH of blood is the *carbonic acid–bicarbonate buffer system*. Carbonic acid (H_2CO_3) and bicarbonate ion (HCO_3^-) are a conjugate acid–base pair. In addition, carbonic acid can decompose into carbon dioxide gas and water. The important equilibria in this buffer system are



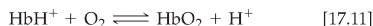
Several aspects of these equilibria are notable. First, although carbonic acid is a diprotic acid, the carbonate ion (CO_3^{2-}) is unimportant in this system. Second, one of the components of this equilibrium, CO_2 , is a gas, which provides a mechanism for the body to adjust the equilibria. Removal of CO_2 via exhalation shifts the equilibria to the right, consuming H^+ ions. Third, the buffer system in blood operates at a pH of 7.4, which is fairly far removed from the $\text{p}K_{a1}$ value of H_2CO_3 (6.1 at physiological temperatures). For the buffer to have a pH of 7.4, the ratio [base]/[acid] must have a value of about 20. In normal blood plasma the concentrations of HCO_3^- and H_2CO_3 are about 0.024 M and 0.0012 M, respectively. Consequently, the buffer has a high capacity to neutralize additional acid, but only a low capacity to neutralize additional base.

The principal organs that regulate the pH of the carbonic acid–bicarbonate buffer system are the lungs and kidneys. Some of the receptors in the brain are sensitive to the concentrations of H^+ and CO_2 in bodily fluids. When the concentration of CO_2 rises, the equilibria in Equation 17.10 shift to the left, which leads to the formation of more H^+ . The receptors trigger a reflex to breathe faster and deeper, increasing the rate of elimination of CO_2 from the lungs and shifting the equilibria back to the right. The kidneys absorb or release H^+ and HCO_3^- ; much of the excess acid leaves the body in urine, which normally has a pH of 5.0 to 7.0.



▲ **Figure 17.4 Red blood cells.** A scanning electronmicrograph of a group of red blood cells traveling through a small branch of an artery. Blood is a buffered solution whose pH is maintained between 7.35 and 7.45.

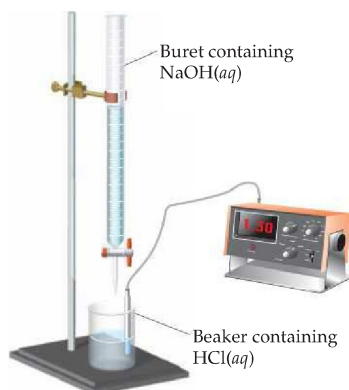
The regulation of the pH of blood plasma relates directly to the effective transport of O_2 to bodily tissues. The protein hemoglobin, which is found in red blood cells, carries oxygen. Hemoglobin (Hb) reversibly binds both H^+ and O_2 . These two substances compete for the Hb, which can be represented approximately by the following equilibrium:



Oxygen enters the blood through the lungs, where it passes into the red blood cells and binds to Hb. When the blood reaches tissue in which the concentration of O_2 is low, the equilibrium in Equation 17.11 shifts to the left and O_2 is released. An increase in H^+ ion concentration (decrease in blood pH) also shifts this equilibrium to the left, as does increasing temperature.

During periods of strenuous exertion, three factors work together to ensure the delivery of O_2 to active tissues: (1) As O_2 is consumed, the equilibrium in Equation 17.11 shifts to the left according to Le Châtelier's principle. (2) Exertion raises the temperature of the body, also shifting the equilibrium to the left. (3) Large amounts of CO_2 are produced by metabolism, which shifts the equilibrium in Equation 17.10 to the left, thus decreasing the pH. Other acids, such as lactic acid, are also produced during strenuous exertion as tissues become starved for oxygen. The decrease in pH shifts the hemoglobin equilibrium to the left, delivering more O_2 . In addition, the decrease in pH stimulates an increase in the rate of breathing, which furnishes more O_2 and eliminates CO_2 . Without this elaborate arrangement, the O_2 in tissues would be rapidly depleted, making further activity impossible.

Related Exercises: 17.29 and 17.90



▲ **Figure 17.5 Measuring pH during a titration.** A typical setup for using a pH meter to measure data for a titration curve. In this case a standard solution of NaOH (the titrant) is added by buret to a solution of HCl. The HCl solution is stirred during the titration to ensure uniform composition.

17.3 ACID–BASE TITRATIONS

In Section 4.6 we briefly described *titrations*. In an acid–base titration, a solution containing a known concentration of base is slowly added to an acid (or the acid is added to the base). Acid–base indicators can be used to signal the *equivalence point* of a titration (the point at which stoichiometrically equivalent quantities of acid and base have been brought together). Alternatively, a pH meter can be used to monitor the progress of the reaction producing a **pH titration curve**, a graph of the pH as a function of the volume of the added titrant. The shape of the titration curve makes it possible to determine the equivalence point in the titration. The titration curve can also be used to select suitable indicators and to determine the K_a of the weak acid or the K_b of the weak base being titrated.

A typical apparatus for measuring pH during a titration is illustrated in Figure 17.5 ◀. The titrant is added to the solution from a buret, and the pH is continually monitored using a pH meter. To understand why titration curves have certain characteristic shapes, we will examine the curves for three kinds of titrations: (1) strong acid–strong base, (2) weak acid–strong base, and (3) polyprotic acid–strong base. We will also briefly consider how these curves relate to those involving weak bases.

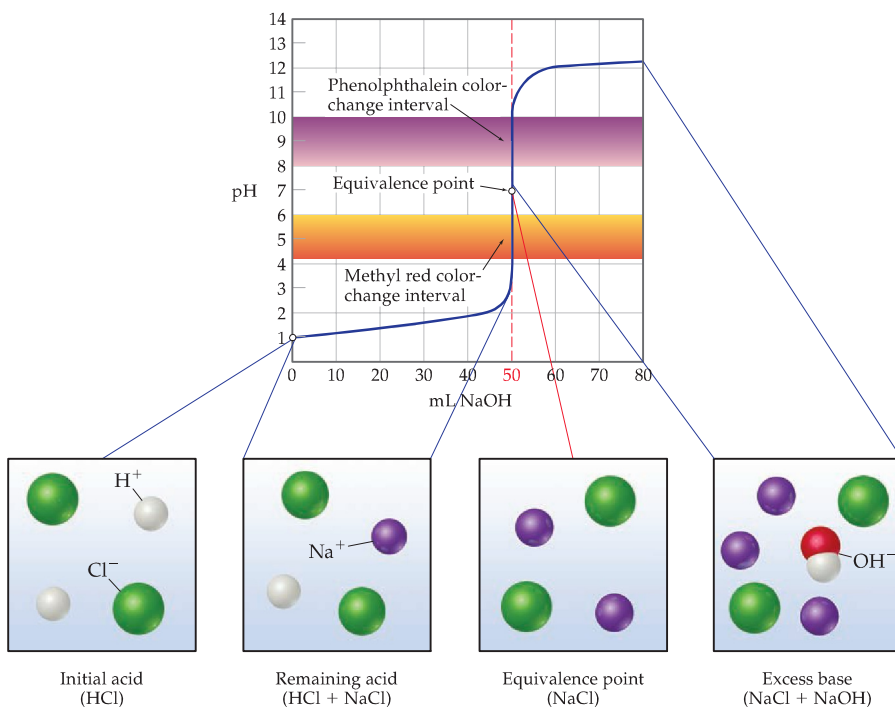
GIVE IT SOME THOUGHT

For the setup shown in Figure 17.5, will pH increase or decrease as titrant is added?

Strong Acid–Strong Base Titrations

The titration curve produced when a strong base is added to a strong acid has the general shape shown in Figure 17.6 ▶. This curve depicts the pH change that occurs as 0.100 M NaOH is added to 50.0 mL of 0.100 M HCl. The pH can be calculated at various stages of the titration. To help understand these calculations, we can divide the curve into four regions:

1. *The initial pH (initial acid):* The pH of the solution before the addition of any base is determined by the initial concentration of the strong acid. For a solution of 0.100 M HCl, $[\text{H}^+] = 0.100 \text{ M}$, and hence $\text{pH} = -\log(0.100) = 1.000$. Thus, the initial pH is low.
2. *Between the initial pH and the equivalence point (remaining acid):* As NaOH is added, the pH increases slowly at first and then rapidly in the vicinity of the equivalence point. The pH of the solution before the equivalence point is determined by the concentration of acid that has not yet been neutralized. This calculation is illustrated in Sample Exercise 17.6(a).
3. *The equivalence point:* At the equivalence point an equal number of moles of the NaOH and HCl have reacted, leaving only a solution of their salt, NaCl. The pH of the solution is 7.00 because the cation of a strong base (in this case Na^+) and the anion of a strong acid (in this case Cl^-) do not hydrolyze and therefore have no appreciable effect on pH. ∞∞ (Section 16.9)
4. *After the equivalence point (excess base):* The pH of the solution after the equivalence point is determined by the concentration of the excess NaOH in the solution. This calculation is illustrated in Sample Exercise 17.6(b).



▲ **Figure 17.6 Adding a strong base to a strong acid.** The pH curve for titration of 50.0 mL of a 0.100 M solution of a strong acid with a 0.100 M solution of a strong base. In this case the acid is HCl and the base is NaOH. The pH starts out at a low value characteristic of the acid and then increases as base is added, rising rapidly at the equivalence point. Both phenolphthalein and methyl red change color at the equivalence point. (For clarity, water molecules have been omitted from the molecular art.)

■ SAMPLE EXERCISE 17.6 | Calculating pH for a Strong Acid–Strong Base Titration

Calculate the pH when the following quantities of 0.100 M NaOH solution have been added to 50.0 mL of 0.100 M HCl solution: (a) 49.0 mL, (b) 51.0 mL.

SOLUTION

Analyze: We are asked to calculate the pH at two points in the titration of a strong acid with a strong base. The first point is just before the equivalence point, so we expect the pH to be determined by the small amount of strong acid that has not yet been neutralized. The second point is just after the equivalence point, so we expect this pH to be determined by the small amount of excess strong base.

Plan: (a) As the NaOH solution is added to the HCl solution, $\text{H}^+(\text{aq})$ reacts with $\text{OH}^-(\text{aq})$ to form H_2O . Both Na^+ and Cl^- are spectator ions, having negligible effect on the pH. To determine the pH of the solution, we must first determine how many moles of H^+ were originally present and how many moles of OH^- were added. We can then calculate how many moles of each ion remain after the neutralization reaction. To calculate $[\text{H}^+]$, and hence pH, we must also remember that the volume of the solution increases as we add titrant, thus diluting the concentration of all solutes present.

Solve: The number of moles of H^+ in the original HCl solution is given by the product of the volume of the solution (50.0 mL = 0.0500 L) and its molarity (0.100 M):

$$(0.0500 \text{ L soln}) \left(\frac{0.100 \text{ mol H}^+}{1 \text{ L soln}} \right) = 5.00 \times 10^{-3} \text{ mol H}^+$$

Likewise, the number of moles of OH^- in 49.0 mL of 0.100 M NaOH is

$$(0.0490 \text{ L soln})\left(\frac{0.100 \text{ mol OH}^-}{1 \text{ L soln}}\right) = 4.90 \times 10^{-3} \text{ mol OH}^-$$

Because we have not yet reached the equivalence point, there are more moles of H^+ present than OH^- . Each mole of OH^- will react with one mole of H^+ . Using the convention introduced in Sample Exercise 17.5,

	$\text{H}^+(aq)$	+	$\text{OH}^-(aq)$	\longrightarrow	$\text{H}_2\text{O}(l)$
Before addition	$5.00 \times 10^{-3} \text{ mol}$		0		—
Addition			$4.90 \times 10^{-3} \text{ mol}$		
After addition	$0.10 \times 10^{-3} \text{ mol}$		0		—

During the course of the titration, the volume of the reaction mixture increases as the NaOH solution is added to the HCl solution. Thus, at this point in the titration, the total volume of the solutions is

$$50.0 \text{ mL} + 49.0 \text{ mL} = 99.0 \text{ mL} = 0.0990 \text{ L}$$

(We assume that the total volume is the sum of the volumes of the acid and base solutions.) Thus, the concentration of $\text{H}^+(aq)$ is

$$[\text{H}^+] = \frac{\text{moles H}^+(aq)}{\text{liters soln}} = \frac{0.10 \times 10^{-3} \text{ mol}}{0.09900 \text{ L}} = 1.0 \times 10^{-3} \text{ M}$$

The corresponding pH equals

$$-\log(1.0 \times 10^{-3}) = 3.00$$

Plan: (b) We proceed in the same way as we did in part (a), except we are now past the equivalence point and have more OH^- in the solution than H^+ . As before, the initial number of moles of each reactant is determined from their volumes and concentrations. The reactant present in smaller stoichiometric amount (the limiting reactant) is consumed completely, leaving an excess of hydroxide ion.

Solve:

	$\text{H}^+(aq)$	+	$\text{OH}^-(aq)$	\longrightarrow	$\text{H}_2\text{O}(l)$
Before addition	$5.00 \times 10^{-3} \text{ mol}$		0		—
Addition			$5.10 \times 10^{-3} \text{ mol}$		
After addition	0		$0.10 \times 10^{-3} \text{ mol}$		—

In this case the total volume of the solution is

$$50.0 \text{ mL} + 51.0 \text{ mL} = 101.0 \text{ mL} = 0.1010 \text{ L}$$

Hence, the concentration of $\text{OH}^-(aq)$ in the solution is

$$[\text{OH}^-] = \frac{\text{moles OH}^-(aq)}{\text{liters soln}} = \frac{0.10 \times 10^{-3} \text{ mol}}{0.1010 \text{ L}} = 1.0 \times 10^{-3} \text{ M}$$

Thus, the pOH of the solution equals

$$\text{pOH} = -\log(1.0 \times 10^{-3}) = 3.00$$

and the pH equals

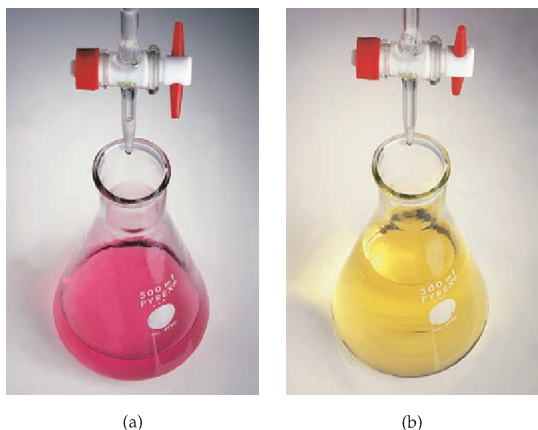
$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 3.00 = 11.00$$

■ PRACTICE EXERCISE

Calculate the pH when the following quantities of 0.100 M HNO_3 have been added to 25.0 mL of 0.100 M KOH solution: (a) 24.9 mL, (b) 25.1 mL.

Answers: (a) 10.30, (b) 3.70

Optimally, an indicator would change color at the equivalence point in a titration. In practice, however, that is unnecessary. The pH changes very rapidly near the equivalence point, and in this region merely a drop of titrant can change the pH by several units. Thus, an indicator beginning and ending its color change anywhere on this rapid-rise portion of the titration curve will give a sufficiently accurate measure of the volume of titrant needed to reach the equivalence point. The point in a titration where the indicator changes color is called the *end point* to distinguish it from the actual equivalence point that it closely approximates.



◀ **Figure 17.7 Methyl red indicator.** Change in appearance of a solution containing methyl red indicator in the pH range 4.2 to 6.3. The characteristic acidic color is shown in (a), and the characteristic basic color in (b).

In Figure 17.6 we see that the pH changes very rapidly from about 4 to about 10 near the equivalence point. Consequently, an indicator for this strong acid–strong base titration can change color anywhere in this range. Most strong acid–strong base titrations are carried out using phenolphthalein as an indicator (Figure 4.20) because it dramatically changes color in this range. From Figure 16.7, we see that phenolphthalein changes color from pH 8.3 to 10.0. Several other indicators would also be satisfactory, including methyl red, which changes color from pH 4.2 to 6.0 (Figure 17.7 ▲).

Titration of a solution of a strong base with a solution of a strong acid would yield an analogous curve of pH versus added acid. In this case, however, the pH would be high at the outset of the titration and low at its completion, as shown in Figure 17.8 ▶.

GIVE IT SOME THOUGHT

What is the pH at the equivalence point when 0.10 M HNO_3 is added to a solution containing 0.30 g of KOH?

Weak Acid–Strong Base Titrations

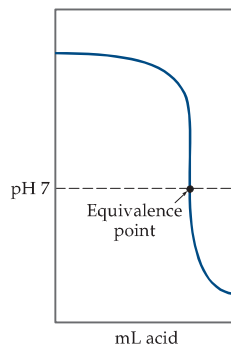
The curve for the titration of a weak acid by a strong base is very similar in shape to that for the titration of a strong acid by a strong base. Consider, for example, the titration curve for the titration of 50.0 mL of 0.100 M acetic acid (CH_3COOH) with 0.100 M NaOH shown in Figure 17.9 ▼. We can calculate the pH at points along this curve, using principles we have discussed earlier. As in the case of the titration of a strong acid by a strong base, we can divide the curve into four regions:

1. *The initial pH (initial acid):* We use K_a of the acid to calculate this pH, as shown in Section 16.6. The calculated pH of 0.100 M CH_3COOH is 2.89.
2. *Between the initial pH and the equivalence point (buffer mixture):* Prior to reaching the equivalence point, the acid is being neutralized, and its conjugate base is being formed:

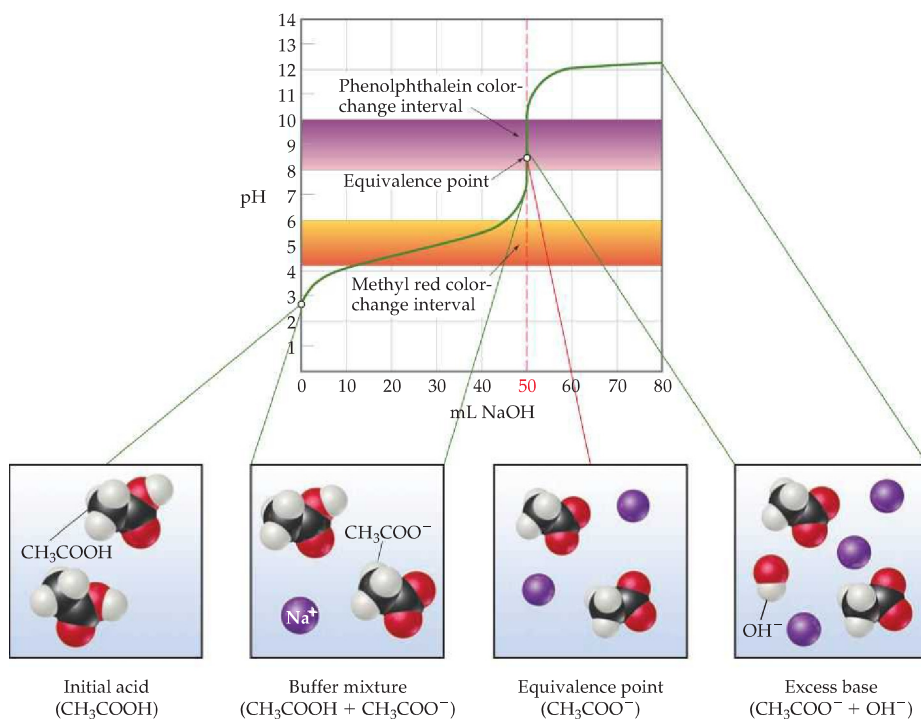


Thus, the solution contains a mixture of CH_3COOH and CH_3COO^- .

The approach we take in calculating the pH in this region of the titration curve involves two main steps. First, we consider the neutralization reaction between CH_3COOH and OH^- to determine the concentrations of



▲ **Figure 17.8 Adding a strong acid to a strong base.** The shape of a pH curve for titration of a strong base with a strong acid. The pH starts out at a high value characteristic of the base and then decreases as acid is added, dropping rapidly at the equivalence point.

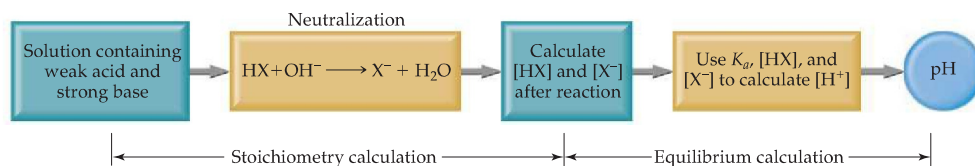


▲ **Figure 17.9 Adding a strong base to a weak acid.** The curve shows the variation in pH as 0.100 M NaOH solution is added to 50.0 mL of 0.100 M acetic acid solution. Phenolphthalein changes color at the equivalence point, but methyl red does not. (For clarity, water molecules have been omitted from the molecular art.)

▼ **Figure 17.10 Procedure for calculating the pH when a weak acid is partially neutralized by a strong base.** First consider the effect of the neutralization reaction (stoichiometry calculation). Then determine the pH of the resultant buffer mixture (equilibrium calculation). An analogous procedure can be used for the addition of strong acid to a weak base.

CH_3COOH and CH_3COO^- in the solution. Next, we calculate the pH of this buffer pair using procedures developed in Sections 17.1 and 17.2. The general procedure is diagrammed in Figure 17.10 ▼ and illustrated in Sample Exercise 17.7.

3. *The equivalence point:* The equivalence point is reached after adding 50.0 mL of 0.100 M NaOH to the 50.0 mL of 0.100 M CH_3COOH . At this point the 5.00×10^{-3} mol of NaOH completely reacts with the 5.00×10^{-3} mol of CH_3COOH to form 5.00×10^{-3} mol of their salt, CH_3COONa . The Na^+ ion of this salt has no significant effect on the pH. The CH_3COO^- ion, however, is a weak base, and the pH at the equivalence point is therefore greater than 7. Indeed, the pH at the equivalence point is always above 7 in a weak acid–strong base titration because the anion of the salt formed is a weak base. The procedure for calculating the pH of the solution of a weak base is described in Section 16.7 and is shown in Sample Exercise 17.8.
4. *After the equivalence point (excess base):* In this region of the titration curve, $[\text{OH}^-]$ from the reaction of CH_3COO^- with water is negligible compared to $[\text{OH}^-]$ from the excess NaOH. Thus, the pH is determined by the concentration of OH^- from the excess NaOH. The method for calculating pH



in this region is therefore like that for the strong acid–strong base titration illustrated in Sample Exercise 17.6(b). Thus, the addition of 51.0 mL of 0.100 M NaOH to 50.0 mL of either 0.100 M HCl or 0.100 M CH₃COOH yields the same pH, 11.00. Notice in Figures 17.6 and 17.9 that the titration curves for the titrations of both the strong acid and the weak acid are the same after the equivalence point.

SAMPLE EXERCISE 17.7 | Calculating pH for a Weak Acid–Strong Base Titration

Calculate the pH of the solution formed when 45.0 mL of 0.100 M NaOH is added to 50.0 mL of 0.100 M CH₃COOH ($K_a = 1.8 \times 10^{-5}$).

SOLUTION

Analyze: We are asked to calculate the pH before the equivalence point of the titration of a weak acid with a strong base.

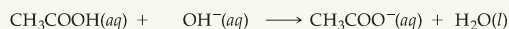
Plan: We first must determine the number of moles of CH₃COOH and CH₃COO[−] that are present after the neutralization reaction. We then calculate pH using K_a together with [CH₃COOH] and [CH₃COO[−]].

Solve: *Stoichiometry Calculation:* The product of the volume and concentration of each solution gives the number of moles of each reactant present before the neutralization:

$$(0.0500 \text{ L soln}) \left(\frac{0.100 \text{ mol CH}_3\text{COOH}}{1 \text{ L soln}} \right) = 5.00 \times 10^{-3} \text{ mol CH}_3\text{COOH}$$

$$(0.0450 \text{ L soln}) \left(\frac{0.100 \text{ mol NaOH}}{1 \text{ L soln}} \right) = 4.50 \times 10^{-3} \text{ mol NaOH}$$

The 4.50×10^{-3} mol of NaOH consumes 4.50×10^{-3} mol of CH₃COOH:



Before addition	$5.00 \times 10^{-3} \text{ mol}$	0	0	—
Addition		$4.50 \times 10^{-3} \text{ mol}$		
After addition	$0.50 \times 10^{-3} \text{ mol}$	0	$4.50 \times 10^{-3} \text{ mol}$	—

The total volume of the solution is

$$45.0 \text{ mL} + 50.0 \text{ mL} = 95.0 \text{ mL} = 0.0950 \text{ L}$$

The resulting molarities of CH₃COOH and CH₃COO[−] after the reaction are therefore

$$[\text{CH}_3\text{COOH}] = \frac{0.50 \times 10^{-3} \text{ mol}}{0.0950 \text{ L}} = 0.0053 \text{ M}$$

$$[\text{CH}_3\text{COO}^-] = \frac{4.50 \times 10^{-3} \text{ mol}}{0.0950 \text{ L}} = 0.0474 \text{ M}$$

Equilibrium Calculation: The equilibrium between CH₃COOH and CH₃COO[−] must obey the equilibrium-constant expression for CH₃COOH

$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = 1.8 \times 10^{-5}$$

Solving for [H⁺] gives

$$[\text{H}^+] = K_a \times \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} = (1.8 \times 10^{-5}) \times \left(\frac{0.0053}{0.0474} \right) = 2.0 \times 10^{-6} \text{ M}$$

$$\text{pH} = -\log(2.0 \times 10^{-6}) = 5.70$$

Comment: We could have solved for pH equally well using the Henderson–Hasselbalch equation.

PRACTICE EXERCISE

(a) Calculate the pH in the solution formed by adding 10.0 mL of 0.050 M NaOH to 40.0 mL of 0.0250 M benzoic acid (C₆H₅COOH, $K_a = 6.3 \times 10^{-5}$). (b) Calculate the pH in the solution formed by adding 10.0 mL of 0.100 M HCl to 20.0 mL of 0.100 M NH₃.

Answers: (a) 4.20, (b) 9.26

SAMPLE EXERCISE 17.8 | Calculating the pH at the Equivalence Point

Calculate the pH at the equivalence point in the titration of 50.0 mL of 0.100 M CH₃COOH with 0.100 M NaOH.

SOLUTION

Analyze: We are asked to determine the pH at the equivalence point of the titration of a weak acid with a strong base. Because the neutralization of a weak acid produces its anion, which is a weak base, we expect the pH at the equivalence point to be greater than 7.

Plan: The initial number of moles of acetic acid will equal the number of moles of acetate ion at the equivalence point. We use the volume of the solution at the equivalence point to calculate the concentration of acetate ion. Because the acetate ion is a weak base, we can calculate the pH using K_b and $[\text{CH}_3\text{COO}^-]$.

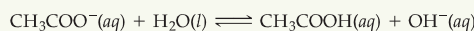
Solve: The number of moles of acetic acid in the initial solution is obtained from the volume and molarity of the solution:

$$\text{Moles} = M \times L = (0.100 \text{ mol/L})(0.0500 \text{ L}) = 5.00 \times 10^{-3} \text{ mol CH}_3\text{COOH}$$

Hence 5.00×10^{-3} mol of CH_3COO^- is formed. It will take 50.0 mL of NaOH to reach the equivalence point (Figure 17.9). The volume of this salt solution at the equivalence point is the sum of the volumes of the acid and base, 50.0 mL + 50.0 mL = 100.0 mL = 0.1000 L. Thus, the concentration of CH_3COO^- is

$$[\text{CH}_3\text{COO}^-] = \frac{5.00 \times 10^{-3} \text{ mol}}{0.1000 \text{ L}} = 0.0500 \text{ M}$$

The CH_3COO^- ion is a weak base.



The K_b for CH_3COO^- can be calculated from the K_a value of its conjugate acid, $K_b = K_w/K_a = (1.0 \times 10^{-14})/(1.8 \times 10^{-5}) = 5.6 \times 10^{-10}$. Using the K_b expression, we have

$$K_b = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} = \frac{(x)(x)}{0.0500 - x} = 5.6 \times 10^{-10}$$

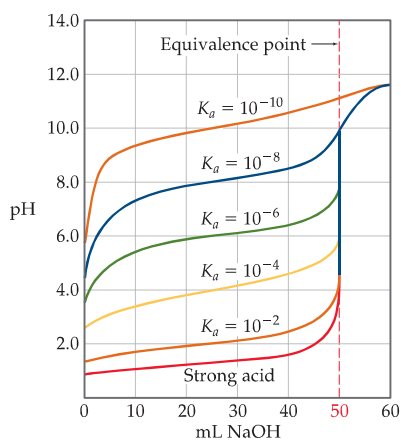
Making the approximation that $0.0500 - x \approx 0.0500$, and then solving for x , we have $x = [\text{OH}^-] = 5.3 \times 10^{-6} \text{ M}$, which gives $\text{pOH} = 5.28$ and $\text{pH} = 8.72$.

Check: The pH is above 7, as expected for the salt of a weak acid and strong base.

■ PRACTICE EXERCISE

Calculate the pH at the equivalence point when (a) 40.0 mL of 0.025 M benzoic acid ($\text{C}_6\text{H}_5\text{COOH}$, $K_a = 6.3 \times 10^{-5}$) is titrated with 0.050 M NaOH; (b) 40.0 mL of 0.100 M NH_3 is titrated with 0.100 M HCl.

Answers: (a) 8.21, (b) 5.28



▲ **Figure 17.11 Effect of K_a on titration curves.** This set of curves shows the influence of acid strength (K_a) on the shape of the curve for titration with NaOH. Each curve represents titration of 50.0 mL of 0.10 M acid with 0.10 M NaOH. The weaker the acid, the higher the initial pH and the smaller the pH change at the equivalence point.

The pH titration curves for weak acid–strong base titrations differ from those for strong acid–strong base titrations in three noteworthy ways:

1. The solution of the weak acid has a higher initial pH than a solution of a strong acid of the same concentration.
2. The pH change at the rapid-rise portion of the curve near the equivalence point is smaller for the weak acid than it is for the strong acid.
3. The pH at the equivalence point is above 7.00 for the weak acid–strong base titration.

To illustrate these differences further, consider the family of titration curves shown in Figure 17.11 ◀. Notice that the initial pH increases as the acid becomes weaker (that is, as K_a becomes smaller), and that the pH change near the equivalence point becomes less marked. Notice also that the pH at the equivalence point steadily increases as K_a decreases. It is virtually impossible to determine the equivalence point when $\text{p}K_a$ is 10 or higher because the pH change is too small and gradual.

Because the pH change near the equivalence point becomes smaller as K_a decreases, the choice of indicator for a weak acid–strong base titration is more critical than it is for a strong acid–strong base titration. When 0.100 M CH_3COOH ($K_a = 1.8 \times 10^{-5}$) is titrated with 0.100 M NaOH, for example, as shown in Figure 17.9, the pH increases rapidly only over the pH range of about 7 to 10. Phenolphthalein is therefore an ideal indicator because it changes color from pH 8.3 to 10.0, close to the pH at the equivalence point. Methyl red is a poor choice, however, because its color change occurs from 4.2 to 6.0, which begins well before the equivalence point is reached.

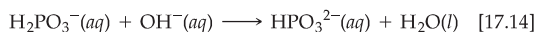
Titration of a weak base (such as 0.100 M NH_3) with a strong acid solution (such as 0.100 M HCl) leads to the titration curve shown in Figure 17.12. In this particular example the equivalence point occurs at pH 5.28. Thus, methyl red would be an ideal indicator, but phenolphthalein would be a poor choice.

GIVE IT SOME THOUGHT

Why is the choice of indicator more crucial for a weak acid–strong base titration than for a strong acid–strong base titration?

Titration of Polyprotic Acids

When weak acids contain more than one ionizable H atom, as in phosphorous acid (H_3PO_3), reaction with OH^- occurs in a series of steps. Neutralization of H_3PO_3 proceeds in two stages. [∞ \(Chapter 16 Sample Integrative Exercise\)](#)



When the neutralization steps of a polyprotic acid or polybasic base are sufficiently separated, the substance exhibits a titration curve with multiple equivalence points. Figure 17.13 shows the two distinct equivalence points in the titration curve for the $\text{H}_3\text{PO}_3\text{--H}_2\text{PO}_3^-\text{--HPO}_3^{2-}$ system.

GIVE IT SOME THOUGHT

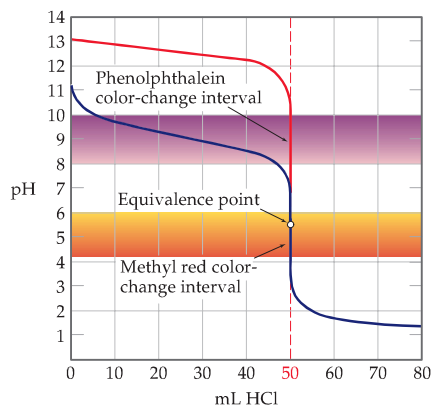
Sketch the titration curve for the titration of Na_2CO_3 with HCl.

17.4 SOLUBILITY EQUILIBRIA

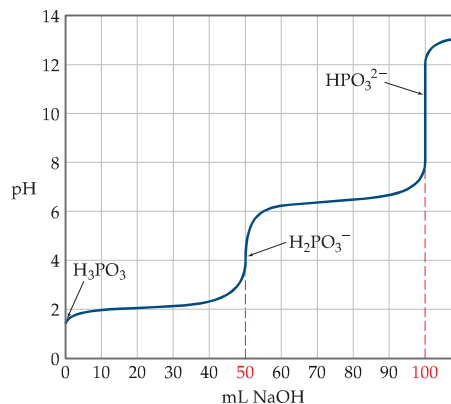
The equilibria that we have considered thus far in this chapter have involved acids and bases. Furthermore, they have been homogeneous; that is, all the species have been in the same phase. Through the rest of this chapter we will consider the equilibria involved in the dissolution or precipitation of ionic compounds. These reactions are heterogeneous.

The dissolving and precipitating of compounds are phenomena that occur both within us and around us. Tooth enamel dissolves in acidic solutions, for example, causing tooth decay. The precipitation of certain salts in our kidneys produces kidney stones. The waters of Earth contain salts dissolved as water passes over and through the ground. Precipitation of CaCO_3 from groundwater is responsible for the formation of stalactites and stalagmites within limestone caves (Figure 4.1).

In our earlier discussion of precipitation reactions, we considered some general rules for predicting the solubility of common salts in water. [∞ \(Section 4.2\)](#) These rules give us a qualitative sense of whether a compound will have a low or high solubility in water. By considering solubility equilibria, in contrast, we can make quantitative predictions about the amount of a given compound that will dissolve. We can also use these equilibria to analyze the factors that affect solubility.



▲ **Figure 17.12 Adding a strong acid to a base.** The blue curve shows pH versus volume of added HCl in the titration of 50.0 mL of 0.10 M ammonia (weak base) with 0.10 M HCl. The red curve shows pH versus added acid for the titration of 0.10 M NaOH (strong base). Both phenolphthalein and methyl red change color at the equivalence point in the titration of the strong base. Phenolphthalein changes color before the equivalence point in the titration of the weak base.



▲ **Figure 17.13 Diprotic acid.** Titration curve for the reaction of 50.0 mL of 0.10 M H_3PO_3 with 0.10 M NaOH.

The Solubility-Product Constant, K_{sp}

Recall that a *saturated solution* is one in which the solution is in contact with undissolved solute. ∞ (Section 13.2) Consider, for example, a saturated aqueous solution of BaSO_4 that is in contact with solid BaSO_4 . Because the solid is an ionic compound, it is a strong electrolyte and yields $\text{Ba}^{2+}(\text{aq})$ and $\text{SO}_4^{2-}(\text{aq})$ ions upon dissolving. The following equilibrium is readily established between the undissolved solid and hydrated ions in solution:



As with any other equilibrium, the extent to which this dissolution reaction occurs is expressed by the magnitude of its equilibrium constant. Because this equilibrium equation describes the dissolution of a solid, the equilibrium constant indicates how soluble the solid is in water and is referred to as the **solubility-product constant** (or simply the **solubility product**). It is denoted K_{sp} , where *sp* stands for solubility product.

The equilibrium-constant expression for the equilibrium between a solid and an aqueous solution of its component ions is written according to the rules that apply to any equilibrium-constant expression. Remember, however, that solids do not appear in the equilibrium-constant expressions for heterogeneous equilibria. ∞ (Section 15.4) Thus, the solubility-product expression for BaSO_4 , which is based on Equation 17.15, is

$$K_{sp} = [\text{Ba}^{2+}][\text{SO}_4^{2-}] \quad [17.16]$$

In general, *the solubility product of a compound equals the product of the concentration of the ions involved in the equilibrium, each raised to the power of its coefficient in the equilibrium equation*. The coefficient for each ion in the equilibrium equation also equals its subscript in the compound's chemical formula.

The values of K_{sp} at 25 °C for many ionic solids are tabulated in Appendix D. The value of K_{sp} for BaSO_4 is 1.1×10^{-10} , a very small number, indicating that only a very small amount of the solid will dissolve in water.

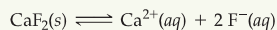
SAMPLE EXERCISE 17.9 | Writing Solubility-Product (K_{sp}) Expressions

Write the expression for the solubility-product constant for CaF_2 , and look up the corresponding K_{sp} value in Appendix D.

SOLUTION

Analyze: We are asked to write an equilibrium-constant expression for the process by which CaF_2 dissolves in water.

Plan: We apply the same rules for writing any equilibrium-constant expression, excluding the solid reactant from the expression. We assume that the compound dissociates completely into its component ions.



Solve: Following the italicized rule stated previously, the expression for K_{sp} is

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

In Appendix D we see that this K_{sp} has a value of 3.9×10^{-11} .

PRACTICE EXERCISE

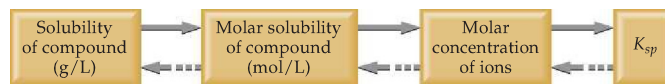
Give the solubility-product-constant expressions and the values of the solubility-product constants (from Appendix D) for the following compounds: (a) barium carbonate, (b) silver sulfate.

Answers: (a) $K_{sp} = [\text{Ba}^{2+}][\text{CO}_3^{2-}] = 5.0 \times 10^{-9}$; (b) $K_{sp} = [\text{Ag}^{+}]^2[\text{SO}_4^{2-}] = 1.5 \times 10^{-5}$

Solubility and K_{sp}

It is important to distinguish carefully between solubility and the solubility-product constant. The solubility of a substance is the quantity that dissolves to form a saturated solution. ∞ (Section 13.2) Solubility is often expressed as grams of solute per liter of solution (g/L). *Molar solubility* is the number of moles of the

solute that dissolve in forming a liter of saturated solution of the solute (mol/L). The solubility-product constant (K_{sp}) is the equilibrium constant for the equilibrium between an ionic solid and its saturated solution and is a unitless number. Thus, the magnitude of K_{sp} is a measure of how much of the solid dissolves to form a saturated solution.



▲ **Figure 17.14 Relationships between solubility and K_{sp} .** The solubility of any compound in grams per liter can be converted to molar solubility. The molar solubility can be used to determine the concentrations of ions in solution. The concentration of ions can be used to calculate K_{sp} . The steps can be reversed, and solubility calculated from K_{sp} .

GIVE IT SOME THOUGHT

Without doing a calculation, predict which of the following compounds will have the greatest molar solubility in water: AgCl ($K_{sp} = 1.8 \times 10^{-10}$), AgBr ($K_{sp} = 5.0 \times 10^{-13}$), or AgI ($K_{sp} = 8.3 \times 10^{-17}$).

The solubility of a substance can change considerably as the concentrations of other solutes change. The solubility of $\text{Mg}(\text{OH})_2$, for example, depends highly on pH. The solubility is also affected by the concentrations of other ions in solution, especially Mg^{2+} . In contrast, the solubility-product constant, K_{sp} , has only one value for a given solute at any specific temperature.*

In principle, it is possible to use the K_{sp} value of a salt to calculate solubility under a variety of conditions. In practice, great care must be taken in doing so for the reasons indicated in “A Closer Look: Limitations of Solubility Products” at the end of this section. Agreement between measured solubility and that calculated from K_{sp} is usually best for salts whose ions have low charges (1+ and 1−) and do not hydrolyze. Figure 17.14▲ summarizes the relationships among various expressions of solubility and K_{sp} .

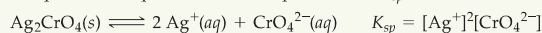
SAMPLE EXERCISE 17.10 | Calculating K_{sp} from Solubility

Solid silver chromate is added to pure water at 25 °C. Some of the solid remains undissolved at the bottom of the flask. The mixture is stirred for several days to ensure that equilibrium is achieved between the undissolved $\text{Ag}_2\text{CrO}_4(\text{s})$ and the solution. Analysis of the equilibrated solution shows that its silver ion concentration is $1.3 \times 10^{-4} \text{ M}$. Assuming that Ag_2CrO_4 dissociates completely in water and that there are no other important equilibria involving the Ag^+ or CrO_4^{2-} ions in the solution, calculate K_{sp} for this compound.

SOLUTION

Analyze: We are given the equilibrium concentration of Ag^+ in a saturated solution of Ag_2CrO_4 . From this information, we are asked to determine the value of the solubility-product constant, K_{sp} , for Ag_2CrO_4 .

Plan: The equilibrium equation and the expression for K_{sp} are



To calculate K_{sp} , we need the equilibrium concentrations of Ag^+ and CrO_4^{2-} . We know that at equilibrium $[\text{Ag}^+] = 1.3 \times 10^{-4} \text{ M}$. All the Ag^+ and CrO_4^{2-} ions in the solution come from the Ag_2CrO_4 that dissolves. Thus, we can use $[\text{Ag}^+]$ to calculate $[\text{CrO}_4^{2-}]$.

Solve: From the chemical formula of silver chromate, we know that there must be 2 Ag^+ ions in solution for each CrO_4^{2-} ion in solution. Consequently, the concentration of CrO_4^{2-} is half the concentration of Ag^+ :

$$[\text{CrO}_4^{2-}] = \left(\frac{1.3 \times 10^{-4} \text{ mol Ag}^+}{\text{L}} \right) \left(\frac{1 \text{ mol CrO}_4^{2-}}{2 \text{ mol Ag}^+} \right) = 6.5 \times 10^{-5} \text{ M}$$

We can now calculate the value of K_{sp} .

$$K_{sp} = [\text{Ag}^+]^2[\text{CrO}_4^{2-}] = (1.3 \times 10^{-4})^2(6.5 \times 10^{-5}) = 1.1 \times 10^{-12}$$

Check: We obtain a small value, as expected for a slightly soluble salt. Furthermore, the calculated value agrees well with the one given in Appendix D, 1.2×10^{-12} .

*This is strictly true only for very dilute solutions. The values of equilibrium constants are somewhat altered when the total concentration of ionic substances in water is increased. However, we will ignore these effects, which are taken into consideration only for work that requires exceptional accuracy.

PRACTICE EXERCISE

A saturated solution of $\text{Mg}(\text{OH})_2$ in contact with undissolved solid is prepared at 25 °C. The pH of the solution is found to be 10.17. Assuming that $\text{Mg}(\text{OH})_2$ dissociates completely in water and that there are no other simultaneous equilibria involving the Mg^{2+} or OH^- ions in the solution, calculate K_{sp} for this compound.

Answer: 1.6×10^{-12}

SAMPLE EXERCISE 17.11 Calculating Solubility from K_{sp}

The K_{sp} for CaF_2 is 3.9×10^{-11} at 25 °C. Assuming that CaF_2 dissociates completely upon dissolving and that there are no other important equilibria affecting its solubility, calculate the solubility of CaF_2 in grams per liter.

SOLUTION

Analyze: We are given K_{sp} for CaF_2 and are asked to determine solubility. Recall that the *solubility* of a substance is the quantity that can dissolve in solvent, whereas the *solubility-product constant*, K_{sp} , is an equilibrium constant.

Plan: We can approach this problem by using our standard techniques for solving equilibrium problems. We write the chemical equation for the dissolution process and set up a table of the initial and equilibrium concentrations. We then use the equilibrium-constant expression. In this case we know K_{sp} , and so we solve for the concentrations of the ions in solution.

Solve: Assume initially that none of the salt has dissolved, and then allow x moles/liter of CaF_2 to dissociate completely when equilibrium is achieved.

Initial	—	0	0
Change	—	+ x M	+2 x M
Equilibrium	—	x M	2 x M

The stoichiometry of the equilibrium dictates that $2x$ moles/liter of F^- are produced for each x moles/liter of CaF_2 that dissolve. We now use the expression for K_{sp} and substitute the equilibrium concentrations to solve for the value of x :

$$K_{sp} = [\text{Ca}^{2+}][\text{F}^-]^2 = (x)(2x)^2 = 4x^3 = 3.9 \times 10^{-11}$$

$$x = \sqrt[3]{\frac{3.9 \times 10^{-11}}{4}} = 2.1 \times 10^{-4} \text{ M}$$

(Remember that $\sqrt[3]{y} = y^{1/3}$; to calculate the cube root of a number, you can use the y^x function on your calculator, with $x = \frac{1}{3}$.) Thus, the molar solubility of CaF_2 is 2.1×10^{-4} mol/L. The mass of CaF_2 that dissolves in water to form a liter of solution is

$$\left(\frac{2.1 \times 10^{-4} \text{ mol CaF}_2}{1 \text{ L soln}} \right) \left(\frac{78.1 \text{ g CaF}_2}{1 \text{ mol CaF}_2} \right) = 1.6 \times 10^{-2} \text{ g CaF}_2/\text{L soln}$$

Check: We expect a small number for the solubility of a slightly soluble salt. If we reverse the calculation, we should be able to recalculate the solubility product: $K_{sp} = (2.1 \times 10^{-4})(4.2 \times 10^{-4})^2 = 3.7 \times 10^{-11}$, close to the starting value for K_{sp} , 3.9×10^{-11} .

Comment: Because F^- is the anion of a weak acid, you might expect that the hydrolysis of the ion would affect the solubility of CaF_2 . The basicity of F^- is so small ($K_b = 1.5 \times 10^{-11}$), however, that the hydrolysis occurs to only a slight extent and does not significantly influence the solubility. The reported solubility is 0.017 g/L at 25 °C, in good agreement with our calculation.

PRACTICE EXERCISE

The K_{sp} for LaF_3 is 2×10^{-19} . What is the solubility of LaF_3 in water in moles per liter?

Answer: 9×10^{-6} mol/L

A Closer Look

LIMITATIONS OF SOLUBILITY PRODUCTS

The concentrations of ions calculated from K_{sp} sometimes deviate appreciably from those found experimentally. In part, these deviations are due to electrostatic interactions between ions in solution, which can lead to ion pairs. (See Section 13.5, “A Closer Look: Colligative Properties of Electrolyte Solutions.”) These interactions increase in magnitude both as the concentrations of the ions increase and as their charges increase. The solubility calculated from K_{sp} tends to be low unless it is corrected to account for these interactions between ions. Chemists have developed procedures for correcting for these “ionic-strength” or “ionic-activity” effects, and these procedures are examined in more advanced chemistry courses. As an example of the effect of these interionic interactions, consider CaCO_3 (calcite), whose solubility product, $K_{sp} = 4.5 \times 10^{-9}$, gives a calculated solubility of 6.7×10^{-5} mol/L. Making corrections for the interionic interactions in the solution yields a higher solubility, 7.3×10^{-5} mol/L. The reported solubility, however, is twice as high (1.4×10^{-4} mol/L), so there must be one or more additional factors involved.

Another common source of error in calculating ion concentrations from K_{sp} is ignoring other equilibria that occur simultaneously in the solution. It is possible, for example, that acid–base equilibria take place simultaneously with solubility equilibria. In particular, both basic anions and cations with high charge-to-size ratios undergo hydrolysis reactions that can measurably increase the solubilities of their salts. For example, CaCO_3 contains the basic carbonate ion ($K_b = 1.8 \times 10^{-4}$), which hydrolyzes in water: $\text{CO}_3^{2-}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HCO}_3^-(aq) + \text{OH}^-(aq)$. If we consider both the effect of the interionic interactions in the solution and the effect of the simultaneous solubility and hydrolysis equilibria, we calculate a solubility of 1.4×10^{-4} mol/L, in agreement with the measured value.

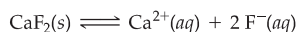
Finally, we generally assume that ionic compounds dissociate completely into their component ions when they dissolve. This assumption is not always valid. When MgF_2 dissolves, for example, it yields not only Mg^{2+} and F^- ions but also MgF^+ ions in solution. Thus, we see that calculating solubility using K_{sp} can be more complicated than it first appears and it requires considerable knowledge of the equilibria occurring in solution.

17.5 FACTORS THAT AFFECT SOLUBILITY

The solubility of a substance is affected by temperature as well as by the presence of other solutes. The presence of an acid, for example, can have a major influence on the solubility of a substance. In Section 17.4 we considered the dissolving of ionic compounds in pure water. In this section we examine three factors that affect the solubility of ionic compounds: (1) the presence of common ions, (2) the pH of the solution, and (3) the presence of complexing agents. We will also examine the phenomenon of *amphoterism*, which is related to the effects of both pH and complexing agents.

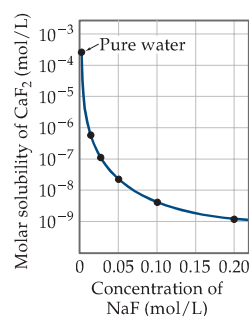
Common-Ion Effect

The presence of either $\text{Ca}^{2+}(aq)$ or $\text{F}^-(aq)$ in a solution reduces the solubility of CaF_2 , shifting the solubility equilibrium of CaF_2 to the left.



Addition of Ca^{2+} or F^- shifts equilibrium, reducing solubility

This reduction in solubility is another application of the common-ion effect. ∞ (Section 17.1) In general, the solubility of a slightly soluble salt is decreased by the presence of a second solute that furnishes a common ion. Figure 17.15 \blacktriangleright shows how the solubility of CaF_2 decreases as NaF is added to the solution. Sample Exercise 17.12 shows how the K_{sp} can be used to calculate the solubility of a slightly soluble salt in the presence of a common ion.



\blacktriangle **Figure 17.15 Common-ion effect.** The way in which NaF concentration affects the solubility of CaF_2 demonstrates the common-ion effect. Notice that the CaF_2 solubility is on a logarithmic scale.

SAMPLE EXERCISE 17.12 | Calculating the Effect of a Common Ion on Solubility

Calculate the molar solubility of CaF_2 at 25°C in a solution that is (a) 0.010 M in $\text{Ca}(\text{NO}_3)_2$, (b) 0.010 M in NaF .

SOLUTION

Analyze: We are asked to determine the solubility of CaF_2 in the presence of two strong electrolytes, each of which contains an ion common to CaF_2 . In (a) the common ion is Ca^{2+} , and NO_3^- is a spectator ion. In (b) the common ion is F^- , and Na^+ is a spectator ion.

Plan: Because the slightly soluble compound is CaF_2 , we need to use the K_{sp} for this compound, which is available in Appendix D:

$$K_{sp} = [\text{Ca}^{2+}][\text{F}^-]^2 = 3.9 \times 10^{-11}$$

The value of K_{sp} is unchanged by the presence of additional solutes. Because of the common-ion effect, however, the solubility of the salt will decrease in the presence of common ions. We can again use our standard equilibrium techniques of starting with the equation for CaF_2 dissolution, setting up a table of initial and equilibrium concentrations, and using the K_{sp} expression to determine the concentration of the ion that comes only from CaF_2 .

Solve: (a) In this instance the initial concentration of Ca^{2+} is 0.010 M because of the dissolved $\text{Ca}(\text{NO}_3)_2$:

	$\text{CaF}_2(\text{s})$	\rightleftharpoons	$\text{Ca}^{2+}(\text{aq})$	+	$2\text{F}^-(\text{aq})$
Initial	—		0.010 M		0
Change	—		$+x\text{ M}$		$+2x\text{ M}$
Equilibrium	—		$(0.010 + x)\text{ M}$		$2x\text{ M}$

Substituting into the solubility-product expression gives

$$K_{sp} = 3.9 \times 10^{-11} = [\text{Ca}^{2+}][\text{F}^-]^2 = (0.010 + x)(2x)^2$$

This would be a messy problem to solve exactly, but fortunately it is possible to simplify matters greatly. Even without the common-ion effect, the solubility of CaF_2 is very small ($2.1 \times 10^{-4}\text{ M}$). Thus, we assume that the 0.010 M concentration of Ca^{2+} from $\text{Ca}(\text{NO}_3)_2$ is very much greater than the small additional concentration resulting from the solubility of CaF_2 ; that is, x is small compared to 0.010 M , and $0.010 + x \approx 0.010$. We then have

$$\begin{aligned} 3.9 \times 10^{-11} &= (0.010)(2x)^2 \\ x^2 &= \frac{3.9 \times 10^{-11}}{4(0.010)} = 9.8 \times 10^{-10} \\ x &= \sqrt{9.8 \times 10^{-10}} = 3.1 \times 10^{-5}\text{ M} \end{aligned}$$

The very small value for x validates the simplifying assumption we have made. Our calculation indicates that 3.1×10^{-5} mol of solid CaF_2 dissolves per liter of the 0.010 M $\text{Ca}(\text{NO}_3)_2$ solution.

(b) In this case the common ion is F^- , and at equilibrium we have

$$[\text{Ca}^{2+}] = x \quad \text{and} \quad [\text{F}^-] = 0.010 + 2x$$

Assuming that $2x$ is small compared to 0.010 M (that is, $0.010 + 2x \approx 0.010$), we have

$$\begin{aligned} 3.9 \times 10^{-11} &= x(0.010)^2 \\ x &= \frac{3.9 \times 10^{-11}}{(0.010)^2} = 3.9 \times 10^{-7}\text{ M} \end{aligned}$$

Thus, 3.9×10^{-7} mol of solid CaF_2 should dissolve per liter of 0.010 M NaF solution.

Comment: The molar solubility of CaF_2 in pure water is $2.1 \times 10^{-4}\text{ M}$ (Sample Exercise 17.11). By comparison, our calculations above show that the solubility of CaF_2 in the presence of 0.010 M Ca^{2+} is $3.1 \times 10^{-5}\text{ M}$, and in the presence of 0.010 M F^- ion it is $3.9 \times 10^{-7}\text{ M}$. Thus, the addition of either Ca^{2+} or F^- to a solution of CaF_2 decreases the solubility. However, the effect of F^- on the solubility is more pronounced than that of Ca^{2+} because $[\text{F}^-]$ appears to the second power in the K_{sp} expression for CaF_2 , whereas Ca^{2+} appears to the first power.

PRACTICE EXERCISE

The value for K_{sp} for manganese(II) hydroxide, $\text{Mn}(\text{OH})_2$, is 1.6×10^{-13} . Calculate the molar solubility of $\text{Mn}(\text{OH})_2$ in a solution that contains 0.020 M NaOH .

Answer: $4.0 \times 10^{-10}\text{ M}$

Solubility and pH

The pH of a solution will affect the solubility of any substance whose anion is basic. Consider $\text{Mg}(\text{OH})_2$, for example, for which the solubility equilibrium is



A saturated solution of $\text{Mg}(\text{OH})_2$ has a calculated pH of 10.52 and contains $[\text{Mg}^{2+}] = 1.7 \times 10^{-4} \text{ M}$. Now suppose that solid $\text{Mg}(\text{OH})_2$ is equilibrated with a solution buffered at a more acidic pH of 9.0. The pOH, therefore, is 5.0, so $[\text{OH}^-] = 1.0 \times 10^{-5}$. Inserting this value for $[\text{OH}^-]$ into the solubility-product expression, we have

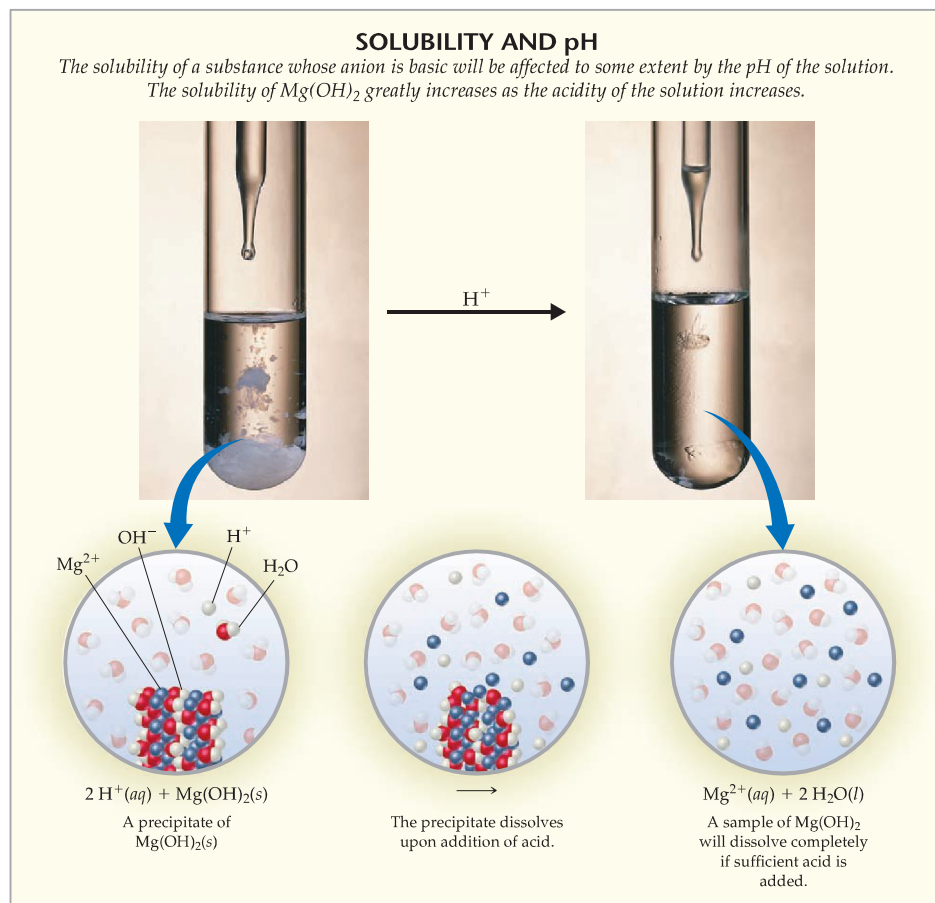
$$K_{sp} = [\text{Mg}^{2+}][\text{OH}^-]^2 = 1.8 \times 10^{-11}$$

$$[\text{Mg}^{2+}](1.0 \times 10^{-5})^2 = 1.8 \times 10^{-11}$$

$$[\text{Mg}^{2+}] = \frac{1.8 \times 10^{-11}}{(1.0 \times 10^{-5})^2} = 0.18 \text{ M}$$

Thus, $\text{Mg}(\text{OH})_2$ dissolves in the solution until $[\text{Mg}^{2+}] = 0.18 \text{ M}$. It is apparent that $\text{Mg}(\text{OH})_2$ is quite soluble in this solution. If the concentration of OH^- were reduced even further by making the solution more acidic, the Mg^{2+} concentration would have to increase to maintain the equilibrium condition. Thus, a sample of $\text{Mg}(\text{OH})_2$ will dissolve completely if sufficient acid is added (Figure 17.16 ▼).

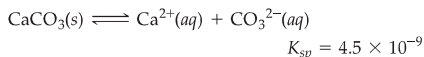
▼ **Figure 17.16 Dissolution of a precipitate in acid.** A white precipitate of $\text{Mg}(\text{OH})_2(\text{s})$ in contact with its saturated solution is in the test tube on the left. The dropper poised above the solution surface contains hydrochloric acid. (The anions accompanying the acid have been omitted to simplify the art.)



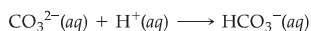
Chemistry and Life

SINKHOLES

A principal cause of sinkholes is the dissolution of limestone, which is calcium carbonate, by groundwater. Although CaCO_3 has a relatively small solubility-product constant, it is quite soluble in the presence of acid.



Rainwater is naturally acidic, with a pH range of 5 to 6, and can become more acidic when it comes into contact with decaying plant matter. Because carbonate ion is the conjugate base of the weak acid, hydrogen carbonate ion (HCO_3^-), it readily combines with hydrogen ion.



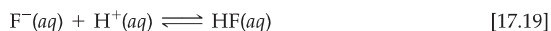
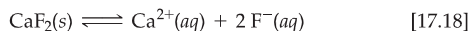
The consumption of carbonate ion shifts the dissolution equilibrium to the right, thus increasing the solubility of CaCO_3 . This can have profound consequences in areas where the terrain consists of porous calcium carbonate bedrock covered by a relatively thin layer of clay and/or topsoil. As acidic water percolates through and gradually dissolves the limestone, it creates underground voids. A sinkhole results when the overlying ground can no longer be supported by the remaining bedrock and collapses into the underground cavity [Figure 17.17 ▶].



▲ **Figure 17.17 Sinkhole formation.** An underground void develops as limestone, $\text{CaCO}_3(s)$, dissolves. Collapse of the overlying ground into an underground cavity causes sinkhole formation. The large sinkhole shown here occurred in Orlando, Florida and destroyed several buildings and part of a highway.

The solubility of almost any ionic compound is affected if the solution is made sufficiently acidic or basic. The effects are very noticeable, however, only when one or both ions involved are at least moderately acidic or basic. The metal hydroxides, such as $\text{Mg}(\text{OH})_2$, are examples of compounds containing a strongly basic ion, the hydroxide ion.

In general, if a compound contains a basic anion (that is, the anion of a weak acid), its solubility will increase as the solution becomes more acidic. As we have seen, the solubility of $\text{Mg}(\text{OH})_2$ greatly increases as the acidity of the solution increases. The solubility of CaF_2 increases as the solution becomes more acidic, too, because the F^- ion is a weak base; it is the conjugate base of the weak acid HF. As a result, the solubility equilibrium of CaF_2 is shifted to the right as the concentration of F^- ions is reduced by protonation to form HF. Thus, the solution process can be understood in terms of two consecutive reactions:



The equation for the overall process is

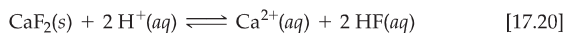
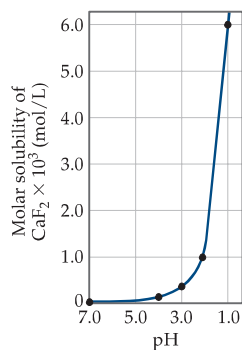


Figure 17.18 ◀ shows how the solubility of CaF_2 changes with pH.

Other salts that contain basic anions, such as CO_3^{2-} , PO_4^{3-} , CN^- , or S^{2-} , behave similarly. These examples illustrate a general rule: *The solubility of slightly soluble salts containing basic anions increases as $[\text{H}^+]$ increases (as pH is lowered).* The more basic the anion, the more the solubility is influenced by pH. Salts with anions of negligible basicity (the anions of strong acids) are unaffected by pH changes.



▲ **Figure 17.18 The effect of pH on the solubility of CaF_2 .** The solubility increases as the solution becomes more acidic (lower pH). Notice that the vertical scale has been multiplied by 10^3 .

SAMPLE EXERCISE 17.13 | Predicting the Effect of Acid on Solubility

Which of the following substances will be more soluble in acidic solution than in basic solution: (a) $\text{Ni}(\text{OH})_2(\text{s})$, (b) $\text{CaCO}_3(\text{s})$, (c) $\text{BaF}_2(\text{s})$, (d) $\text{AgCl}(\text{s})$?

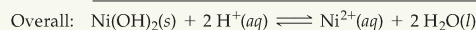
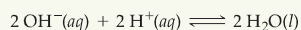
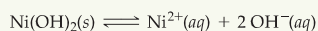
SOLUTION

Analyze: The problem lists four sparingly soluble salts, and we are asked to determine which will be more soluble at low pH than at high pH.

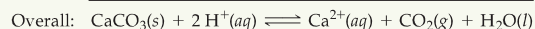
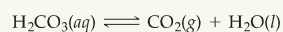
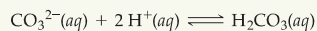
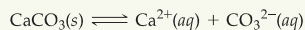
Plan: Ionic compounds that dissociate to produce a basic anion will be more soluble in acid solution.

Solve:

(a) $\text{Ni}(\text{OH})_2(\text{s})$ will be more soluble in acidic solution because of the basicity of OH^- ; the H^+ ion reacts with the OH^- ion, forming water.

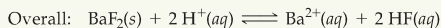
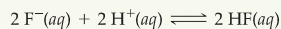
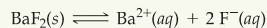


(b) Similarly, $\text{CaCO}_3(\text{s})$ dissolves in acid solutions because CO_3^{2-} is a basic anion.



The reaction between CO_3^{2-} and H^+ occurs in a stepwise fashion, first forming HCO_3^- . H_2CO_3 forms in appreciable amounts only when the concentration of H^+ is sufficiently high.

(c) The solubility of BaF_2 is also enhanced by lowering the pH, because F^- is a basic anion.



(d) The solubility of AgCl is unaffected by changes in pH because Cl^- is the anion of a strong acid and therefore has negligible basicity.

PRACTICE EXERCISE

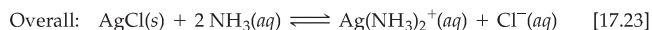
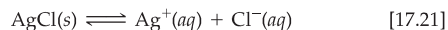
Write the net ionic equation for the reaction of the following copper(II) compounds with acid: (a) CuS , (b) $\text{Cu}(\text{N}_3)_2$.

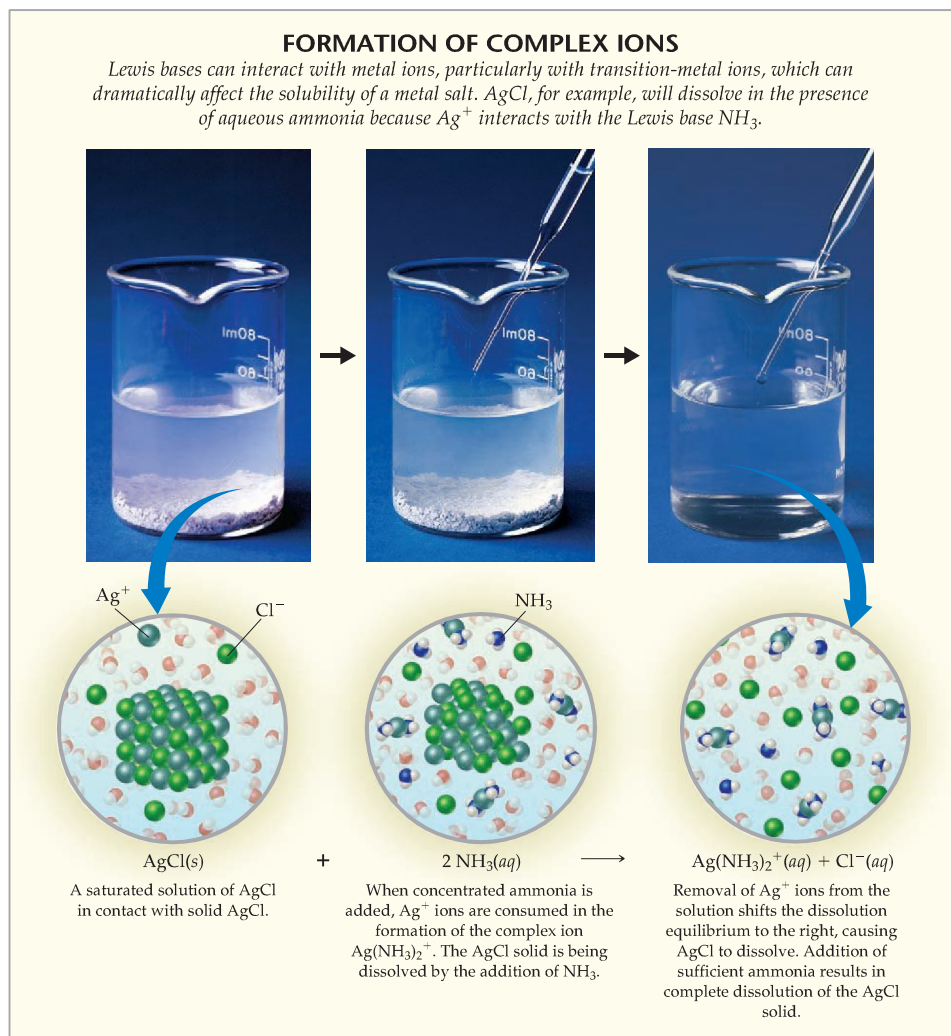
Answers: (a) $\text{CuS}(\text{s}) + \text{H}^+(\text{aq}) \rightleftharpoons \text{Cu}^{2+}(\text{aq}) + \text{HS}^-(\text{aq})$

(b) $\text{Cu}(\text{N}_3)_2(\text{s}) + 2 \text{H}^+(\text{aq}) \rightleftharpoons \text{Cu}^{2+}(\text{aq}) + 2 \text{HN}_3(\text{aq})$

Formation of Complex Ions

A characteristic property of metal ions is their ability to act as Lewis acids, or electron-pair acceptors, toward water molecules, which act as Lewis bases, or electron-pair donors. ∞ (Section 16.11) Lewis bases other than water can also interact with metal ions, particularly with transition-metal ions. Such interactions can dramatically affect the solubility of a metal salt. AgCl , for example, which has $K_{sp} = 1.8 \times 10^{-10}$, will dissolve in the presence of aqueous ammonia because Ag^+ interacts with the Lewis base NH_3 , as shown in Figure 17.19 \blacktriangledown . This process can be viewed as the sum of two reactions, the dissolution of AgCl and the Lewis acid–base interaction between Ag^+ and NH_3 .

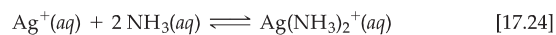




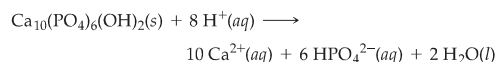
▲ Figure 17.19 Using NH₃(aq) to dissolve AgCl(s).

The presence of NH₃ drives the reaction, the dissolution of AgCl, to the right as Ag⁺(aq) is consumed to form Ag(NH₃)₂⁺.

For a Lewis base such as NH₃ to increase the solubility of a metal salt, it must be able to interact more strongly with the metal ion than water does. The NH₃ must displace solvating H₂O molecules (Sections 13.1 and 16.11) in order to form Ag(NH₃)₂⁺:



Tooth enamel consists mainly of a mineral called hydroxyapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$. It is the hardest substance in the body. Tooth cavities are caused when acids dissolve tooth enamel.

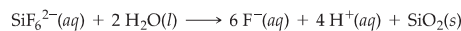


The resultant Ca^{2+} and HPO_4^{2-} ions diffuse out of the tooth enamel and are washed away by saliva. The acids that attack the hydroxyapatite are formed by the action of specific bacteria on sugars and other carbohydrates present in the plaque adhering to the teeth.

Fluoride ion, present in drinking water, toothpaste, and other sources, can react with hydroxyapatite to form fluorapatite, $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$. This mineral, in which F^- has replaced

OH^- , is much more resistant to attack by acids because the fluoride ion is a much weaker Brønsted–Lowry base than the hydroxide ion.

Because the fluoride ion is so effective in preventing cavities, it is added to the public water supply in many places to give a concentration of 1 mg/L (1 ppm). The compound added may be NaF or Na_2SiF_6 . Na_2SiF_6 reacts with water to release fluoride ions by the following reaction:



About 80% of all toothpastes now sold in the United States contain fluoride compounds, usually at the level of 0.1% fluoride by mass. The most common compounds in toothpastes are sodium fluoride (NaF), sodium monofluorophosphate ($\text{Na}_2\text{PO}_3\text{F}$), and stannous fluoride (SnF_2).

Related Exercise: 17.110

An assembly of a metal ion and the Lewis bases bonded to it, such as $\text{Ag}(\text{NH}_3)_2^+$, is called a **complex ion**. The stability of a complex ion in aqueous solution can be judged by the size of the equilibrium constant for its formation from the hydrated metal ion. For example, the equilibrium constant for formation of $\text{Ag}(\text{NH}_3)_2^+$ (Equation 17.24) is 1.7×10^7 :

$$K_f = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}^+][\text{NH}_3]^2} = 1.7 \times 10^7 \quad [17.25]$$

The equilibrium constant for this kind of reaction is called a **formation constant**, K_f . The formation constants for several complex ions are listed in Table 17.1 ▼.

TABLE 17.1 ■ Formation Constants for Some Metal Complex Ions in Water at 25 °C

Complex Ion	K_f	Equilibrium Equation
$\text{Ag}(\text{NH}_3)_2^+$	1.7×10^7	$\text{Ag}^+(aq) + 2 \text{NH}_3(aq) \rightleftharpoons \text{Ag}(\text{NH}_3)_2^+(aq)$
$\text{Ag}(\text{CN})_2^-$	1×10^{21}	$\text{Ag}^+(aq) + 2 \text{CN}^-(aq) \rightleftharpoons \text{Ag}(\text{CN})_2^-(aq)$
$\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$	2.9×10^{13}	$\text{Ag}^+(aq) + 2 \text{S}_2\text{O}_3^{2-}(aq) \rightleftharpoons \text{Ag}(\text{S}_2\text{O}_3)_2^{3-}(aq)$
CdBr_4^{2-}	5×10^3	$\text{Cd}^{2+}(aq) + 4 \text{Br}^-(aq) \rightleftharpoons \text{CdBr}_4^{2-}(aq)$
$\text{Cr}(\text{OH})_4^-$	8×10^{29}	$\text{Cr}^{3+}(aq) + 4 \text{OH}^-(aq) \rightleftharpoons \text{Cr}(\text{OH})_4^-(aq)$
$\text{Co}(\text{SCN})_4^{2-}$	1×10^3	$\text{Co}^{2+}(aq) + 4 \text{SCN}^-(aq) \rightleftharpoons \text{Co}(\text{SCN})_4^{2-}(aq)$
$\text{Cu}(\text{NH}_3)_4^{2+}$	5×10^{12}	$\text{Cu}^{2+}(aq) + 4 \text{NH}_3(aq) \rightleftharpoons \text{Cu}(\text{NH}_3)_4^{2+}(aq)$
$\text{Cu}(\text{CN})_4^{2-}$	1×10^{25}	$\text{Cu}^{2+}(aq) + 4 \text{CN}^-(aq) \rightleftharpoons \text{Cu}(\text{CN})_4^{2-}(aq)$
$\text{Ni}(\text{NH}_3)_6^{2+}$	1.2×10^9	$\text{Ni}^{2+}(aq) + 6 \text{NH}_3(aq) \rightleftharpoons \text{Ni}(\text{NH}_3)_6^{2+}(aq)$
$\text{Fe}(\text{CN})_6^{4-}$	1×10^{35}	$\text{Fe}^{2+}(aq) + 6 \text{CN}^-(aq) \rightleftharpoons \text{Fe}(\text{CN})_6^{4-}(aq)$
$\text{Fe}(\text{CN})_6^{3-}$	1×10^{42}	$\text{Fe}^{3+}(aq) + 6 \text{CN}^-(aq) \rightleftharpoons \text{Fe}(\text{CN})_6^{3-}(aq)$

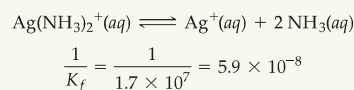
SAMPLE EXERCISE 17.14 | Evaluating an Equilibrium Involving a Complex Ion

Calculate the concentration of Ag^+ present in solution at equilibrium when concentrated ammonia is added to a 0.010 M solution of AgNO_3 to give an equilibrium concentration of $[\text{NH}_3] = 0.20\text{ M}$. Neglect the small volume change that occurs when NH_3 is added.

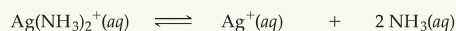
SOLUTION

Analyze: When $\text{NH}_3(aq)$ is added to $\text{Ag}^+(aq)$, a reaction occurs forming $\text{Ag}(\text{NH}_3)_2^+$ as shown in Equation 17.22. We are asked to determine what concentration of $\text{Ag}^+(aq)$ will remain uncombined when the NH_3 concentration is brought to 0.20 M in a solution originally 0.010 M in AgNO_3 .

Plan: We first assume that the AgNO_3 is completely dissociated, giving 0.010 M Ag^+ . Because K_f for the formation of $\text{Ag}(\text{NH}_3)_2^+$ is quite large, we assume that essentially all the Ag^+ is then converted to $\text{Ag}(\text{NH}_3)_2^+$ and approach the problem as though we are concerned with the *dissociation* of $\text{Ag}(\text{NH}_3)_2^+$ rather than its *formation*. To facilitate this approach, we will need to reverse the equation to represent the formation of Ag^+ and NH_3 from $\text{Ag}(\text{NH}_3)_2^+$ and also make the corresponding change to the equilibrium constant.



Solve: If $[\text{Ag}^+]$ is 0.010 M initially, then $[\text{Ag}(\text{NH}_3)_2^+]$ will be 0.010 M following addition of the NH_3 . We now construct a table to solve this equilibrium problem. Note that the NH_3 concentration given in the problem is an *equilibrium* concentration rather than an initial concentration.



Initial	0.010 M	0 M	
Change	$-x\text{ M}$	$+x\text{ M}$	
Equilibrium	$0.010 - x\text{ M}$	$x\text{ M}$	0.20 M

Because the concentration of Ag^+ is very small, we can ignore x in comparison with 0.010 . Thus, $0.010 - x \approx 0.010\text{ M}$. Substituting these values into the equilibrium-constant expression for the dissociation of $\text{Ag}(\text{NH}_3)_2^+$, we obtain

$$\frac{[\text{Ag}^+][\text{NH}_3]^2}{[\text{Ag}(\text{NH}_3)_2^+]} = \frac{(x)(0.20)^2}{0.010} = 5.9 \times 10^{-8}$$

Solving for x , we obtain $x = 1.5 \times 10^{-8}\text{ M} = [\text{Ag}^+]$. Thus, formation of the $\text{Ag}(\text{NH}_3)_2^+$ complex drastically reduces the concentration of free Ag^+ ion in solution.

PRACTICE EXERCISE

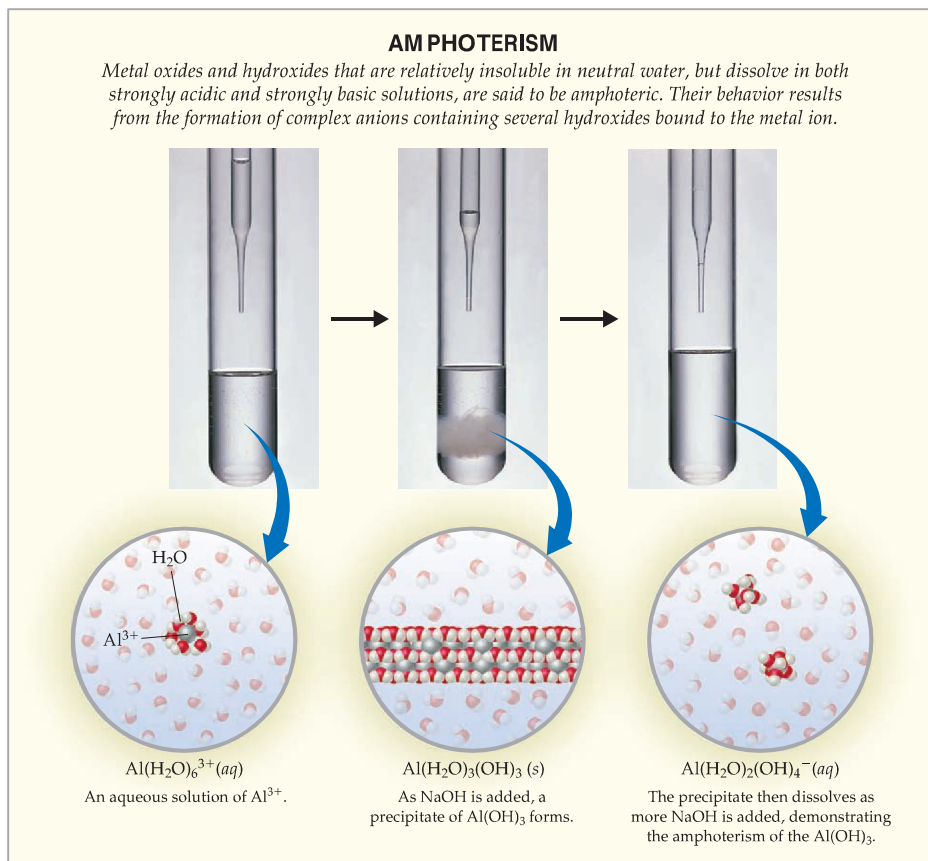
Calculate $[\text{Cr}^{3+}]$ in equilibrium with $\text{Cr}(\text{OH})_4^-$ when 0.010 mol of $\text{Cr}(\text{NO}_3)_3$ is dissolved in a liter of solution buffered at $\text{pH } 10.0$.

Answer: $1 \times 10^{-16}\text{ M}$

The general rule is that the solubility of metal salts increases in the presence of suitable Lewis bases, such as NH_3 , CN^- , or OH^- , if the metal forms a complex with the base. The ability of metal ions to form complexes is an extremely important aspect of their chemistry. In Chapter 24 we will take a much closer look at complex ions. In that chapter and others we will see applications of complex ions to areas such as biochemistry, metallurgy, and photography.

Amphoterism

Some metal oxides and hydroxides that are relatively insoluble in neutral water dissolve in strongly acidic and strongly basic solutions. These substances are soluble in strong acids and bases because they themselves are capable of behaving as either an acid or base; they are **amphoteric oxides and hydroxides**.



▲ Figure 17.20 Amphotericism.

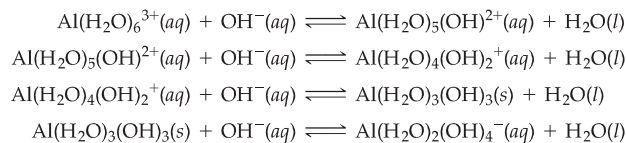
Amphoteric oxides and hydroxides include those of Al^{3+} , Cr^{3+} , Zn^{2+} , and Sn^{2+} . Notice that the term *amphoteric* is applied to the behavior of insoluble oxides and hydroxides that can be made to dissolve in either acidic or basic solutions. The similar term *amphiprotic*, which we encountered in Section 16.2, relates more generally to any molecule or ion that can either gain or lose a proton.

Amphoteric species dissolve in acidic solutions because they contain basic anions. What makes amphoteric oxides and hydroxides special, though, is that they also dissolve in strongly basic solutions (Figure 17.20 ▲). This behavior results from the formation of complex anions containing several (typically four) hydroxides bound to the metal ion.



Amphotericism is often explained by the behavior of the water molecules that surround the metal ion and that are bonded to it by Lewis acid–base interactions. ∞ (Section 16.11) For example, $\text{Al}^{3+}(\text{aq})$ is more accurately represented as $\text{Al}(\text{H}_2\text{O})_6^{3+}(\text{aq})$ because six water molecules are bonded to the Al^{3+} in aqueous solution. Recall from Section 16.11 that this hydrated ion is a weak acid.

As a strong base is added, $\text{Al}(\text{H}_2\text{O})_6^{3+}$ loses protons in a stepwise fashion, eventually forming neutral and water-insoluble $\text{Al}(\text{H}_2\text{O})_3(\text{OH})_3$. This substance then dissolves upon removal of an additional proton to form the anion $\text{Al}(\text{H}_2\text{O})_2(\text{OH})_4^-$. The reactions that occur are as follows:



Removing additional protons is possible, but each successive reaction occurs less readily than the one before. As the charge on the ion becomes more negative, it becomes increasingly difficult to remove a positively charged proton. Addition of an acid reverses these reactions. The proton adds in a stepwise fashion to convert the OH^- groups to H_2O , eventually re-forming $\text{Al}(\text{H}_2\text{O})_6^{3+}$. The common practice is to simplify the equations for these reactions by excluding the bound H_2O molecules. Thus, we usually write Al^{3+} instead of $\text{Al}(\text{H}_2\text{O})_6^{3+}$, $\text{Al}(\text{OH})_3$ instead of $\text{Al}(\text{H}_2\text{O})_3(\text{OH})_3$, $\text{Al}(\text{OH})_4^-$ instead of $\text{Al}(\text{H}_2\text{O})_2(\text{OH})_4^-$, and so forth.

The extent to which an insoluble metal hydroxide reacts with either acid or base varies with the particular metal ion involved. Many metal hydroxides—such as $\text{Ca}(\text{OH})_2$, $\text{Fe}(\text{OH})_2$, and $\text{Fe}(\text{OH})_3$ —are capable of dissolving in acidic solution but do not react with excess base. These hydroxides are not amphoteric.

The purification of aluminum ore in the manufacture of aluminum metal provides an interesting application of the property of amphoterism. As we have seen, $\text{Al}(\text{OH})_3$ is amphoteric, whereas $\text{Fe}(\text{OH})_3$ is not. Aluminum occurs in large quantities as the ore *bauxite*, which is essentially Al_2O_3 with additional water molecules. The ore is contaminated with Fe_2O_3 as an impurity. When bauxite is added to a strongly basic solution, the Al_2O_3 dissolves because the aluminum forms complex ions, such as $\text{Al}(\text{OH})_4^-$. The Fe_2O_3 impurity, however, is not amphoteric and remains as a solid. The solution is filtered, getting rid of the iron impurity. Aluminum hydroxide is then precipitated by addition of acid. The purified hydroxide receives further treatment and eventually yields aluminum metal. [∞ \(Section 23.3\)](#)



GIVE IT SOME THOUGHT

What kind of behavior characterizes an amphoteric oxide or an amphoteric hydroxide?

17.6 PRECIPITATION AND SEPARATION OF IONS

Equilibrium can be achieved starting with the substances on either side of a chemical equation. The equilibrium among $\text{BaSO}_4(\text{s})$, $\text{Ba}^{2+}(\text{aq})$, and $\text{SO}_4^{2-}(\text{aq})$ (Equation 17.15) can be achieved starting with solid BaSO_4 . It can also be reached starting with solutions of salts containing Ba^{2+} and SO_4^{2-} , say BaCl_2 and Na_2SO_4 . When these two solutions are mixed, BaSO_4 will precipitate if the product of the initial ion concentrations, $Q = [\text{Ba}^{2+}][\text{SO}_4^{2-}]$, is greater than K_{sp} .

The use of the reaction quotient, Q , to determine the direction in which a reaction must proceed to reach equilibrium was discussed earlier. [∞ \(Section 15.6\)](#) The possible relationships between Q and K_{sp} are summarized as follows:

- If $Q > K_{sp}$, precipitation occurs until $Q = K_{sp}$.
- If $Q = K_{sp}$, equilibrium exists (saturated solution).
- If $Q < K_{sp}$, solid dissolves until $Q = K_{sp}$.

SAMPLE EXERCISE 17.15 | Predicting Whether a Precipitate Will Form

Will a precipitate form when 0.10 L of $8.0 \times 10^{-3} M$ $\text{Pb}(\text{NO}_3)_2$ is added to 0.40 L of $5.0 \times 10^{-3} M$ Na_2SO_4 ?

SOLUTION

Analyze: The problem asks us to determine whether a precipitate will form when two salt solutions are combined.

Plan: We should determine the concentrations of all ions immediately upon mixing of the solutions and compare the value of the reaction quotient, Q , to the solubility-product constant, K_{sp} , for any potentially insoluble product. The possible metathesis products are PbSO_4 and NaNO_3 . Sodium salts are quite soluble; PbSO_4 has a K_{sp} of 6.3×10^{-7} (Appendix D), however, and will precipitate if the Pb^{2+} and SO_4^{2-} ion concentrations are high enough for Q to exceed K_{sp} for the salt.

Solve: When the two solutions are mixed, the total volume becomes 0.10 L + 0.40 L = 0.50 L. The number of moles of Pb^{2+} in 0.10 L of $8.0 \times 10^{-3} M$ $\text{Pb}(\text{NO}_3)_2$ is

$$(0.10 \text{ L}) \left(8.0 \times 10^{-3} \frac{\text{mol}}{\text{L}} \right) = 8.0 \times 10^{-4} \text{ mol}$$

The concentration of Pb^{2+} in the 0.50-L mixture is therefore

$$[\text{Pb}^{2+}] = \frac{8.0 \times 10^{-4} \text{ mol}}{0.50 \text{ L}} = 1.6 \times 10^{-3} M$$

The number of moles of SO_4^{2-} in 0.40 L of $5.0 \times 10^{-3} M$ Na_2SO_4 is

$$(0.40 \text{ L}) \left(5.0 \times 10^{-3} \frac{\text{mol}}{\text{L}} \right) = 2.0 \times 10^{-3} \text{ mol}$$

Therefore, $[\text{SO}_4^{2-}]$ in the 0.50-L mixture is

$$[\text{SO}_4^{2-}] = \frac{2.0 \times 10^{-3} \text{ mol}}{0.50 \text{ L}} = 4.0 \times 10^{-3} M$$

We then have

$$Q = [\text{Pb}^{2+}][\text{SO}_4^{2-}] = (1.6 \times 10^{-3})(4.0 \times 10^{-3}) = 6.4 \times 10^{-6}$$

Because $Q > K_{sp}$, PbSO_4 will precipitate.

PRACTICE EXERCISE

Will a precipitate form when 0.050 L of $2.0 \times 10^{-2} M$ NaF is mixed with 0.010 L of $1.0 \times 10^{-2} M$ $\text{Ca}(\text{NO}_3)_2$?

Answer: Yes, CaF_2 precipitates because $Q = 4.6 \times 10^{-8}$ is larger than $K_{sp} = 3.9 \times 10^{-11}$

Selective Precipitation of Ions

Ions can be separated from each other based on the solubilities of their salts. Consider a solution containing both Ag^+ and Cu^{2+} . If HCl is added to the solution, AgCl ($K_{sp} = 1.8 \times 10^{-10}$) precipitates, while Cu^{2+} remains in solution because CuCl_2 is soluble. Separation of ions in an aqueous solution by using a reagent that forms a precipitate with one or a few of the ions is called *selective precipitation*.

SAMPLE EXERCISE 17.16 | Calculating Ion Concentrations for Precipitation

A solution contains $1.0 \times 10^{-2} M$ Ag^+ and $2.0 \times 10^{-2} M$ Pb^{2+} . When Cl^- is added to the solution, both AgCl ($K_{sp} = 1.8 \times 10^{-10}$) and PbCl_2 ($K_{sp} = 1.7 \times 10^{-9}$) precipitate from the solution. What concentration of Cl^- is necessary to begin the precipitation of each salt? Which salt precipitates first?

SOLUTION

Analyze: We are asked to determine the concentration of Cl^- necessary to begin the precipitation from a solution containing Ag^+ and Pb^{2+} ions, and to predict which metal chloride will begin to precipitate first.

Plan: We are given K_{sp} values for the two possible precipitates. Using these and the metal ion concentrations, we can calculate what concentration of Cl^- ion would be necessary to begin precipitation of each. The salt requiring the lower Cl^- ion concentration will precipitate first.

Solve: For AgCl we have

$$K_{sp} = [\text{Ag}^+][\text{Cl}^-] = 1.8 \times 10^{-10}$$

Because $[\text{Ag}^+] = 1.0 \times 10^{-2} M$, the greatest concentration of Cl^- that can be present without causing precipitation of AgCl can be calculated from the K_{sp} expression:

$$K_{sp} = [1.0 \times 10^{-2}][\text{Cl}^-] = 1.8 \times 10^{-10}$$

$$[\text{Cl}^-] = \frac{1.8 \times 10^{-10}}{1.0 \times 10^{-2}} = 1.8 \times 10^{-8} M$$

Any Cl^- in excess of this very small concentration will cause AgCl to precipitate from solution. Proceeding similarly for PbCl_2 , we have

$$\begin{aligned}K_{sp} &= [\text{Pb}^{2+}][\text{Cl}^-]^2 = 1.7 \times 10^{-5} \\[2.0 \times 10^{-2}][\text{Cl}^-]^2 &= 1.7 \times 10^{-5} \\[\text{Cl}^-]^2 &= \frac{1.7 \times 10^{-5}}{2.0 \times 10^{-2}} = 8.5 \times 10^{-4} \\[\text{Cl}^-] &= \sqrt{8.5 \times 10^{-4}} = 2.9 \times 10^{-2} \text{ M}\end{aligned}$$

Thus, a concentration of Cl^- in excess of $2.9 \times 10^{-2} \text{ M}$ will cause PbCl_2 to precipitate.

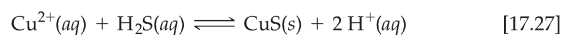
Comparing the concentrations of Cl^- required to precipitate each salt, we see that as Cl^- is added to the solution, AgCl will precipitate first because it requires a much smaller concentration of Cl^- . Thus, Ag^+ can be separated from Pb^{2+} by slowly adding Cl^- so $[\text{Cl}^-]$ is between $1.8 \times 10^{-8} \text{ M}$ and $2.9 \times 10^{-2} \text{ M}$.

PRACTICE EXERCISE

A solution consists of 0.050 M Mg^{2+} and 0.020 M Cu^{2+} . Which ion will precipitate first as OH^- is added to the solution? What concentration of OH^- is necessary to begin the precipitation of each cation? [$K_{sp} = 1.8 \times 10^{-11}$ for $\text{Mg}(\text{OH})_2$, and $K_{sp} = 4.8 \times 10^{-20}$ for $\text{Cu}(\text{OH})_2$.]

Answer: $\text{Cu}(\text{OH})_2$ precipitates first. $\text{Cu}(\text{OH})_2$ begins to precipitate when $[\text{OH}^-]$ exceeds $1.5 \times 10^{-9} \text{ M}$; $\text{Mg}(\text{OH})_2$ begins to precipitate when $[\text{OH}^-]$ exceeds $1.9 \times 10^{-5} \text{ M}$.

Sulfide ion is often used to separate metal ions because the solubilities of sulfide salts span a wide range and depend greatly on the pH of the solution. Cu^{2+} and Zn^{2+} , for example, can be separated by bubbling H_2S gas through an acidified solution. Because CuS ($K_{sp} = 6 \times 10^{-37}$) is less soluble than ZnS ($K_{sp} = 2 \times 10^{-25}$), CuS precipitates from an acidified solution ($\text{pH} = 1$) while ZnS does not (Figure 17.21 ▼):



SELECTIVE PRECIPITATION OF IONS

Separation of ions in an aqueous solution by using a reagent that forms a precipitate with one or a few of the ions is called selective precipitation.

Add H_2S Remove CuS and increase pH

Cu^{2+}
 Zn^{2+}
 H^+

S^{2-}

Solution containing $\text{Zn}^{2+}(\text{aq})$ and $\text{Cu}^{2+}(\text{aq})$.
 When H_2S is added to a solution whose pH exceeds 0.6, CuS precipitates.
 After CuS is removed, the pH is increased allowing ZnS to precipitate.

▲ Figure 17.21 Selective precipitation.

The CuS can be separated from the Zn^{2+} solution by filtration. The CuS can then be dissolved by using a high concentration of H^+ , shifting the equilibrium shown in Equation 17.27 to the left.

GIVE IT SOME THOUGHT

What experimental conditions will leave the smallest concentration of Cu^{2+} ions in solution according to Equation 17.27?

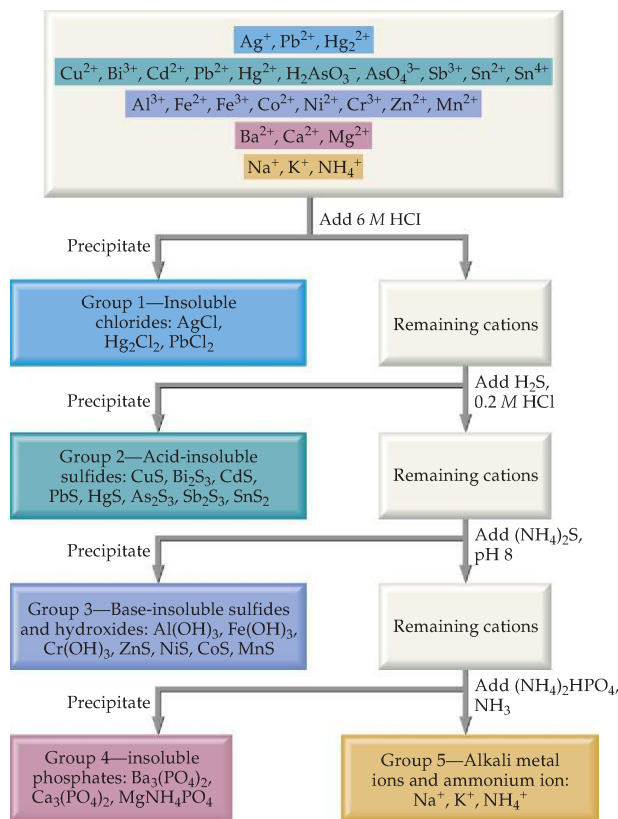
17.7 QUALITATIVE ANALYSIS FOR METALLIC ELEMENTS

In this chapter we have seen several examples of equilibria involving metal ions in aqueous solution. In this final section we look briefly at how solubility equilibria and complex-ion formation can be used to detect the presence of particular metal ions in solution. Before the development of modern analytical instrumentation, it was necessary to analyze mixtures of metals in a sample by so-called wet chemical methods. For example, a metallic sample that might contain several metallic elements was dissolved in a concentrated acid solution. This solution was then tested in a systematic way for the presence of various metal ions.

Qualitative analysis determines only the presence or absence of a particular metal ion, whereas **quantitative analysis** determines how much of a given substance is present. Wet methods of qualitative analysis have become less important as a means of analysis. They are frequently used in general chemistry laboratory programs, however, to illustrate equilibria, to teach the properties of common metal ions in solution, and to develop laboratory skills. Typically, such analyses proceed in three stages: (1) The ions are separated into broad groups on the basis of solubility properties. (2) The individual ions within each group are then separated by selectively dissolving members in the group. (3) The ions are then identified by means of specific tests.

A scheme in general use divides the common cations into five groups, as shown in Figure 17.22. The order of addition of reagents is important. The most selective separations—those that involve the smallest number of ions—are carried out first. The reactions that are used must proceed so far toward completion that any concentration of cations remaining in the solution is too small to interfere with subsequent tests. Let's take a closer look at each of these five groups of cations, briefly examining the logic used in this qualitative analysis scheme.

- Insoluble chlorides:** Of the common metal ions, only Ag^+ , Hg_2^{2+} , and Pb^{2+} form insoluble chlorides. When dilute HCl is added to a mixture of cations, therefore, only AgCl , Hg_2Cl_2 , and PbCl_2 will precipitate, leaving the other cations in solution. The absence of a precipitate indicates that the starting solution contains no Ag^+ , Hg_2^{2+} , or Pb^{2+} .



▲ **Figure 17.22 Qualitative analysis.** A flowchart showing the separation of cations into groups as a part of a common scheme for identifying cations.

- 2. Acid-insoluble sulfides:** After any insoluble chlorides have been removed, the remaining solution, now acidic, is treated with H_2S . Only the most insoluble metal sulfides— CuS , Bi_2S_3 , CdS , PbS , HgS , As_2S_3 , Sb_2S_3 , and SnS_2 —can precipitate. (Note the very small values of K_{sp} for some of these sulfides in Appendix D.) Those metal ions whose sulfides are somewhat more soluble—for example, ZnS or NiS —remain in solution.
- 3. Base-insoluble sulfides and hydroxides:** After the solution is filtered to remove any acid-insoluble sulfides, the remaining solution is made slightly basic, and $(\text{NH}_4)_2\text{S}$ is added. In basic solutions the concentration of S^{2-} is higher than in acidic solutions. Thus, the ion products for many of the more soluble sulfides are made to exceed their K_{sp} values and precipitation occurs. The metal ions precipitated at this stage are Al^{3+} , Cr^{3+} , Fe^{3+} , Zn^{2+} , Ni^{2+} , Co^{2+} , and Mn^{2+} . (Actually, the Al^{3+} , Fe^{3+} , and Cr^{3+} ions do not form insoluble sulfides; instead they are precipitated as insoluble hydroxides at the same time.)
- 4. Insoluble phosphates:** At this point the solution contains only metal ions from periodic table groups 1A and 2A. Adding $(\text{NH}_4)_2\text{HPO}_4$ to a basic solution precipitates the group 2A elements Mg^{2+} , Ca^{2+} , Sr^{2+} , and Ba^{2+} because these metals form insoluble phosphates.
- 5. The alkali metal ions and NH_4^+ :** The ions that remain after removing the insoluble phosphates form a small group. We can test the original solution for each ion individually. A flame test can be used to determine the presence of K^+ , for example, because the flame turns a characteristic violet color if K^+ is present.

GIVE IT SOME THOUGHT

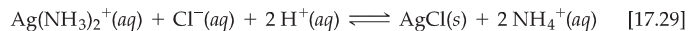
If a precipitate forms upon addition of HCl to an aqueous solution, what conclusions can you draw about the contents of the solution?

Additional separation and testing is necessary to determine which ions are present within each of the groups. Consider, for example, the ions of the insoluble chloride group. The precipitate containing the metal chlorides is boiled in water. The PbCl_2 is relatively soluble in hot water, whereas AgCl and Hg_2Cl_2 are not. The hot solution is filtered, and a solution of Na_2CrO_4 is added to the filtrate. If Pb^{2+} is present, a yellow precipitate of PbCrO_4 forms. The test for Ag^+ consists of treating the metal chloride precipitate with dilute ammonia.

Only Ag^+ forms an ammonia complex. If AgCl is present in the precipitate, it will dissolve in the ammonia solution.



After treatment with ammonia, the solution is filtered and the filtrate made acidic by adding nitric acid. The nitric acid removes ammonia from solution by forming NH_4^+ , thus releasing Ag^+ , which re-forms the AgCl precipitate.



The analyses for individual ions in the acid-insoluble and base-insoluble sulfides are a bit more complex, but the same general principles are involved. The detailed procedures for carrying out such analyses are given in many laboratory manuals.

SAMPLE INTEGRATIVE EXERCISE | Putting Concepts Together

A sample of 1.25 L of HCl gas at 21 °C and 0.950 atm is bubbled through 0.500 L of 0.150 M NH₃ solution. Calculate the pH of the resulting solution assuming that all the HCl dissolves and that the volume of the solution remains 0.500 L.

SOLUTION

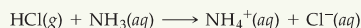
The number of moles of HCl gas is calculated from the ideal-gas law.

$$n = \frac{PV}{RT} = \frac{(0.950 \text{ atm})(1.25 \text{ L})}{(0.0821 \text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K})(294 \text{ K})} = 0.0492 \text{ mol HCl}$$

The number of moles of NH₃ in the solution is given by the product of the volume of the solution and its concentration.

$$\text{Moles NH}_3 = (0.500 \text{ L})(0.150 \text{ mol NH}_3/\text{L}) = 0.0750 \text{ mol NH}_3$$

The acid HCl and base NH₃ react, transferring a proton from HCl to NH₃, producing NH₄⁺ and Cl⁻ ions.



To determine the pH of the solution, we first calculate the amount of each reactant and each product present at the completion of the reaction.



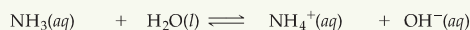
Before addition	0.0492 mol	0 mol	0 mol	0 mol
Addition		0.0750 mol		
After addition	0 mol	0.0258 mol	0.0492 mol	0.0492 mol

Thus, the reaction produces a solution containing a mixture of NH₃, NH₄⁺, and Cl⁻. The NH₃ is a weak base ($K_b = 1.8 \times 10^{-5}$), NH₄⁺ is its conjugate acid, and Cl⁻ is neither acidic nor basic. Consequently, the pH depends on [NH₃] and [NH₄⁺].

$$[\text{NH}_3] = \frac{0.0258 \text{ mol NH}_3}{0.500 \text{ L soln}} = 0.0516 \text{ M}$$

$$[\text{NH}_4^+] = \frac{0.0492 \text{ mol NH}_4^+}{0.500 \text{ L soln}} = 0.0984 \text{ M}$$

We can calculate the pH using either K_b for NH₃ or K_a for NH₄⁺. Using the K_b expression, we have



Initial	0.0516 M	—	0.0984 M	0
Change	-x M	—	+x M	+x M
Equilibrium	(0.0516 - x) M	—	(0.0984 + x) M	x M

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{(0.0984 + x)(x)}{(0.0516 - x)} \approx \frac{(0.0984)x}{0.0516} = 1.8 \times 10^{-5}$$

$$x = [\text{OH}^-] = \frac{(0.0516)(1.8 \times 10^{-5})}{0.0984} = 9.4 \times 10^{-6} \text{ M}$$

Hence, pOH = $-\log(9.4 \times 10^{-6}) = 5.03$ and pH = 14.00 - pOH = 14.00 - 5.03 = 8.97.

CHAPTER REVIEW

SUMMARY AND KEY TERMS

Section 17.1 In this chapter we have considered several types of important equilibria that occur in aqueous solution. Our primary emphasis has been on acid–base equilibria in solutions containing two or more solutes and on solubility equilibria. The dissociation of a weak acid or weak base is repressed by the presence of a strong electrolyte that provides an ion common to the equilibrium. This phenomenon is called the **common-ion effect**.

Section 17.2 A particularly important type of acid–base mixture is that of a weak conjugate acid–base pair. Such mixtures function as **buffered solutions (buffers)**. Addition of small amounts of a strong acid or a strong base to a buffered solution causes only small changes in pH because the buffer reacts with the added acid or base. (Strong acid–strong base, strong acid–weak base, and weak acid–strong base reactions proceed essentially to completion.) Buffered solutions are usually prepared from a weak acid and a salt of that acid or from a weak base and a salt of that base. Two important characteristics of a buffered solution are its **buffer capacity** and its pH. The pH can be calculated using K_a or K_b . The relationship between pH, pK_a , and the concentrations of an acid and its conjugate base can be expressed by the **Henderson–Hasselbalch**

$$\text{equation: } \text{pH} = \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]}$$

Section 17.3 The plot of the pH of an acid (or base) as a function of the volume of added base (or acid) is called a **pH titration curve**. Titration curves aid in selecting a proper pH indicator for an acid–base titration. The titration curve of a strong acid–strong base titration exhibits a large change in pH in the immediate vicinity of the equivalence point; at the equivalence point for this titration, $\text{pH} = 7$. For strong acid–weak base or weak acid–strong base titrations, the pH change in the vicinity of the equivalence point is not as large. Furthermore, the pH at the equivalence point is not 7 in either of these cases. Rather, it is the pH of the salt solution that results from the neutralization reaction. It is possible to calculate the pH at any point of the titration curve by first considering the effects of the reaction between the acid and base on solution concentrations and then examining equilibria involving remaining solute species.

Section 17.4 The equilibrium between a solid compound and its ions in solution provides an example of heterogeneous equilibrium. The **solubility-product**

constant (or simply the **solubility product**), K_{sp} , is an equilibrium constant that expresses quantitatively the extent to which the compound dissolves. The K_{sp} can be used to calculate the solubility of an ionic compound, and the solubility can be used to calculate K_{sp} .

Section 17.5 Several experimental factors, including temperature, affect the solubilities of ionic compounds in water. The solubility of a slightly soluble ionic compound is decreased by the presence of a second solute that furnishes a common ion (the common-ion effect). The solubility of compounds containing basic anions increases as the solution is made more acidic (as pH decreases). Salts with anions of negligible basicity (the anions of strong acids) are unaffected by pH changes.

The solubility of metal salts is also affected by the presence of certain Lewis bases that react with metal ions to form stable **complex ions**. Complex-ion formation in aqueous solution involves the displacement by Lewis bases (such as NH_3 and CN^-) of water molecules attached to the metal ion. The extent to which such complex formation occurs is expressed quantitatively by the **formation constant** for the complex ion. **Amphoteric oxides and hydroxides** are those that are only slightly soluble in water but dissolve on addition of either acid or base. Acid–base reactions involving the OH^- or H_2O groups bound to the metal ions give rise to the amphoterism.

Section 17.6 Comparison of the ion product, Q , with the value of K_{sp} can be used to judge whether a precipitate will form when solutions are mixed or whether a slightly soluble salt will dissolve under various conditions. Precipitates form when $Q > K_{sp}$. Ions can be separated from each other based on the solubilities of their salts.

Section 17.7 Metallic elements vary a great deal in the solubilities of their salts, in their acid–base behavior, and in their tendencies to form complex ions. These differences can be used to separate and detect the presence of metal ions in mixtures. **Qualitative analysis** determines the presence or absence of species in a sample, whereas **quantitative analysis** determines how much of each species is present. The qualitative analysis of metal ions in solution can be carried out by separating the ions into groups on the basis of precipitation reactions and then analyzing each group for individual metal ions.

KEY SKILLS

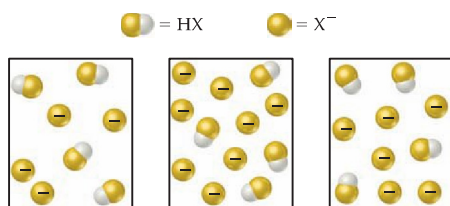
- Describe the common-ion effect.
- Explain how a buffer functions.
- Calculate the pH of a buffer solution.
- Calculate the pH of a buffer after the addition of small amounts of a strong acid or a strong base.
- Calculate the pH at any point in an acid–base titration of a strong acid and strong base.
- Calculate the pH at any point in a titration of a weak acid with a strong base or a weak base with a strong acid.
- Understand the differences between the titration curves for a strong acid–strong base titration and those when either the acid or base is weak.
- Calculate K_{sp} from molar solubility and molar solubility from K_{sp} .
- Calculate molar solubility in the presence of a common ion.
- Predict the effect of pH on solubility.
- Predict whether a precipitate will form when solutions are mixed by comparing Q and K_{sp} .
- Calculate the ion concentrations required to begin precipitation.
- Explain the effect of complex-ion formation on solubility.

KEY EQUATIONS

- $\text{pH} = \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]}$ [17.9] The Henderson–Hasselbalch equation, used to calculate the pH of a buffer from the concentrations of a conjugate acid–base pair

VISUALIZING CONCEPTS

17.1 The following boxes represent aqueous solutions containing a weak acid, HX, and its conjugate base, X^- . Water molecules and cations are not shown. Which solution has the highest pH? Explain. [Section 17.1]



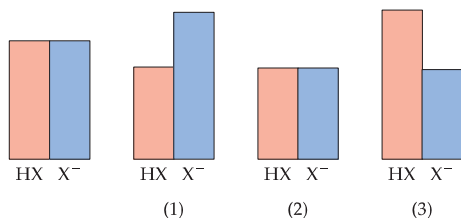
17.2 The beaker on the right contains 0.1 M acetic acid solution with methyl orange as an indicator. The beaker on the left contains a mixture of 0.1 M acetic acid and 0.1 M sodium acetate with methyl orange. (a) Using Figure

16.7, estimate the pH of each solution, and explain the difference. (b) Which solution is better able to maintain its pH when small amounts of NaOH are added? Explain. [Sections 17.1 and 17.2]

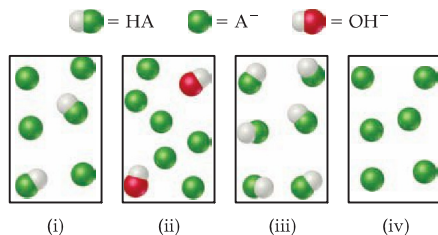


17.3 A buffer contains a weak acid, HX, and its conjugate base. The weak acid has a pK_a of 4.5, and the buffer solution has a pH of 4.3. Without doing a calculation, predict whether $[HX] = [X^-]$, $[HX] > [X^-]$, or $[HX] < [X^-]$. Explain. [Section 17.2]

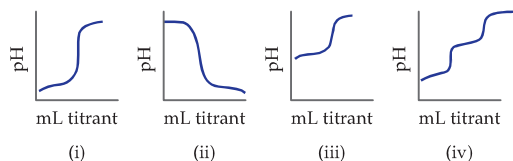
17.4 The drawing on the left represents a buffer composed of equal concentrations of a weak acid, HX, and its conjugate base, X^- . The heights of the columns are proportional to the concentrations of the components of the buffer. (a) Which of the three drawings, (1), (2), or (3), represents the buffer after the addition of a strong acid? (b) Which of the three represents the buffer after the addition of a strong base? (c) Which of the three represents a situation that cannot arise from the addition of either an acid or a base? [Section 17.2]



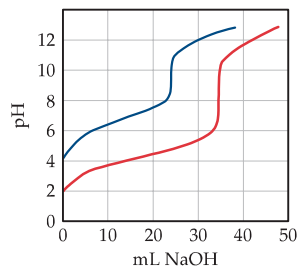
17.5 The following drawings represent solutions at various stages of the titration of a weak acid, HA, with NaOH. (The Na^+ ions and water molecules have been omitted for clarity.) To which of the following regions of the titration curve does each drawing correspond: (a) before addition of NaOH, (b) after addition of NaOH but before equivalence point, (c) at equivalence point, (d) after equivalence point? [Section 17.3]



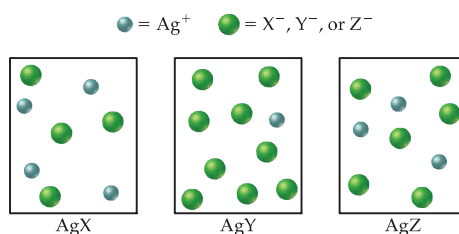
17.6 Match the following descriptions of titration curves with the diagrams: (a) strong acid added to strong base, (b) strong base added to weak acid, (c) strong base added to strong acid, (d) strong base added to polyprotic acid. [Section 17.3]



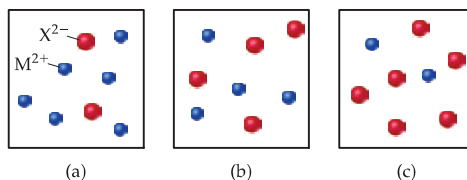
17.7 Equal volumes of two acids are titrated with 0.10 M NaOH resulting in the two titration curves shown in the following figure. (a) Which curve corresponds to the more concentrated acid solution? (b) Which corresponds to the acid with the largest K_a ? Explain. [Section 17.3]



17.8 The following drawings represent saturated solutions of three ionic compounds of silver—AgX, AgY, and AgZ. (Na^+ cations, which might also be present for charge balance, are not shown.) Which compound has the smallest K_{sp} ? [Section 17.4]

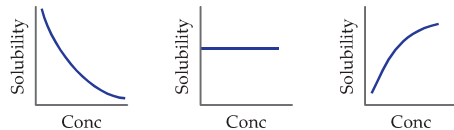


17.9 The figures below represent the ions in a saturated aqueous solution of the slightly soluble ionic compound MX: $MX(s) \rightleftharpoons M^{2+}(aq) + X^{2-}(aq)$. (Only the M^{2+} and X^{2-} ions are shown.) (a) Which figure represents a solution prepared by dissolving MX in water? (b) Which figure represents a solution prepared by dissolving MX in a solution containing Na_2X ? (c) If X^{2-} is a basic anion, which figure represents a saturated solution with the lowest pH? (d) If you were to calculate the K_{sp} for MX, would you get the same value in each of the three scenarios? Why or why not? [Sections 17.4 and 17.5]

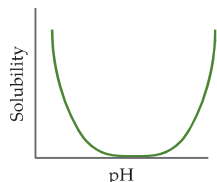


17.10 The following graphs represent the behavior of $BaCO_3$ under different circumstances. In each case the vertical axis indicates the solubility of the $BaCO_3$ and the

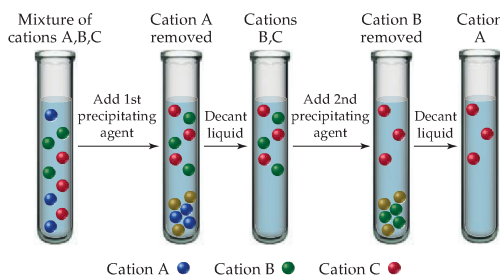
horizontal axis represents the concentration of some other reagent. (a) Which graph represents what happens to the solubility of BaCO_3 as HNO_3 is added? (b) Which graph represents what happens to the BaCO_3 solubility as Na_2CO_3 is added? (c) Which represents what happens to the BaCO_3 solubility as NaNO_3 is added? [Section 17.5]



- 17.11 What is the name given to the kind of behavior demonstrated by a metal hydroxide in this graph? [Section 17.5]



- 17.12 Three cations, Ni^{2+} , Cu^{2+} , and Ag^+ , are separated using two different precipitating agents. Based on Figure 17.22, what two precipitating agents could be used? Using these agents, indicate which of the cations is A, which is B, and which is C. [Section 17.7]



EXERCISES

Common-Ion Effect

- 17.13 (a) What is the common-ion effect? (b) Give an example of a salt that can decrease the ionization of HNO_2 in solution.
- 17.14 (a) Consider the equilibrium $\text{B}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HB}^+(aq) + \text{OH}^-(aq)$. Using Le Châtelier's principle, explain the effect of the presence of a salt of HB^+ on the ionization of B. (b) Give an example of a salt that can decrease the ionization of NH_3 in solution.
- 17.15 Use information from Appendix D to calculate the pH of (a) a solution that is 0.060 M in potassium propionate ($\text{C}_2\text{H}_5\text{COOK}$ or $\text{KC}_2\text{H}_5\text{O}_2$) and 0.085 M in propionic acid ($\text{C}_2\text{H}_5\text{COOH}$ or $\text{HC}_2\text{H}_5\text{O}_2$); (b) a solution that is 0.075 M in trimethylamine, $(\text{CH}_3)_3\text{N}$, and 0.10 M in trimethylammonium chloride, $(\text{CH}_3)_3\text{NHCl}$; (c) a solution that is made by mixing 50.0 mL of 0.15 M acetic acid and 50.0 mL of 0.20 M sodium acetate.
- 17.16 Use information from Appendix D to calculate the pH of (a) a solution that is 0.150 M in sodium formate (HCOONa) and 0.200 M in formic acid (HCOOH); (b) a solution that is 0.210 M in pyridine ($\text{C}_5\text{H}_5\text{N}$) and 0.350 M in pyridinium chloride ($\text{C}_5\text{H}_5\text{NHCl}$); (c) a solution that is made by combining 125 mL of 0.050 M hydrofluoric acid with 50.0 mL of 0.10 M sodium fluoride.
- 17.17 (a) Calculate the percent ionization of 0.0075 M butanoic acid ($K_a = 1.5 \times 10^{-5}$). (b) Calculate the percent ionization of 0.0075 M butanoic acid in a solution containing 0.085 M sodium butanoate.
- 17.18 (a) Calculate the percent ionization of 0.085 M lactic acid ($K_a = 1.4 \times 10^{-4}$). (b) Calculate the percent ionization of 0.095 M lactic acid in a solution containing 0.0075 M sodium lactate.

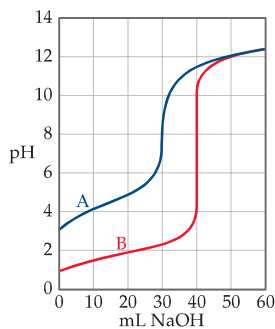
Buffers

- 17.19 Explain why a mixture of CH_3COOH and CH_3COONa can act as a buffer while a mixture of HCl and NaCl cannot.
- 17.20 Explain why a mixture formed by mixing 100 mL of 0.100 M CH_3COOH and 50 mL of 0.100 M NaOH will act as a buffer.
- 17.21 (a) Calculate the pH of a buffer that is 0.12 M in lactic acid and 0.11 M in sodium lactate. (b) Calculate the pH of a buffer formed by mixing 85 mL of 0.13 M lactic acid with 95 mL of 0.15 M sodium lactate.
- 17.22 (a) Calculate the pH of a buffer that is 0.105 M in NaHCO_3 and 0.125 M in Na_2CO_3 . (b) Calculate the pH of a solution formed by mixing 65 mL of 0.20 M NaHCO_3 with 75 mL of 0.15 M Na_2CO_3 .

- 17.23** A buffer is prepared by adding 20.0 g of acetic acid (CH_3COOH) and 20.0 g of sodium acetate (CH_3COONa) to enough water to form 2.00 L of solution. (a) Determine the pH of the buffer. (b) Write the complete ionic equation for the reaction that occurs when a few drops of hydrochloric acid are added to the buffer. (c) Write the complete ionic equation for the reaction that occurs when a few drops of sodium hydroxide solution are added to the buffer.
- 17.24** A buffer is prepared by adding 7.00 g of ammonia (NH_3) and 20.0 g of ammonium chloride (NH_4Cl) to enough water to form 2.50 L of solution. (a) What is the pH of this buffer? (b) Write the complete ionic equation for the reaction that occurs when a few drops of nitric acid are added to the buffer. (c) Write the complete ionic equation for the reaction that occurs when a few drops of potassium hydroxide solution are added to the buffer.
- 17.25** How many moles of sodium hypobromite (NaBrO) should be added to 1.00 L of 0.050 M hypobromous acid (HBrO) to form a buffer solution of pH 9.15? Assume that no volume change occurs when the NaBrO is added.
- 17.26** How many grams of sodium lactate [$\text{CH}_3\text{CH}(\text{OH})\text{COONa}$ or $\text{NaC}_3\text{H}_5\text{O}_3$] should be added to 1.00 L of 0.150 M lactic acid [$\text{CH}_3\text{CH}(\text{OH})\text{COOH}$ or $\text{HC}_3\text{H}_5\text{O}_3$] to form a buffer solution with pH 4.00? Assume that no volume change occurs when the sodium lactate is added.
- 17.27** A buffer solution contains 0.10 mol of acetic acid and 0.13 mol of sodium acetate in 1.00 L. (a) What is the pH of this buffer? (b) What is the pH of the buffer after the addition of 0.02 mol of KOH ? (c) What is the pH of the buffer after the addition of 0.02 mol of HNO_3 ?
- 17.28** A buffer solution contains 0.10 mol of propionic acid ($\text{C}_2\text{H}_5\text{COOH}$) and 0.13 mol of sodium propionate ($\text{C}_2\text{H}_5\text{COONa}$) in 1.50 L. (a) What is the pH of this buffer? (b) What is the pH of the buffer after the addition of 0.01 mol of NaOH ? (c) What is the pH of the buffer after the addition of 0.01 mol of HI ?
- 17.29** (a) What is the ratio of HCO_3^- to H_2CO_3 in blood of pH 7.4? (b) What is the ratio of HCO_3^- to H_2CO_3 in an exhausted marathon runner whose blood pH is 7.1?
- 17.30** A buffer, consisting of H_2PO_4^- and HPO_4^{2-} , helps control the pH of physiological fluids. Many carbonated soft drinks also use this buffer system. What is the pH of a soft drink in which the major buffer ingredients are 6.5 g of NaH_2PO_4 and 8.0 g of Na_2HPO_4 per 355 mL of solution?
- 17.31** You have to prepare a pH 3.50 buffer, and you have the following 0.10 M solutions available: HCOOH , CH_3COOH , H_3PO_4 , HCOONa , CH_3COONa , and NaH_2PO_4 . Which solutions would you use? How many milliliters of each solution would you use to make approximately a liter of the buffer?
- 17.32** You have to prepare a pH 4.80 buffer, and you have the following 0.10 M solutions available: formic acid, sodium formate, propionic acid, sodium propionate, phosphoric acid, and sodium dihydrogen phosphate. Which solutions would you use? How many milliliters of each solution would you use to make approximately a liter of the buffer?

Acid–Base Titrations

- 17.33** The accompanying graph shows the titration curves for two monoprotic acids. (a) Which curve is that of a strong acid? (b) What is the approximate pH at the equivalence point of each titration? (c) How do the original concentrations of the two acids compare if 40.0 mL of each is titrated to the equivalence point with 0.100 M base?



- 17.34** How does titration of a strong, monoprotic acid with a strong base differ from titration of a weak, monoprotic acid with a strong base with respect to the following: (a) quantity of base required to reach the equivalence point, (b) pH at the beginning of the titration, (c) pH at the equivalence point, (d) pH after addition of a slight excess of base, (e) choice of indicator for determining the equivalence point?
- 17.35** Predict whether the equivalence point of each of the following titrations is below, above, or at pH 7: (a) NaHCO_3 titrated with NaOH , (b) NH_3 titrated with HCl , (c) KOH titrated with HBr .
- 17.36** Predict whether the equivalence point of each of the following titrations is below, above, or at pH 7: (a) formic acid titrated with NaOH , (b) calcium hydroxide titrated with perchloric acid, (c) pyridine titrated with nitric acid.
- 17.37** Two monoprotic acids, both 0.100 M in concentration, are titrated with 0.100 M NaOH . The pH at the equivalence point for HX is 8.8, and that for HY is 7.9. (a) Which is the weaker acid? (b) Which indicators in Figure 16.7 could be used to titrate each of these acids?

- 17.38** Assume that 30.0 mL of a 0.10 M solution of a weak base B that accepts one proton is titrated with a 0.10 M solution of the monoprotic strong acid HX. (a) How many moles of HX have been added at the equivalence point? (b) What is the predominant form of B at the equivalence point? (c) What factor determines the pH at the equivalence point? (d) Which indicator, phenolphthalein or methyl red, is likely to be the better choice for this titration?
- 17.39** How many milliliters of 0.0850 M NaOH are required to titrate each of the following solutions to the equivalence point: (a) 40.0 mL of 0.0900 M HNO₃, (b) 35.0 mL of 0.0850 M CH₃COOH, (c) 50.0 mL of a solution that contains 1.85 g of HCl per liter?
- 17.40** How many milliliters of 0.105 M HCl are needed to titrate each of the following solutions to the equivalence point: (a) 45.0 mL of 0.0950 M NaOH, (b) 22.5 mL of 0.118 M NH₃, (c) 125.0 mL of a solution that contains 1.35 g of NaOH per liter?
- 17.41** A 20.0-mL sample of 0.200 M HBr solution is titrated with 0.200 M NaOH solution. Calculate the pH of the solution after the following volumes of base have been added: (a) 15.0 mL, (b) 19.9 mL, (c) 20.0 mL, (d) 20.1 mL, (e) 35.0 mL.
- 17.42** A 30.0-mL sample of 0.150 M KOH is titrated with 0.125 M HClO₄ solution. Calculate the pH after the following volumes of acid have been added: (a) 30.0 mL, (b) 35.0 mL, (c) 36.0 mL, (d) 37.0 mL, (e) 40.0 mL.
- 17.43** A 35.0-mL sample of 0.150 M acetic acid (CH₃COOH) is titrated with 0.150 M NaOH solution. Calculate the pH after the following volumes of base have been added: (a) 0 mL, (b) 17.5 mL, (c) 34.5 mL, (d) 35.0 mL, (e) 35.5 mL, (f) 50.0 mL.
- 17.44** Consider the titration of 30.0 mL of 0.030 M NH₃ with 0.025 M HCl. Calculate the pH after the following volumes of titrant have been added: (a) 0 mL, (b) 10.0 mL, (c) 20.0 mL, (d) 35.0 mL, (e) 36.0 mL, (f) 37.0 mL.
- 17.45** Calculate the pH at the equivalence point for titrating 0.200 M solutions of each of the following bases with 0.200 M HBr: (a) sodium hydroxide (NaOH), (b) hydroxylamine (NH₂OH), (c) aniline (C₆H₅NH₂).
- 17.46** Calculate the pH at the equivalence point in titrating 0.100 M solutions of each of the following with 0.080 M NaOH: (a) hydrobromic acid (HBr), (b) lactic acid [CH₃CH(OH)COOH], (c) sodium hydrogen chromate (NaHCrO₄).

Solubility Equilibria and Factors Affecting Solubility

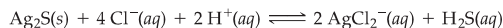
- 17.47** (a) Why is the concentration of undissolved solid not explicitly included in the expression for the solubility-product constant? (b) Write the expression for the solubility-product constant for each of the following strong electrolytes: AgI, SrSO₄, Fe(OH)₂, and Hg₂Br₂.
- 17.48** (a) Explain the difference between solubility and solubility-product constant. (b) Write the expression for the solubility-product constant for each of the following ionic compounds: MnCO₃, Hg(OH)₂, and Cu₃(PO₄)₂.
- 17.49** (a) If the molar solubility of CaF₂ at 35 °C is 1.24×10^{-3} mol/L, what is K_{sp} at this temperature? (b) It is found that 1.1×10^{-2} g of SrF₂ dissolves per 100 mL of aqueous solution at 25 °C. Calculate the solubility product for SrF₂. (c) The K_{sp} of Ba(IO₃)₂ at 25 °C is 6.0×10^{-10} . What is the molar solubility of Ba(IO₃)₂?
- 17.50** (a) The molar solubility of PbBr₂ at 25 °C is 1.0×10^{-2} mol/L. Calculate K_{sp} . (b) If 0.0490 g of AgIO₃ dissolves per liter of solution, calculate the solubility-product constant. (c) Using the appropriate K_{sp} value from Appendix D, calculate the solubility of Cu(OH)₂ in grams per liter of solution.
- 17.51** A 1.00-L solution saturated at 25 °C with calcium oxalate (CaC₂O₄) contains 0.0061 g of CaC₂O₄. Calculate the solubility-product constant for this salt at 25 °C.
- 17.52** A 1.00-L solution saturated at 25 °C with lead(II) iodide contains 0.54 g of PbI₂. Calculate the solubility-product constant for this salt at 25 °C.
- 17.53** Using Appendix D, calculate the molar solubility of AgBr in (a) pure water, (b) 3.0×10^{-2} M AgNO₃ solution, (c) 0.10 M NaBr solution.
- 17.54** Calculate the solubility of LaF₃ in grams per liter in (a) pure water, (b) 0.010 M KF solution, (c) 0.050 M LaCl₃ solution.
- 17.55** Calculate the solubility of Mn(OH)₂ in grams per liter when buffered at pH (a) 7.0, (b) 9.5, (c) 11.8.
- 17.56** Calculate the molar solubility of Fe(OH)₂ when buffered at pH (a) 8.0, (b) 10.0, (c) 12.0.
- 17.57** Which of the following salts will be substantially more soluble in acidic solution than in pure water: (a) ZnCO₃, (b) ZnS, (c) BiI₃, (d) AgCN, (e) Ba₃(PO₄)₂?
- 17.58** For each of the following slightly soluble salts, write the net ionic equation, if any, for reaction with acid: (a) MnS, (b) PbF₂, (c) AuCl₃, (d) Hg₂C₂O₄, (e) CuBr.
- 17.59** From the value of K_f listed in Table 17.1, calculate the concentration of Cu²⁺ in 1.0 L of a solution that contains a total of 1×10^{-3} mol of copper(II) ion and that is 0.10 M in NH₃.

17.60 To what final concentration of NH_3 must a solution be adjusted to just dissolve 0.020 mol of NiC_2O_4 ($K_{sp} = 4 \times 10^{-10}$) in 1.0 L of solution? (*Hint*: You can neglect the hydrolysis of $\text{C}_2\text{O}_4^{2-}$ because the solution will be quite basic.)

17.61 By using the values of K_{sp} for AgI and K_f for $\text{Ag}(\text{CN})_2^-$, calculate the equilibrium constant for the reaction



17.62 Using the value of K_{sp} for Ag_2S , K_{a1} and K_{a2} for H_2S , and $K_f = 1.1 \times 10^5$ for AgCl_2^- , calculate the equilibrium constant for the following reaction:



Precipitation; Qualitative Analysis

17.63 (a) Will $\text{Ca}(\text{OH})_2$ precipitate from solution if the pH of a 0.050 M solution of CaCl_2 is adjusted to 8.0? (b) Will Ag_2SO_4 precipitate when 100 mL of 0.050 M AgNO_3 is mixed with 10 mL of 5.0×10^{-2} M Na_2SO_4 solution?

17.64 (a) Will $\text{Co}(\text{OH})_2$ precipitate from solution if the pH of a 0.020 M solution of $\text{Co}(\text{NO}_3)_2$ is adjusted to 8.5? (b) Will AgIO_3 precipitate when 20 mL of 0.010 M AgNO_3 is mixed with 10 mL of 0.015 M NaIO_3 ? (K_{sp} of AgIO_3 is 3.1×10^{-8} .)

17.65 Calculate the minimum pH needed to precipitate $\text{Mn}(\text{OH})_2$ so completely that the concentration of Mn^{2+} is less than 1 μg per liter [1 part per billion (ppb)].

17.66 Suppose that a 10-mL sample of a solution is to be tested for Cl^- ion by addition of 1 drop (0.2 mL) of 0.10 M AgNO_3 . What is the minimum number of grams of Cl^- that must be present for $\text{AgCl}(s)$ to form?

17.67 A solution contains 2.0×10^{-4} M Ag^+ and 1.5×10^{-3} M Pb^{2+} . If NaI is added, will AgI ($K_{sp} = 8.3 \times 10^{-17}$) or PbI_2 ($K_{sp} = 7.9 \times 10^{-9}$) precipitate first? Specify the concentration of I^- needed to begin precipitation.

17.68 A solution of Na_2SO_4 is added dropwise to a solution that is 0.010 M in Ba^{2+} and 0.010 M in Sr^{2+} . (a) What concentration of SO_4^{2-} is necessary to begin precipitation? (Neglect volume changes. BaSO_4 : $K_{sp} = 1.1 \times 10^{-10}$; SrSO_4 : $K_{sp} = 3.2 \times 10^{-7}$.) (b) Which cation precipitates first? (c) What is the concentration of SO_4^{2-} when the second cation begins to precipitate?

17.69 A solution containing an unknown number of metal ions is treated with dilute HCl ; no precipitate forms. The pH is adjusted to about 1, and H_2S is bubbled through. Again, no precipitate forms. The pH of the solution is then adjusted to about 8. Again, H_2S is bubbled through. This time a precipitate forms. The filtrate from this solution is treated with $(\text{NH}_4)_2\text{HPO}_4$. No precipitate forms.

Which metal ions discussed in Section 17.7 are possibly present? Which are definitely absent within the limits of these tests?

17.70 An unknown solid is entirely soluble in water. On addition of dilute HCl , a precipitate forms. After the precipitate is filtered off, the pH is adjusted to about 1 and H_2S is bubbled in; a precipitate again forms. After filtering off this precipitate, the pH is adjusted to 8 and H_2S is again added; no precipitate forms. No precipitate forms upon addition of $(\text{NH}_4)_2\text{HPO}_4$. The remaining solution shows a yellow color in a flame test. Based on these observations, which of the following compounds might be present, which are definitely present, and which are definitely absent: CdS , $\text{Pb}(\text{NO}_3)_2$, HgO , ZnSO_4 , $\text{Cd}(\text{NO}_3)_2$, and Na_2SO_4 ?

17.71 In the course of various qualitative analysis procedures, the following mixtures are encountered: (a) Zn^{2+} and Cd^{2+} , (b) $\text{Cr}(\text{OH})_3$ and $\text{Fe}(\text{OH})_3$, (c) Mg^{2+} and K^+ , (d) Ag^+ and Mn^{2+} . Suggest how each mixture might be separated.

17.72 Suggest how the cations in each of the following solution mixtures can be separated: (a) Na^+ and Cd^{2+} , (b) Cu^{2+} and Mg^{2+} , (c) Pb^{2+} and Al^{3+} , (d) Ag^+ and Hg^{2+} .

17.73 (a) Precipitation of the group 4 cations (Figure 17.22) requires a basic medium. Why is this so? (b) What is the most significant difference between the sulfides precipitated in group 2 and those precipitated in group 3? (c) Suggest a procedure that would serve to redissolve the group 3 cations following their precipitation.

17.74 A student who is in a great hurry to finish his laboratory work decides that his qualitative analysis unknown contains a metal ion from the insoluble phosphate group, group 4 (Figure 17.22). He therefore tests his sample directly with $(\text{NH}_4)_2\text{HPO}_4$, skipping earlier tests for the metal ions in groups 1, 2, and 3. He observes a precipitate and concludes that a metal ion from group 4 is indeed present. Why is this possibly an erroneous conclusion?

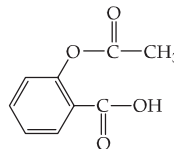
ADDITIONAL EXERCISES

- 17.75** Derive an equation similar to the Henderson–Hasselbalch equation relating the pOH of a buffer to the pK_b of its base component.
- 17.76** Benzenesulfonic acid is a monoprotic acid with $pK_a = 2.25$. Calculate the pH of a buffer composed of 0.150 M benzenesulfonic acid and 0.125 M sodium benzenesulfonate.
- 17.77** Furoic acid ($\text{HC}_5\text{H}_3\text{O}_3$) has a K_a value of 6.76×10^{-4} at 25 °C. Calculate the pH at 25 °C of (a) a solution formed by adding 25.0 g of furoic acid and 30.0 g of sodium furoate ($\text{NaC}_5\text{H}_3\text{O}_3$) to enough water to form 0.250 L of solution; (b) a solution formed by mixing 30.0 mL of 0.250 M $\text{HC}_5\text{H}_3\text{O}_3$ and 20.0 mL of 0.22 M $\text{NaC}_5\text{H}_3\text{O}_3$ and diluting the total volume to 125 mL; (c) a solution prepared by adding 50.0 mL of 1.65 M NaOH solution to 0.500 L of 0.0850 M $\text{HC}_5\text{H}_3\text{O}_3$.
- 17.78** The acid–base indicator bromocresol green is a weak acid. The yellow acid and blue base forms of the indicator are present in equal concentrations in a solution when the pH is 4.68. What is the pK_a for bromocresol green?
- 17.79** Equal quantities of 0.010 M solutions of an acid HA and a base B are mixed. The pH of the resulting solution is 9.2. (a) Write the equilibrium equation and equilibrium-constant expression for the reaction between HA and B. (b) If K_a for HA is 8.0×10^{-5} , what is the value of the equilibrium constant for the reaction between HA and B? (c) What is the value of K_b for B?
- 17.80** Two buffers are prepared by adding an equal number of moles of formic acid (HCOOH) and sodium formate (HCOONa) to enough water to make 1.00 L of solution. Buffer A is prepared using 1.00 mol each of formic acid and sodium formate. Buffer B is prepared by using 0.010 mol of each. (a) Calculate the pH of each buffer, and explain why they are equal. (b) Which buffer will have the greater buffer capacity? Explain. (c) Calculate the change in pH for each buffer upon the addition of 1.0 mL of 1.00 M HCl. (d) Calculate the change in pH for each buffer upon the addition of 10 mL of 1.00 M HCl. (e) Discuss your answers for parts (c) and (d) in light of your response to part (b).
- 17.81** A biochemist needs 750 mL of an acetic acid–sodium acetate buffer with pH 4.50. Solid sodium acetate (CH_3COONa) and glacial acetic acid (CH_3COOH) are available. Glacial acetic acid is 99% CH_3COOH by mass and has a density of 1.05 g/mL. If the buffer is to be 0.15 M in CH_3COOH , how many grams of CH_3COONa and how many milliliters of glacial acetic acid must be used?
- 17.82** A sample of 0.2140 g of an unknown monoprotic acid was dissolved in 25.0 mL of water and titrated with 0.0950 M NaOH. The acid required 27.4 mL of base to reach the equivalence point. (a) What is the molar mass of the acid? (b) After 15.0 mL of base had been added in the titration, the pH was found to be 6.50. What is the K_a for the unknown acid?
- 17.83** Show that the pH at the halfway point of a titration of a weak acid with a strong base (where the volume of added base is half of that needed to reach the equivalence point) is equal to pK_a for the acid.
- 17.84** Potassium hydrogen phthalate, often abbreviated KHP, can be obtained in high purity and is used to determine the concentrations of solutions of strong bases. Strong bases react with the hydrogen phthalate ion as follows:
- $$\text{HP}^-(aq) + \text{OH}^-(aq) \longrightarrow \text{H}_2\text{O}(l) + \text{P}^{2-}(aq)$$
- The molar mass of KHP is 204.2 g/mol and K_a for the HP^- ion is 3.1×10^{-6} . (a) If a titration experiment begins with 0.4885 g of KHP and has a final volume of about 100 mL, which indicator from Figure 16.7 would be most appropriate? (b) If the titration required 38.55 mL of NaOH solution to reach the end point, what is the concentration of the NaOH solution?
- 17.85** If 40.00 mL of 0.100 M Na_2CO_3 is titrated with 0.100 M HCl, calculate (a) the pH at the start of the titration; (b) the volume of HCl required to reach the first equivalence point and the predominant species present at this point; (c) the volume of HCl required to reach the second equivalence point and the predominant species present at this point; (d) the pH at the second equivalence point.
- 17.86** A hypothetical weak acid, HA, was combined with NaOH in the following proportions: 0.20 mol of HA, 0.080 mol of NaOH. The mixture was diluted to a total volume of 1.0 L, and the pH measured. (a) If pH = 4.80, what is the pK_a of the acid? (b) How many additional moles of NaOH should be added to the solution to increase the pH to 5.00?
- [17.87]** What is the pH of a solution made by mixing 0.30 mol NaOH, 0.25 mol Na_2HPO_4 , and 0.20 mol H_3PO_4 with water and diluting to 1.00 L?
- [17.88]** Suppose you want to do a physiological experiment that calls for a pH 6.5 buffer. You find that the organism with which you are working is not sensitive to the weak acid H_2X ($K_{a1} = 2 \times 10^{-2}$; $K_{a2} = 5.0 \times 10^{-7}$) or its sodium salts. You have available a 1.0 M solution of this acid and a 1.0 M solution of NaOH. How much of the NaOH solution should be added to 1.0 L of the acid to give a buffer at pH 6.50? (Ignore any volume change.)
- [17.89]** How many microliters of 1.000 M NaOH solution must be added to 25.00 mL of a 0.1000 M solution of lactic acid [$\text{CH}_3\text{CH}(\text{OH})\text{COOH}$ or $\text{HC}_3\text{H}_5\text{O}_3$] to produce a buffer with pH = 3.75?

- 17.90** A person suffering from anxiety begins breathing rapidly and as a result suffers alkalosis, an increase in blood pH. (a) Using Equation 17.10, explain how rapid breathing can cause the pH of blood to increase. (b) One cure for this problem is breathing in a paper bag. Why does this procedure lower blood pH?
- 17.91** For each pair of compounds, use K_{sp} values to determine which has the greater molar solubility: (a) CdS or CuS, (b) $PbCO_3$ or $BaCrO_4$, (c) $Ni(OH)_2$ or $NiCO_3$, (d) AgI or Ag_2SO_4 .
- 17.92** Describe the solubility of $CaCO_3$ in each of the following solutions compared to its solubility in water: (a) in 0.10 M NaCl solution; (b) in 0.10 M $Ca(NO_3)_2$ solution; (c) 0.10 M Na_2CO_3 ; (d) 0.10 M HCl solution. (Answer same, less soluble, or more soluble.)
- 17.93** Tooth enamel is composed of hydroxyapatite, whose simplest formula is $Ca_5(PO_4)_3OH$, and whose corresponding $K_{sp} = 6.8 \times 10^{-27}$. As discussed in the "Chemistry and Life" box in Section 17.5, fluoride in fluorinated water or in toothpaste reacts with hydroxyapatite to form fluoroapatite, $Ca_5(PO_4)_3F$, whose $K_{sp} = 1.0 \times 10^{-60}$. (a) Write the expression for the solubility-constant for hydroxyapatite and for fluoroapatite. (b) Calculate the molar solubility of each of these compounds.
- 17.94** Calculate the solubility of $Mg(OH)_2$ in 0.50 M NH_4Cl .
- [17.95]** Seawater contains 0.13% magnesium by mass, and has a density of 1.025 g/mL. What fraction of the magnesium can be removed by adding a stoichiometric quantity of CaO (that is, one mole of CaO for each mole of Mg^{2+})?
- 17.96** The solubility-product constant for barium permanganate, $Ba(MnO_4)_2$, is 2.5×10^{-10} . Assume that solid $Ba(MnO_4)_2$ is in equilibrium with a solution of $KMnO_4$. What concentration of $KMnO_4$ is required to establish a concentration of 2.0×10^{-8} M for the Ba^{2+} ion in solution?
- 17.97** Calculate the ratio of $[Ca^{2+}]$ to $[Fe^{2+}]$ in a lake in which the water is in equilibrium with deposits of both $CaCO_3$ and $FeCO_3$. Assume that the water is slightly basic and that the hydrolysis of the carbonate ion can therefore be ignored.
- [17.98]** The solubility products of $PbSO_4$ and $SrSO_4$ are 6.3×10^{-7} and 3.2×10^{-7} , respectively. What are the values of $[SO_4^{2-}]$, $[Pb^{2+}]$, and $[Sr^{2+}]$ in a solution at equilibrium with both substances?
- [17.99]** What pH buffer solution is needed to give a Mg^{2+} concentration of 3.0×10^{-2} M in equilibrium with solid magnesium oxalate?
- [17.100]** The value of K_{sp} for $Mg_3(AsO_4)_2$ is 2.1×10^{-20} . The AsO_4^{3-} ion is derived from the weak acid H_3AsO_4 ($pK_{a1} = 2.22$; $pK_{a2} = 6.98$; $pK_{a3} = 11.50$). When asked to calculate the molar solubility of $Mg_3(AsO_4)_2$ in water, a student used the K_{sp} expression and assumed that $[Mg^{2+}] = 1.5[AsO_4^{3-}]$. Why was this a mistake?
- [17.101]** The solubility product for $Zn(OH)_2$ is 3.0×10^{-16} . The formation constant for the hydroxo complex, $Zn(OH)_4^{2-}$, is 4.6×10^{-17} . What concentration of OH^- is required to dissolve 0.015 mol of $Zn(OH)_2$ in a liter of solution?

INTEGRATIVE EXERCISES

- 17.102** (a) Write the net ionic equation for the reaction that occurs when a solution of hydrochloric acid (HCl) is mixed with a solution of sodium formate ($NaCHO_2$). (b) Calculate the equilibrium constant for this reaction. (c) Calculate the equilibrium concentrations of Na^+ , Cl^- , H^+ , CHO_2^- , and $HCHO_2$ when 50.0 mL of 0.15 M HCl is mixed with 50.0 mL of 0.15 M $NaCHO_2$.
- 17.103** (a) A 0.1044-g sample of an unknown monoprotic acid requires 22.10 mL of 0.0500 M NaOH to reach the end point. What is the molecular weight of the unknown? (b) As the acid is titrated, the pH of the solution after the addition of 11.05 mL of the base is 4.89. What is the K_a for the acid? (c) Using Appendix D, suggest the identity of the acid. Do both the molecular weight and K_a value agree with your choice?
- 17.104** A sample of 7.5 L of NH_3 gas at 22 °C and 735 torr is bubbled into a 0.50-L solution of 0.40 M HCl. Assuming that all the NH_3 dissolves and that the volume of the solution remains 0.50 L, calculate the pH of the resulting solution.
- 17.105** Aspirin has the structural formula



At body temperature (37 °C), K_a for aspirin equals 3×10^{-5} . If two aspirin tablets, each having a mass of 325 mg, are dissolved in a full stomach whose volume is 1 L and whose pH is 2, what percent of the aspirin is in the form of neutral molecules?

- 17.106** What is the pH at 25 °C of water saturated with CO_2 at a partial pressure of 1.10 atm? The Henry's law constant for CO_2 at 25 °C is 3.1×10^{-2} mol/L-atm. The CO_2 is an acidic oxide, reacting with H_2O to form H_2CO_3 .

- 17.107** Excess $\text{Ca}(\text{OH})_2$ is shaken with water to produce a saturated solution. The solution is filtered, and a 50.00-mL sample titrated with HCl requires 11.23 mL of 0.0983 M HCl to reach the end point. Calculate K_{sp} for $\text{Ca}(\text{OH})_2$. Compare your result with that in Appendix D. Do you think the solution was kept at 25 °C?
- 17.108** The osmotic pressure of a saturated solution of strontium sulfate at 25 °C is 21 torr. What is the solubility product of this salt at 25 °C?
- 17.109** A concentration of 10–100 parts per billion (by mass) of Ag^+ is an effective disinfectant in swimming pools. However, if the concentration exceeds this range, the Ag^+ can cause adverse health effects. One way to maintain an appropriate concentration of Ag^+ is to add a slightly soluble salt to the pool. Using K_{sp} values from Appendix D, calculate the equilibrium concentration of Ag^+ in parts per billion that would exist in equilibrium with (a) AgCl, (b) AgBr, (c) AgI.
- [17.110]** Fluoridation of drinking water is employed in many places to aid in the prevention of dental caries. Typically the F^- ion concentration is adjusted to about 1 ppb. Some water supplies are also “hard”; that is, they contain certain cations such as Ca^{2+} that interfere with the action of soap. Consider a case where the concentration of Ca^{2+} is 8 ppb. Could a precipitate of CaF_2 form under these conditions? (Make any necessary approximations.)