

# 17

## ADDITIONAL ASPECTS OF AQUEOUS EQUILIBRIA

### WHAT'S AHEAD

- 17.1 ► The Common-Ion Effect
- 17.2 ► Buffers
- 17.3 ► Acid-Base Titrations
- 17.4 ► Solubility Equilibria
- 17.5 ► Factors That Affect Solubility
- 17.6 ► Precipitation and Separation of Ions

### 17.1 | The Common-Ion Effect



Water, the most common and most important solvent on Earth, occupies its position of importance because of its abundance and its exceptional ability to dissolve a wide variety of substances. 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. The discussions and calculations in this chapter are extensions of those in Chapters 15 and 16. We start our

examination with what we call the common-ion effect. By the end of this section, you should be able to

- Describe 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 ( $\text{CH}_3\text{COOH}$ ), and a soluble salt of that acid, such as sodium acetate ( $\text{CH}_3\text{COONa}$ ). Notice that these solutions contain two substances that share a *common ion*,  $\text{CH}_3\text{COO}^-$ . It is instructive to view these solutions from the perspective of Le Châtelier's principle.

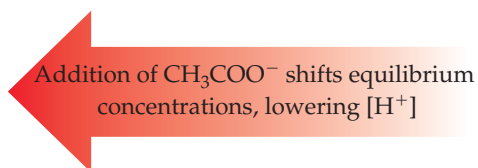
Sodium acetate is a soluble ionic compound and therefore a strong electrolyte. Consequently, it dissociates completely in aqueous solution to form  $\text{Na}^+$  and  $\text{CH}_3\text{COO}^-$  ions:



In contrast,  $\text{CH}_3\text{COOH}$  is a weak electrolyte that ionizes only partially, represented by the dynamic equilibrium



The equilibrium constant for Equation 17.1 is  $K_a = 1.8 \times 10^{-5}$  at  $25^\circ\text{C}$  (Table 16.2). If we add sodium acetate to a solution of acetic acid in water, the  $\text{CH}_3\text{COO}^-$  from  $\text{CH}_3\text{COONa}$  causes the equilibrium concentrations of the substances in Equation 17.1 to shift to the left as expected from Le Châtelier's principle, 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. We call this observation the **common-ion effect**.

*Whenever a weak electrolyte and a strong electrolyte containing a common ion are together in solution, the weak electrolyte ionizes less than it would if it were alone in solution.*

Note that the equilibrium constant itself does not change; it is the relative concentrations of products and reactants in the equilibrium expression that change.



### 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 ( $\text{CH}_3\text{COOH}$ ) and a strong electrolyte ( $\text{CH}_3\text{COONa}$ ) that share a common ion,  $\text{CH}_3\text{COO}^-$ .

**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:

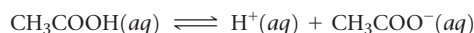
- (1) Consider which solutes are strong electrolytes and which are weak electrolytes, and identify the major species in solution.

- (2) Identify the important equilibrium reaction that is the source of  $\text{H}^+$  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  $\text{CH}_3\text{COOH}$  is a weak electrolyte and  $\text{CH}_3\text{COONa}$  is a strong electrolyte, the major species in the solution are  $\text{CH}_3\text{COOH}$  (a weak acid),  $\text{Na}^+$  (which is neither acidic nor basic and is therefore a spectator in the acid-base chemistry), and  $\text{CH}_3\text{COO}^-$  (which is the conjugate base of  $\text{CH}_3\text{COOH}$ ).

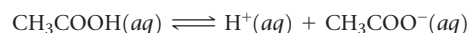
Second,  $[\text{H}^+]$  and, therefore, the pH are controlled by the dissociation equilibrium of  $\text{CH}_3\text{COOH}$ :



(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:

The equilibrium concentration of  $\text{CH}_3\text{COO}^-$  (the common ion) is the initial concentration that is due to  $\text{CH}_3\text{COONa}$  (0.30 M) plus the change in concentration ( $x$ ) that is due to the ionization of  $\text{CH}_3\text{COOH}$ .



Initial (M)	0.30	0	0.30
Change (M)	$-x$	$+x$	$+x$
Equilibrium (M)	$(0.30 - x)$	$x$	$(0.30 + x)$

Now we can use the equilibrium 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  $\text{CH}_3\text{COOH}$  at 25 °C is from Table 16.2, or Appendix D; addition of  $\text{CH}_3\text{COONa}$  does not change the value of this constant. Substituting the equilibrium 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  $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COO}^-$  (0.30 M each). Thus, we can ignore the very small  $x$  relative to 0.30 M, giving:

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

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

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

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

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

**Comment** In Section 16.5, we calculated that a 0.30 M solution of  $\text{CH}_3\text{COOH}$  has a pH of 2.64, corresponding to  $[\text{H}^+] = 2.3 \times 10^{-3} \text{ M}$ . Thus, the addition of  $\text{CH}_3\text{COONa}$  has substantially decreased  $[\text{H}^+]$ , as we expect from Le Châtelier's principle.

### Practice Exercise

For the generic equilibrium  $\text{HA}(aq) \rightleftharpoons \text{H}^+(aq) + \text{A}^-(aq)$ , which of these statements is true?

- The equilibrium constant for this reaction changes as the pH changes.
- If you add the soluble salt KA to a solution of HA that is at equilibrium, the concentration of HA would decrease.
- If you add the soluble salt KA to a solution of HA that is at equilibrium, the concentration of  $\text{A}^-$  would decrease.
- If you add the soluble salt KA to a solution of HA that is at equilibrium, the pH would increase.

## 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

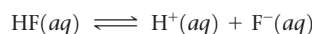
**Analyze** We are asked to determine the concentration of  $F^-$  and the pH in a solution containing the weak acid HF and the strong acid HCl. In this case the common ion is  $H^+$ .

**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, this is the important equilibrium:

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 (M)	0.20	0.10	0
Change (M)	$-x$	$+x$	$+x$
Equilibrium (M)	$(0.20 - x)$	$(0.10 + x)$	$x$

The equilibrium constant for the ionization of HF, from Appendix D, is  $6.8 \times 10^{-4}$ . 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,

$$pH = 1.00$$

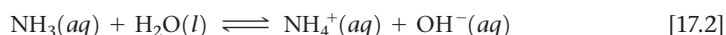
**Comment** Notice that for all practical purposes, the hydrogen ion concentration is due entirely to the HCl; the HF makes a negligible contribution by comparison.

#### Practice Exercise

Calculate the concentration of the lactate ion in a solution that is 0.100 *M* in lactic acid ( $CH_3CH(OH)COOH$ ,  $pK_a = 3.86$ ) and 0.080 *M* in HCl.

- (a) 4.83 *M*      (b) 0.0800 *M*  
 (c)  $7.3 \times 10^{-3} M$       (d)  $3.65 \times 10^{-3} M$   
 (e)  $1.73 \times 10^{-4} M$

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 equilibrium concentrations of the reagents in Equation 17.2 to shift to the left, decreasing the equilibrium concentration of  $OH^-$  and lowering the pH:



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

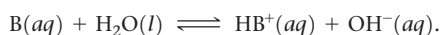
## Self-Assessment Exercise

**17.1** In a solution made from the weak base ammonia,  $\text{NH}_3$ , and the soluble salt  $\text{Ca}(\text{OH})_2$ , which is the common ion?

- (a)  $\text{NH}_3$
- (b)  $\text{NH}_4^+$
- (c)  $\text{Ca}^{2+}$
- (d)  $\text{OH}^-$

## Exercises

**17.2** Consider the equilibrium



Suppose that a salt of  $\text{HB}^+(aq)$  is added to a solution of  $\text{B}(aq)$  at equilibrium. (a) Will the equilibrium constant for the reaction increase, decrease, or stay the same? (b) Will the concentration of  $\text{B}(aq)$  increase, decrease, or stay the same? (c) Will the pH of the solution increase, decrease, or stay the same?

**17.3** Use information from Appendix D to calculate the pH of (a) a solution that is 0.250 M in sodium methanoate

( $\text{HCOONa}$ ) and 0.150 M in methanoic acid ( $\text{HCOOH}$ ), (b) a solution that is 0.490 M in pyridine ( $\text{C}_5\text{H}_5\text{N}$ ) and 0.450 M in pyridinium chloride ( $\text{C}_5\text{H}_5\text{NHCl}$ ), (c) a solution that is made by combining 80 mL of 0.050 M hydrofluoric acid with 100 mL of 0.10 M sodium fluoride.

**17.4** (a) Calculate the percent ionization of 0.250 M lactic acid ( $K_a = 1.4 \times 10^{-4}$ ). (b) Calculate the percent ionization of 0.250 M lactic acid in a solution containing 0.050 M sodium lactate.

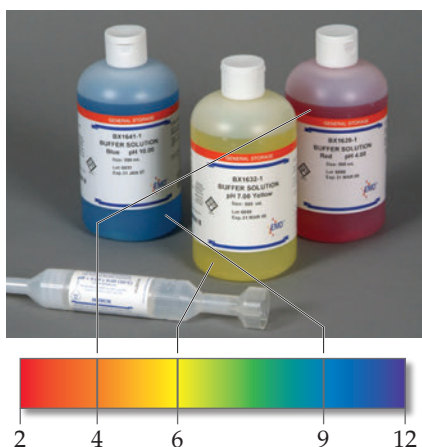
17.1 (d)

Answers to Self-Assessment Exercises

## 17.2 | Buffers



Buffers are used in many areas of industry. For example, to control the pH of a dying process, in fermentation to counter the acidity resulting from  $\text{CO}_2$  release, in the culture medium used in microbiology labs, and in the manufacture of pharmaceuticals. Buffers are used in processed food to maintain color and flavor and delay spoilage. For example, sodium citrate (assigned the number E331 on food packaging) is added to fruit products such as jams and jellies to act with the naturally present citric acid as a buffer, maintaining color and helping preserve the fruit.



▲ **Figure 17.1** Standard buffers. For laboratory work, prepackaged buffers at specific pH values can be purchased.

By the end of this section, you should be able to

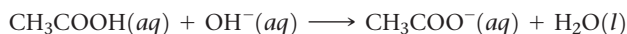
- Explain how a buffer functions and calculate the pH of a buffered solution.
- Calculate the pH of a buffer after the addition of small amounts of a strong acid or a strong base.
- Calculate the appropriate quantities of compounds to make a buffer at a given pH.

Solutions that contain high concentrations ( $10^{-3} M$  or more) of a weak conjugate acid–base pair and that resist drastic changes in pH when small amounts of strong acid or strong base are added to them are called **buffered solutions** (or merely **buffers**). Human blood, for example, is a complex buffered solution that maintains the blood pH at about 7.4 (The *Chemistry and Life* box, “Blood as a Buffered Solution” later in 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 due to the  $\text{HCO}_3^-/\text{CO}_3^{2-}$  acid–base pair. Buffers find many important applications in the laboratory and in medicine (Figure 17.1). Many biological reactions occur at the optimal rates only when properly buffered. If you ever work in a biochemistry lab, you will very likely have to prepare specific buffers in which to run your biochemical reactions.

## Composition and Action of Buffers

A buffer resists changes in pH because it contains both an acid to neutralize added  $\text{OH}^-$  ions and a base to neutralize added  $\text{H}^+$  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  $\text{NH}_4^+/\text{NH}_3$ . The key is to have roughly equal concentrations of both the weak acid and its conjugate base. There are two ways to make a buffer.

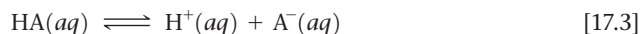
- Mix a weak acid or a weak base with a salt of that acid or base. For example, the  $\text{CH}_3\text{COOH}/\text{CH}_3\text{COO}^-$  buffer can be prepared by adding  $\text{CH}_3\text{COONa}$  to a solution of  $\text{CH}_3\text{COOH}$ . Similarly, the  $\text{NH}_4^+/\text{NH}_3$  buffer can be prepared by adding  $\text{NH}_4\text{Cl}$  to a solution of  $\text{NH}_3$ .
- Make the conjugate acid or base from a solution of weak base or acid by the addition of a strong acid or base. For example, to make the  $\text{CH}_3\text{COOH}/\text{CH}_3\text{COO}^-$  buffer, you could start with a solution of  $\text{CH}_3\text{COOH}$  and add some  $\text{NaOH}$  to the solution—enough to neutralize about half of  $\text{CH}_3\text{COOH}$  according to the reaction



Neutralization reactions have very large equilibrium constants, and so the amount of acetate formed will only be limited by the relative amounts of the acid and strong base that are mixed. The resulting solution is the same as if you added sodium acetate to the acetic acid solution: You will have comparable quantities of both acetic acid and its conjugate base in solution.

By choosing appropriate components and adjusting their relative concentrations, we can buffer a solution at virtually any pH.

To understand how a buffer works, let's consider one composed of a weak acid HA and one of its salts MA, where  $\text{M}^+$  could be  $\text{Na}^+$ ,  $\text{K}^+$ , or any other cation that does not react with water. The acid-dissociation equilibrium in this buffered solution involves both the acid and its conjugate base:



The corresponding acid-dissociation-constant expression is

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

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

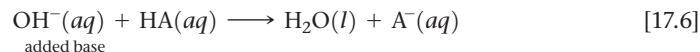
$$[\text{H}^+] = K_a \frac{[\text{HA}]}{[\text{A}^-]} \quad [17.5]$$



We see from this expression that  $[H^+]$  and, thus, the pH are determined by two factors:

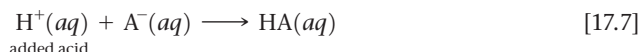
- the value of  $K_a$  for the weak-acid component of the buffer;
- the ratio of the concentrations of the conjugate acid-base pair,  $[HA]/[A^-]$ .

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



This neutralization reaction causes  $[HA]$  to decrease and  $[A^-]$  to increase. As long as the amounts of  $HA$  and  $A^-$  in the buffer are large relative to the amount of  $OH^-$  added, the ratio  $[HA]/[A^-]$  does not change much and, thus, the change in pH is small.

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 this reaction causes  $[A^-]$  to decrease and  $[HA]$  to increase. As long as the change in the ratio  $[HA]/[A^-]$  is small, the change in pH will be small.

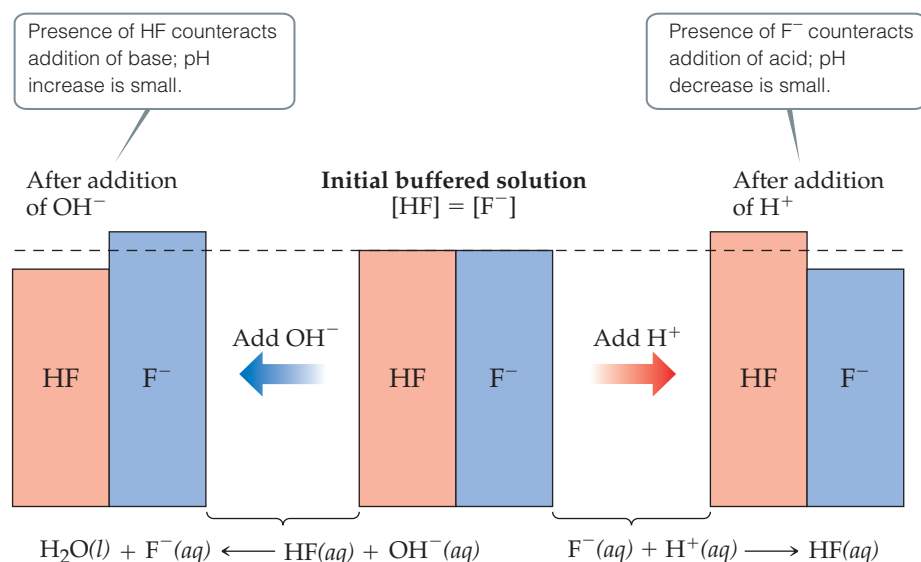
An example of an  $HA/A^-$  buffer is the  $HF/F^-$  buffered solution shown in **Figure 17.2**. The buffer consists of equal concentrations of hydrofluoric acid,  $HF$ , and fluoride ion,  $F^-$  (center). The addition of  $OH^-$  reduces  $[HF]$  and slightly increases  $[F^-]$ , whereas the addition of  $H^+$  reduces  $[F^-]$  and slightly increases  $[HF]$ .

It is possible to overwhelm a buffer by adding too much strong acid or strong base. We will examine this in more detail a little later in this chapter.

## 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 in Sample Exercise 17.1. Alternatively, we can take an approach based on an equation derived from Equation 17.5. Taking the negative logarithm of both sides of Equation 17.5, we have

$$-\log[H^+] = -\log\left(K_a \frac{[HA]}{[A^-]}\right) = -\log K_a - \log \frac{[HA]}{[A^-]}$$



▲ **Figure 17.2 Buffer action.** The pH of an  $HF/F^-$  buffered solution changes by only a small amount in response to addition of an acid or base.

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

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

(Remember the logarithm rules in Appendix A.2, if you are not sure how this calculation works.)

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  $[\text{base}] = [\text{acid}]$ , we have  $\text{pH} = \text{p}K_a$ .

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 initial concentrations of the acid and base components of the buffer directly in Equation 17.9, as seen in Sample Exercise 17.3. However, the assumption that the initial concentrations of the acid and base components in the buffer are equal to the equilibrium concentrations is just that: an assumption. There may be times when you will need to be more careful, as seen in Sample Exercise 17.4.

### 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  $\text{HC}_3\text{H}_5\text{O}_3$ ,  $\text{Na}^+$ , and  $\text{C}_3\text{H}_5\text{O}_3^-$ . The  $\text{Na}^+$  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:

	$\text{CH}_3\text{CH}(\text{OH})\text{COOH}(aq) \rightleftharpoons \text{H}^+(aq) + \text{CH}_3\text{CH}(\text{OH})\text{COO}^-(aq)$		
Initial (M)	0.12	0	0.10
Change (M)	$-x$	$+x$	$+x$
Equilibrium (M)	$(0.12 - x)$	$x$	$(0.10 + x)$

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:

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

Then, we can solve for pH:

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

Alternatively, we can use the Henderson-Hasselbalch equation with the initial concentrations of acid and base to calculate pH directly:

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



**Practice Exercise**

If the pH of a buffer solution is equal to the  $pK_a$  of the acid in the buffer, what does this tell you about the relative concentrations of the acid and conjugate base forms of the buffer components?

(a) The acid concentration must be zero. (b) The base concentration must be zero. (c) The acid and base concentrations must be equal. (d) The acid and base concentrations must be equal to the  $K_a$ . (e) The base concentration must be 2.3 times as large as the acid concentration.

**Sample Exercise 17.4****Calculating pH When the Henderson–Hasselbalch Equation May Not Be Accurate**

Calculate the pH of a buffer that initially contains  $1.00 \times 10^{-3} M$   $CH_3COOH$  and  $1.00 \times 10^{-4} M$   $CH_3COONa$  in the following two ways: (i) using the Henderson–Hasselbalch equation and (ii) making no assumptions about quantities (which means you will need to use the quadratic equation). The  $K_a$  of  $CH_3COOH$  is  $1.80 \times 10^{-5}$ .

**SOLUTION**

**Analyze** We are asked to calculate the pH of a buffer two different ways. We know the initial concentrations of the weak acid and its conjugate base, and the  $K_a$  of the weak acid.

**Plan** We will first use the Henderson–Hasselbalch equation, which relates  $pK_a$  and ratio of acid–base concentrations to the pH. This will be straightforward. Then, we will redo the calculation making

no assumptions about any quantities, which means we will need to write out the initial/change/equilibrium concentrations, as we have done before. In addition, we will need to solve for quantities using the quadratic equation (since we cannot make assumptions about unknowns being small).

**Solve**

(i) The Henderson–Hasselbalch equation is:

$$pH = pK_a + \log \frac{[\text{base}]}{[\text{acid}]}$$

We know the  $K_a$  of the acid ( $1.8 \times 10^{-5}$ ), so we know  $pK_a$  ( $pK_a = -\log K_a = 4.74$ ). We know the initial concentrations of the base, sodium acetate, and the acid, acetic acid, which we will assume are the same as the equilibrium concentrations.

Therefore, we have:

$$\begin{aligned} pH &= 4.74 + \log \frac{(1.00 \times 10^{-4})}{(1.00 \times 10^{-3})} \\ &= 4.74 - 1.00 = 3.74 \end{aligned}$$

(ii) Now we will redo the calculation, without making any assumptions at all. We will solve for  $x$ , which represents the  $H^+$  concentration at equilibrium, in order to calculate pH.

	$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$		
Initial (M)	$1.00 \times 10^{-3}$	$1.00 \times 10^{-4}$	0
Change (M)	$-x$	$+x$	$+x$
Equilibrium (M)	$(1.00 \times 10^{-3} - x)$	$(1.00 \times 10^{-4} + x)$	$x$

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

$$\frac{(1.00 \times 10^{-4} + x)(x)}{(1.00 \times 10^{-3} - x)} = 1.8 \times 10^{-5}$$

$$1.00 \times 10^{-4}x + x^2 = 1.8 \times 10^{-5}(1.00 \times 10^{-3} - x)$$

$$x^2 + 1.00 \times 10^{-4}x = 1.8 \times 10^{-8} - 1.8 \times 10^{-5}x$$

$$x^2 + 1.18 \times 10^{-4}x - 1.8 \times 10^{-8} = 0$$

$$x = \frac{-1.18 \times 10^{-4} \pm \sqrt{(1.18 \times 10^{-4})^2 - 4(1)(-1.8 \times 10^{-8})}}{2(1)}$$

$$= \frac{-1.18 \times 10^{-4} \pm \sqrt{8.5924 \times 10^{-8}}}{2}$$

$$= 8.76 \times 10^{-5} = [H^+]$$

$$pH = 4.06$$

*Continued*

**Comment** In Sample Exercise 17.3, the calculated pH is the same whether we solve exactly using the quadratic equation or make the simplifying assumption that the equilibrium concentrations of acid and base are equal to their initial concentrations. The simplifying assumption works because the concentrations of the acid–base conjugate pair are both a thousand times larger than  $K_a$ . In this Sample Exercise, the acid–base conjugate pair concentrations are only 10–100 as large as  $K_a$ . Therefore, we cannot assume that  $x$  is small compared to the initial concentrations (that is, that the initial concentrations are essentially equal to the equilibrium concentrations). The best answer to this Sample Exercise is  $\text{pH} = 4.06$ , obtained without assuming  $x$  is small. Therefore, we see that the assumptions behind the

Henderson–Hasselbalch equation are not valid when the initial concentration of the weak acid (or base) is small compared to its  $K_a$  (or  $K_b$ ).

### Practice Exercise

A buffer is made with sodium acetate ( $\text{CH}_3\text{COONa}$ ) and acetic acid ( $\text{CH}_3\text{COOH}$ ); the  $K_a$  for acetic acid is  $1.80 \times 10^{-5}$ . The pH of the buffer is 3.98. What is the ratio of the equilibrium concentration of sodium acetate to that of acetic acid? (a)  $-0.760$  (b)  $0.174$  (c)  $0.840$  (d)  $5.75$  (e) Not enough information is given to answer this question.

In Sample Exercise 17.3 we calculated the pH of a buffered solution. Often we will need to work in the opposite direction by calculating the amounts of the acid and its conjugate base needed to achieve a specific pH. This calculation is illustrated in Sample Exercise 17.5.



## Sample Exercise 17.5

### Preparing a Buffer

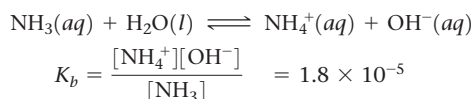
How many moles of  $\text{NH}_4\text{Cl}$  must be added to 2.0 L of 0.10 M  $\text{NH}_3$  to form a buffer whose pH is 9.00? (Assume that the addition of  $\text{NH}_4\text{Cl}$  does not change the volume of the solution.)

### SOLUTION

**Analyze** We are asked to determine the amount of  $\text{NH}_4^+$  ion required to prepare a buffer of a specific pH.

**Plan** The major species in the solution will be  $\text{NH}_4^+$ ,  $\text{Cl}^-$ , and  $\text{NH}_3$ . Of these, the  $\text{Cl}^-$  ion is a spectator (it is the conjugate base of a strong acid). Thus, the  $\text{NH}_4^+/\text{NH}_3$  conjugate acid–base pair will determine the pH of the buffer. The equilibrium relationship

between  $\text{NH}_4^+$  and  $\text{NH}_3$  is given by the base-dissociation reaction for  $\text{NH}_3$ :



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:

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

Because  $K_b$  is small and the common ion  $[\text{NH}_4^+]$  is present, the equilibrium concentration of  $\text{NH}_3$  essentially equals its initial concentration:

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

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

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

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

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

**Comment** Because  $\text{NH}_4^+$  and  $\text{NH}_3$  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  $\text{NH}_4^+$  from the value of  $\text{p}K_b$  for  $\text{NH}_3$ . 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 number of grams of ammonium chloride that must be added to 2.00 L of a 0.500 M ammonia solution to obtain a buffer of  $\text{pH} = 9.20$ . Assume the volume of the solution does not change as the solid is added.  $K_b$  for ammonia is  $1.80 \times 10^{-5}$ .  
(a) 60.7 g (b) 30.4 g (c) 1.52 g (d) 0.568 g  
(e)  $1.59 \times 10^{-5}$  g

## 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 used to prepare the buffer. According to Equation 17.5, for example, the pH of a 1 L solution that is 1 M in  $\text{CH}_3\text{COOH}$  and 1 M in  $\text{CH}_3\text{COONa}$  is the same as the pH of a 1 L solution that is 0.1 M in  $\text{CH}_3\text{COOH}$  and 0.1 M in  $\text{CH}_3\text{COONa}$ . The first solution has a greater buffering capacity, however, because it contains more  $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COO}^-$ .

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  $\pm 1$  pH unit of  $\text{p}K_a$*  (that is, a range of  $\text{pH} = \text{p}K_a \pm 1$ ).

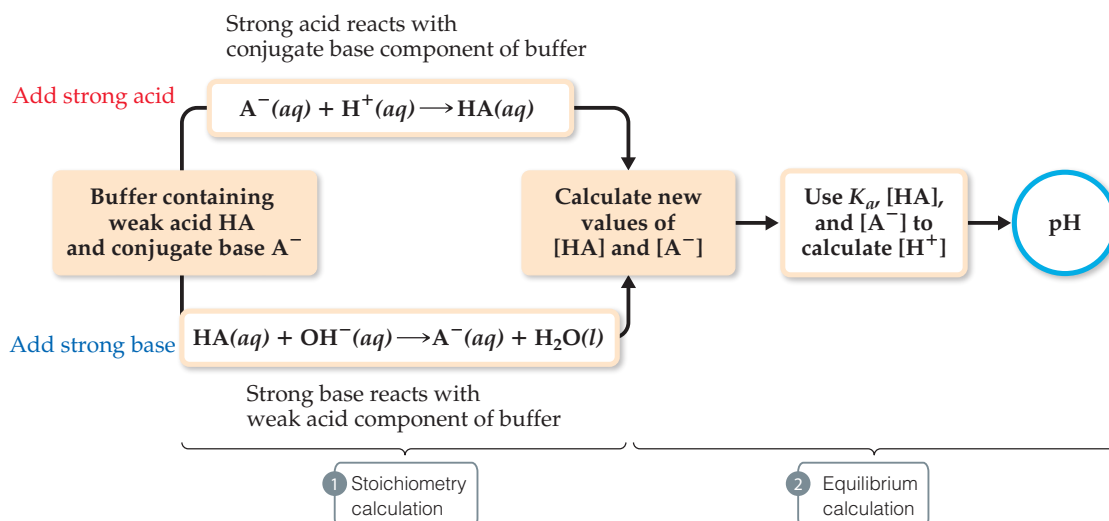
## Addition of Strong Acids or Bases to Buffers

Let's now consider in a more quantitative way how a buffered solution responds to addition of a strong acid or base. In this discussion, it is important to understand that *neutralization reactions between strong acids and weak bases proceed essentially to completion, as do those between strong bases and weak acids*. This is because water is a product of the reaction, and you have an equilibrium constant of  $1/K_w = 10^{14}$  in your favor when making water. 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 HA and its conjugate base  $\text{A}^-$ . When a strong acid is added to this buffer, the added  $\text{H}^+$  is consumed by  $\text{A}^-$  to produce HA; thus,  $[\text{HA}]$  increases and  $[\text{A}^-]$  decreases. (See Equation 17.7.) Upon addition of a strong base, the added  $\text{OH}^-$  is consumed by HA to produce  $\text{A}^-$ ; in this case  $[\text{HA}]$  decreases and  $[\text{A}^-]$  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  $[\text{HA}]$  and  $[\text{A}^-]$ . This step is a *limiting reactant stoichiometry calculation*.
2. Use the calculated values of  $[\text{HA}]$  and  $[\text{A}^-]$  along with  $K_a$  to calculate  $[\text{H}^+]$ . This step is an *equilibrium calculation* and is most easily done using the Henderson–Hasselbalch equation (if the concentrations of the weak acid–base pair are very large compared to  $K_a$  for the acid).



▲ Figure 17.3 Calculating the pH of a buffer after addition of a strong acid or strong base.

## Sample Exercise 17.6

## Calculating pH Changes in Buffers

A buffer is made by adding 0.300 mol  $\text{CH}_3\text{COOH}$  and 0.300 mol  $\text{CH}_3\text{COONa}$  to enough water to make 1.000 L of solution. The pH of the buffer is 4.74 (Sample Exercise 17.1). (a) Calculate the pH of this solution after 5.0 mL of 4.0 M  $\text{NaOH}(aq)$  solution is added. (b) For comparison, calculate the pH of a solution made by adding 5.0 mL of 4.0 M  $\text{NaOH}(aq)$  solution to 1.000 L of pure water.

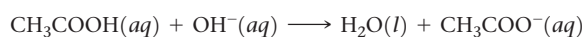
## SOLUTION

**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 with the pH that would result if we were to add the same amount of strong base to pure water.

**Plan** Solving this problem involves the two steps outlined in Figure 17.3. First we do a stoichiometry calculation to determine how the added  $\text{OH}^-$  affects the buffer composition. Then we use the resulting buffer composition and either the Henderson–Hasselbalch equation or the equilibrium-constant expression for the buffer to determine the pH.

## Solve

(a) **Stoichiometry Calculation:** The  $\text{OH}^-$  provided by  $\text{NaOH}$  reacts with  $\text{CH}_3\text{COOH}$ , the weak acid component of the buffer. Since volumes are changing, it is prudent to figure out how many moles of reactants and products would be produced, then divide by the final volume later to obtain concentrations. Prior to this neutralization reaction, there are 0.300 mol each of  $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COO}^-$ . The amount of base added is  $0.0050 \text{ L} \times 4.0 \text{ mol/L} = 0.020 \text{ mol}$ . Neutralizing the 0.020 mol  $\text{OH}^-$  requires 0.020 mol of  $\text{CH}_3\text{COOH}$ . Consequently, the amount of  $\text{CH}_3\text{COOH}$  decreases by 0.020 mol, and the amount of the product of the neutralization,  $\text{CH}_3\text{COO}^-$ , 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  $\text{OH}^-$ :



Before reaction (mol)	0.300	0.020	—	0.300
Change (limiting reactant) (mol)	−0.020	−0.020	—	+0.020
After reaction (mol)	0.280	0	—	0.320

**Equilibrium Calculation:** We now turn our attention to the equilibrium for the ionization of acetic acid, the relationship that determines the buffer pH:



Using the quantities of  $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COO}^-$  remaining in the buffer after the reaction with strong base, we determine the pH using the Henderson–Hasselbalch equation.

The volume of the solution is now  $1.000 \text{ L} + 0.0050 \text{ L} = 1.005 \text{ L}$  due to addition of the  $\text{NaOH}$  solution:

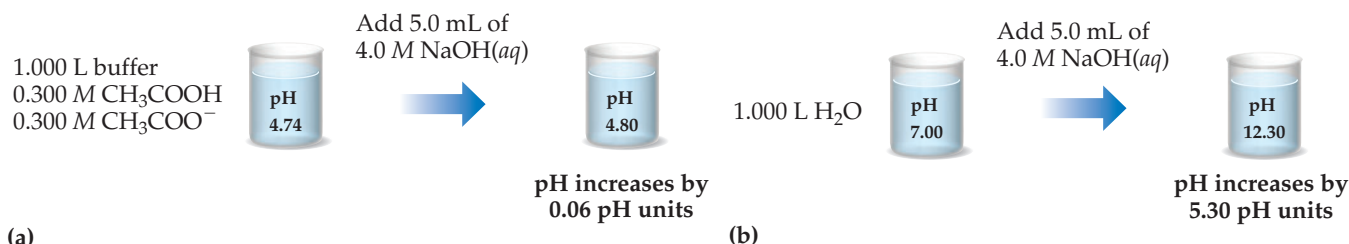
$$\text{pH} = 4.74 + \log \frac{0.320 \text{ mol}/1.005 \text{ L}}{0.280 \text{ mol}/1.005 \text{ L}} = 4.80$$

(b) To determine the pH of a solution made by adding 0.020 mol of  $\text{NaOH}$  to 1.000 L of pure water, we first determine the concentration of  $\text{OH}^-$  ions in solution:

$$[\text{OH}^-] = 0.020 \text{ mol}/1.005 \text{ L} = 0.020 \text{ M}$$

We use this value in Equation 16.18 to calculate pOH and then use our calculated pOH value to obtain pH:

$$\begin{aligned} \text{pOH} &= -\log[\text{OH}^-] = -\log(0.020) = +1.70 \\ \text{pH} &= 14 - (+1.70) = 12.30 \end{aligned}$$



▲ Figure 17.4 Effect of adding a strong base to (a) a buffered solution and to (b) water.

**Comment** Note that the small amount of added NaOH changes the pH of water significantly. In contrast, the pH of the buffer changes very little when the NaOH is added, as summarized in [Figure 17.4](#).

### Practice Exercise

Which of these statements is true? (a) If you add strong acid or base to a buffer, the pH will never change. (b) In order

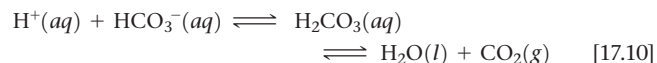
to do calculations in which strong acid or base is added to a buffer, you only need to use the Henderson–Hasselbalch equation. (c) Strong bases react with strong acids, but not weak acids. (d) If you add a strong acid or base to a buffer, the buffer's  $pK_a$  or  $pK_b$  will change. (e) In order to do calculations in which a strong acid or base is added to a buffer, you need to calculate the amounts of substances from the neutralization reaction and then equilibrate.

## CHEMISTRY AND LIFE Blood as a Buffered Solution

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

Human blood has a normal pH of 7.35 to 7.45. Any deviation from this 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 metabolism generates several acids in the body.

The major buffer system used to control blood pH is the *carbonic acid–bicarbonate buffer system*. Carbonic acid ( $\text{H}_2\text{CO}_3$ ) and bicarbonate ion ( $\text{HCO}_3^-$ ) are a conjugate acid–base pair. In addition, carbonic acid decomposes 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 diprotic, the carbonate ion ( $\text{CO}_3^{2-}$ ) is unimportant in this system. Second, one component of this equilibrium,  $\text{CO}_2$ , is a gas, which provides a mechanism for the body to adjust the equilibria. Removal of  $\text{CO}_2$  via exhalation shifts the equilibria to the right, consuming  $\text{H}^+$  ions. Third, the buffer system in blood operates at pH 7.4, which is fairly far removed from the  $pK_{a1}$  value of  $\text{H}_2\text{CO}_3$  (6.1 at physiological temperatures). For the buffer to have a pH of 7.4, the ratio  $[\text{base}]/[\text{acid}]$  must be about 20. In normal blood plasma, the concentrations of  $\text{HCO}_3^-$  and  $\text{H}_2\text{CO}_3$  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. When the concentration of  $\text{CO}_2$  rises, the equilibrium concentrations in Equation 17.10 shift to the left, which leads to the formation of more  $\text{H}^+$  and a drop in pH. This change is detected by receptors in the brain that trigger a reflex to breathe faster and deeper, increasing the rate at which  $\text{CO}_2$  is expelled from the lungs and thereby shifting the equilibrium concentrations back to the right. When the blood pH becomes too high, the kidneys remove  $\text{HCO}_3^-$  from the blood. This shifts the equilibrium concentrations to the left, increasing the concentration of  $\text{H}^+$ . As a result, the pH decreases.

Regulation of blood pH relates directly to the effective transport of  $\text{O}_2$  throughout the body. The protein hemoglobin, found in red blood cells ([Figure 17.5](#)), carries oxygen. Hemoglobin (Hb) reversibly

binds both  $\text{O}_2$  and  $\text{H}^+$ . These two substances compete for the Hb, which can be represented approximately by the equilibrium



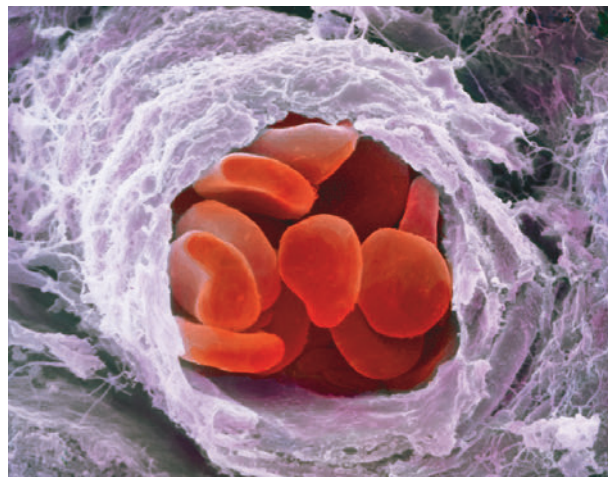
Oxygen enters the blood through the lungs, where it passes into the red blood cells and binds to Hb. When the blood reaches tissue in which the concentration of  $\text{O}_2$  is low, the equilibrium concentrations in Equation 17.11 shift to the left and  $\text{O}_2$  is released.

During periods of strenuous exertion, three factors work together to ensure delivery of  $\text{O}_2$  to active tissues. The role of each factor can be understood by applying Le Châtelier's principle to Equation 17.11:

1.  $\text{O}_2$  is consumed, causing the equilibrium concentrations to shift to the left, releasing more  $\text{O}_2$ .
2. Large amounts of  $\text{CO}_2$  are produced by metabolism, which increases  $[\text{H}^+]$  and causes the equilibrium concentrations to shift to the left, releasing  $\text{O}_2$ .
3. Body temperature rises. Because Equation 17.11 is exothermic, the increase in temperature shifts the equilibrium concentrations to the left, releasing  $\text{O}_2$ .

In addition to the factors causing release of  $\text{O}_2$  to tissues, the decrease in pH stimulates an increase in breathing rate, which furnishes more  $\text{O}_2$  and eliminates  $\text{CO}_2$ . Without this elaborate series of equilibrium shifts and pH changes, the  $\text{O}_2$  in tissues would be rapidly depleted, making further activity impossible. Under such conditions, the buffering capacity of the blood and the exhalation of  $\text{CO}_2$  through the lungs are essential to keep the pH from dropping too low, thereby triggering acidosis.

### Related Exercise: 17.66



**Figure 17.5** Red blood cells. A scanning electron micrograph of red blood cells traveling through a small branch of an artery. The red blood cells are approximately 0.010 mm in diameter.



## Self-Assessment Exercises

- 17.5** Which of the following pairs of substances will function as a buffer?
- (a) HBr and  $\text{Br}^-$   
 (b)  $\text{H}_3\text{PO}_4$  and  $\text{PO}_4^{3-}$   
 (c)  $\text{CH}_3\text{COOH}$  and  $\text{NO}_3^-$   
 (d)  $\text{CH}_3\text{NH}_2$  and  $\text{CH}_3\text{NH}_3^+$
- 17.6** The  $K_a$  values for methanoic acid ( $\text{HCOOH}$ ) and carbonic acid ( $\text{H}_2\text{CO}_3$ ) are  $1.77 \times 10^{-4}$  and  $4.3 \times 10^{-7}$ , respectively. Which one would be more suitable for use in a solution buffered at  $\text{pH} = 7.00$ ?
- (a)  $\text{HCOOH}$   
 (b)  $\text{H}_2\text{CO}_3$
- 17.7** Starting with the same buffer as that used in sample exercise 17.6 (1.000 L that is 0.300 M in both  $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COONa}$ ,  $\text{p}K_a = 4.74$ ), calculate the pH after the addition of 0.020 mol of  $\text{HCl}$  (g). Assume there is no change in volume of the buffer as the  $\text{HCl}$  dissolves.
- (a) 1.70  
 (b) 4.68  
 (c) 4.80  
 (d) 5.62

## Exercises

- 17.8** Which of the following solutions is a buffer? (a) A solution made by mixing 50 mL of 0.200 M formic acid ( $\text{HCOOH}$ ) and 250 mL of 0.200 M  $\text{KOH}$ , (b) A solution made by mixing 50 mL of 0.200 M formic acid ( $\text{HCOOH}$ ) and 25 mL of 0.200 M nitric acid ( $\text{HNO}_3$ ), (c) A solution made by mixing 50 mL of 0.200 M potassium formate ( $\text{HCOOK}$ ) and 25 mL of 0.200 M  $\text{KNO}_3$ , (d) A solution made by mixing 50 mL of 0.200 M formic acid ( $\text{HCOOH}$ ), and 25 mL of 0.200 M  $\text{KOH}$ .
- 17.9** (a) Calculate the pH of a buffer that is 0.125 M in  $\text{NaHCO}_3$  and 0.095 M in  $\text{Na}_2\text{CO}_3$ . (b) Calculate the pH of a solution formed by mixing 25 mL of 0.25 M  $\text{NaHCO}_3$  with 75 mL of 0.15 M  $\text{Na}_2\text{CO}_3$ .
- 17.10** A buffer is prepared by adding 3.5 g of ammonium chloride ( $\text{NH}_4\text{Cl}$ ) to 100 mL of 1.00 M  $\text{NH}_3$  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 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.
- 17.11** You are asked to prepare a  $\text{pH} = 3.00$  buffer starting from 2.00 L of 0.025 M solution of benzoic acid ( $\text{C}_6\text{H}_5\text{COOH}$ ) and any amount you need of sodium benzoate ( $\text{C}_6\text{H}_5\text{COONa}$ ). (a) What is the pH of the benzoic acid solution prior to adding sodium benzoate? (b) How many grams of sodium benzoate should be added to prepare the buffer? Neglect the small volume change that occurs when the sodium benzoate is added.
- 17.12** A buffer contains 0.30 mol of propanoic acid ( $\text{C}_2\text{H}_5\text{COOH}$ ) and 0.25 mol of potassium propanoate ( $\text{C}_2\text{H}_5\text{COOK}$ ) in 1.80 L. (a) What is the pH of this buffer? (b) What is the pH of the buffer after the addition of 0.10 mol of  $\text{NaOH}$ ? (c) What is the pH of the buffer after the addition of 0.10 mol of  $\text{HCl}$ ?
- 17.13** A buffer, consisting of  $\text{H}_2\text{PO}_4^-$  and  $\text{HPO}_4^{2-}$ , 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 10.0 g of  $\text{KH}_2\text{PO}_4$  and 10.0 g of  $\text{K}_2\text{HPO}_4$  per 0.500 L of solution?
- 17.14** You have to prepare a  $\text{pH} = 4.00$  buffer, and you have the following 0.20 M solutions available:  $\text{HCOOH}$ ,  $\text{CH}_3\text{COOH}$ ,  $\text{HCN}$ ,  $\text{KCH}_3\text{COO}$ ,  $\text{KHCOO}$ , and  $\text{KCN}$ . Which solutions would you use? How many milliliters of each solution would you use to make approximately 2 L of the buffer?

17.5 (d) 17.6 (b) 17.7 (b)

## Answers to Self-Assessment Exercises

## 17.3 | Acid–Base Titrations





The word *titration* originated in mid-sixteenth century France, where it referred to the proportion of gold or silver in coins. While the technique may seem old fashioned in these days of instrumental analysis, it can be an accurate and quick way to determine the concentration of a solution. In addition, plotting a titration curve can give the  $K_a$  of the analyte, and the shape of the curve tells us if we have a weak or strong acid/base present.

By the end of this section, you should be able to

- Calculate the pH at any point for an acid–base titration curve.
- Estimate the  $pK_a$  for monoprotic or polyprotic acids from their titration curves.

Titration is a procedure in which one reactant is slowly added into a solution of another reactant, while equilibrium concentrations along the way are monitored. There are two main reasons to do titrations:

- to determine the concentration of one of the reactants
- to determine the equilibrium constant for the reaction

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 (Figure 17.6), producing a **pH titration curve**, a graph of the pH as a function of the volume of titrant added. The shape of the titration curve makes it possible to determine the equivalence point. The 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.

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.

## Strong Acid–Strong Base Titrations

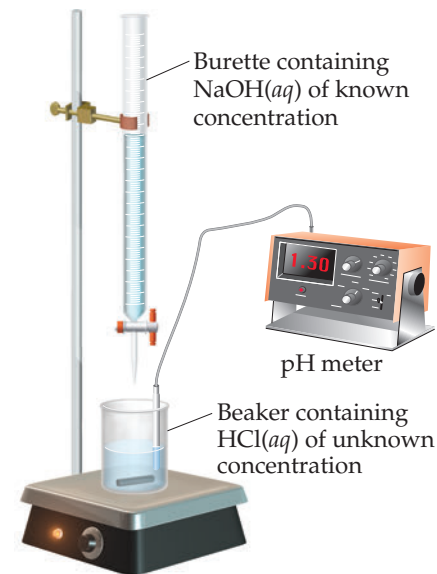
The titration curve produced when a strong base is added to a strong acid has the general shape shown in Figure 17.7, which depicts the pH change that occurs as 0.100 M NaOH is added to 50.0 mL of 0.100 M HCl. The pH can be calculated at various stages of the titration. To help understand these calculations, we can divide the curve into four regions:

- 1. Initial pH:** 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,  $[H^+] = 0.100\text{ M}$  and  $pH = -\log(0.100) = 1.000$ . Thus, the initial pH is low.
- 2. Between initial pH and equivalence point:** As NaOH is added, the pH increases slowly at first and then rapidly in the vicinity of the equivalence point. The pH before the equivalence point is determined by the concentration of acid not yet neutralized. This calculation is illustrated in Sample Exercise 17.7(a).
- 3. Equivalence point:** At the equivalence point an equal number of moles of 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  $Cl^-$ ) are neither acids nor bases and, therefore, have no appreciable effect on pH.
- 4. After equivalence point:** The pH of the solution after the equivalence point is determined by the concentration of excess NaOH in the solution. This calculation is illustrated in Sample Exercise 17.7(b).

Titration of a solution of a strong base with a solution of a strong acid yields an analogous curve of pH versus added acid. In this case, however, the pH is high at the outset

### Go Figure

In which direction do you expect the pH to change as NaOH is added to the HCl solution?

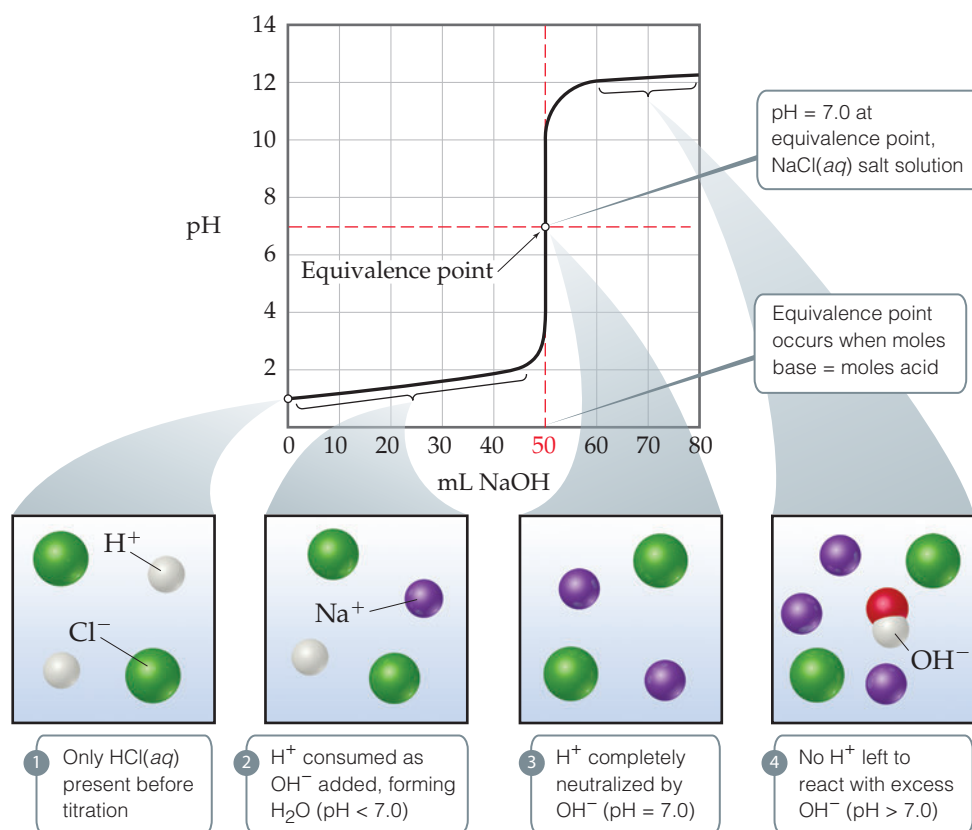


▲ Figure 17.6 Measuring pH during a titration.



## Go Figure

What volume of NaOH(aq) would be needed to reach the equivalence point if the concentration of the added base were 0.200 M?



**Figure 17.7** Titration of a strong acid with a strong base. The pH curve for titration of 50.0 mL of a 0.100 M solution of hydrochloric acid with a 0.100 M solution of NaOH(aq). For clarity, water molecules have been omitted from the molecular art.



## Sample Exercise 17.7

## Calculations for a Strong Acid–Strong Base Titration

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

## 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, H<sup>+</sup>(aq) reacts with OH<sup>-</sup>(aq) to form H<sub>2</sub>O. Both Na<sup>+</sup> and Cl<sup>-</sup> 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<sup>+</sup> were originally present and how many moles of OH<sup>-</sup> were added. We can then calculate how many moles of each ion remain after the neutralization reaction. To calculate [H<sup>+</sup>], 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. Therefore, it is best to deal with moles first, and then convert to molarities using total solution volumes (volume of acid plus volume of base). (b) We proceed in the same way as in part (a) except we are now past the equivalence point and have more OH<sup>-</sup> in the solution than H<sup>+</sup>.

## Solve

- (a) The number of moles of H<sup>+</sup> in the original HCl solution is given by the product of the volume of the solution and its molarity:

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

Likewise, the number of moles of OH<sup>-</sup> 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 reached the equivalence point, there are more moles of  $\text{H}^+$  present than  $\text{OH}^-$ . Therefore,  $\text{OH}^-$  is the limiting reactant. Each mole of  $\text{OH}^-$  reacts with 1 mol of  $\text{H}^+$ . Using the convention introduced in Sample Exercise 17.6, we have:

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

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 volume in the titration flask is:

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

Thus, the concentration of  $\text{H}^+(aq)$  in the flask is:

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

The corresponding pH is:

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

- (b) 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.

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

In this case, the volume in the titration flask is: Hence, the concentration of  $\text{OH}^-(aq)$  in the flask is:

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

and we have:

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

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

**Comment** Note that the pH increased by only two pH units, from 1.00 (Figure 17.7) to 3.00, after the first 49.0 mL of NaOH solution was added, but jumped by eight pH units, from 3.00 to 11.00, as 2.0 mL of base solution was added near the equivalence point. Such a rapid rise in pH near the equivalence point is a characteristic of titrations involving strong acids and strong bases.

### Practice Exercise

An acid–base titration is performed: 250.0 mL of an unknown concentration of HCl ( $aq$ ) is titrated to the equivalence

point with 36.7 mL of a 0.1000 M aqueous solution of NaOH. Which of the following statements is *not* true of this titration?

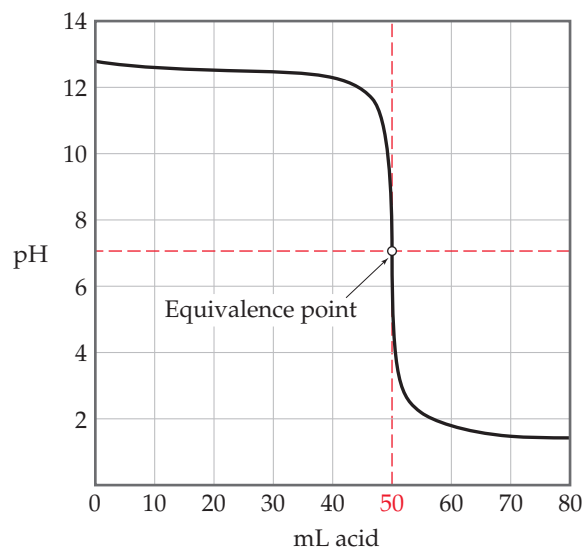
- (a) The HCl solution is less concentrated than the NaOH solution. (b) The pH is less than 7 after adding 25 mL of NaOH solution. (c) The pH at the equivalence point is 7.00. (d) If an additional 1.00 mL of NaOH solution is added beyond the equivalence point, the pH of the solution is more than 7.00. (e) At the equivalence point, the  $\text{OH}^-$  concentration in the solution is  $3.67 \times 10^{-3} \text{ M}$ .

of the titration and low at its completion (Figure 17.8). The pH at the equivalence point is still 7.0 (at 25 °C), just like the strong acid–strong base titration.

## Weak Acid–Strong Base Titrations

The curve for titration of a weak acid by a strong base is similar to the curve in Figure 17.7. Consider, for example, the curve for titration of 50.0 mL of 0.100 M acetic acid with 0.100 M NaOH shown in Figure 17.9. We can calculate the pH at points along this curve, using principles we discussed earlier, which means again dividing the curve into four regions:

- Initial pH:** We use  $K_a$  to calculate this pH, as shown in Section 16.5. The calculated pH of 0.100 M  $\text{CH}_3\text{COOH}$  is 2.89.
- Between initial pH and equivalence point:** Prior to reaching the equivalence point, the acid is being neutralized, and its conjugate base is being formed:

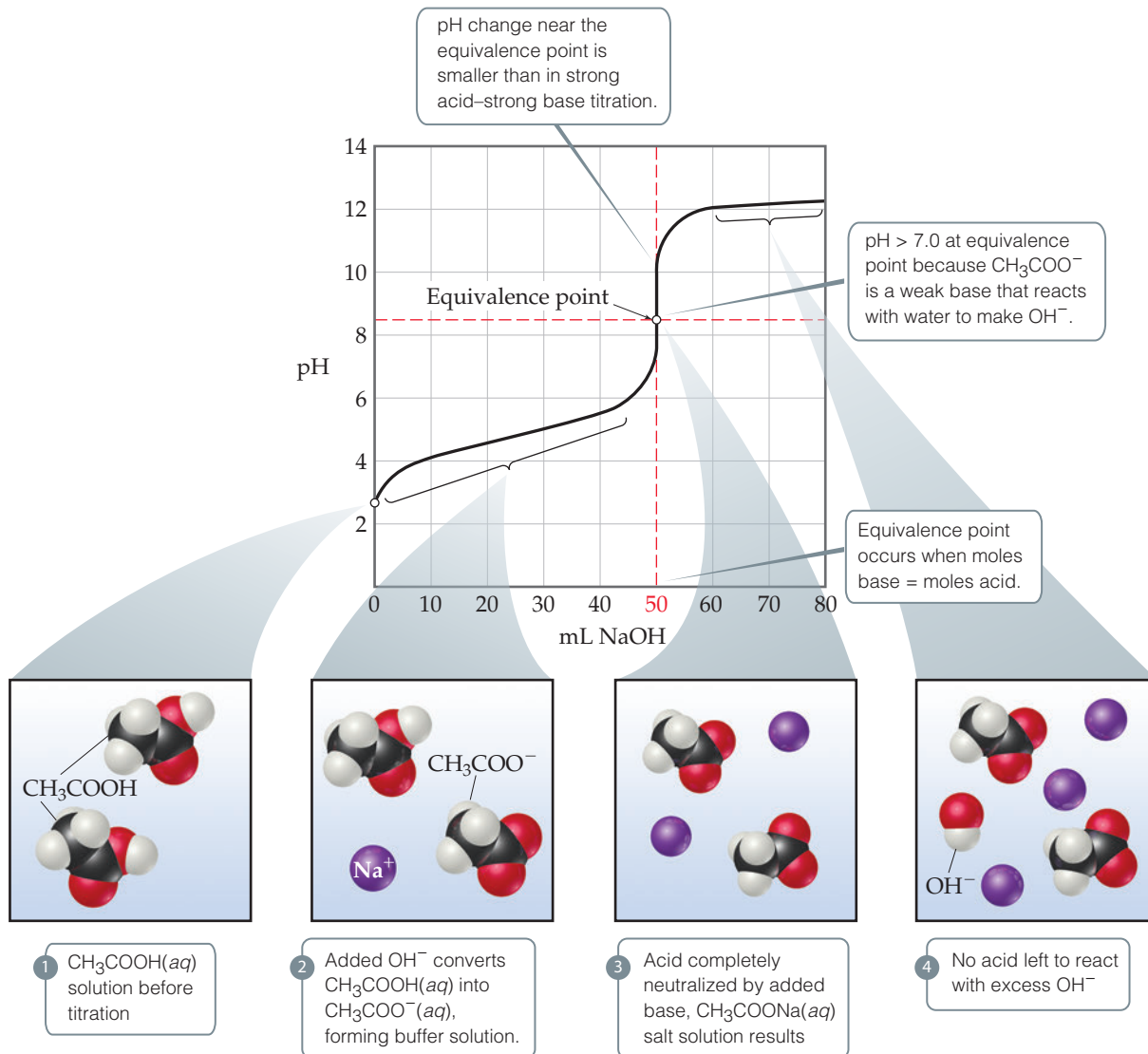


▲ **Figure 17.8** Titration of a strong base with a strong acid. The pH curve for titration of 50.0 mL of a 0.100 M solution of a strong base with a 0.100 M solution of a strong acid.



## Go Figure

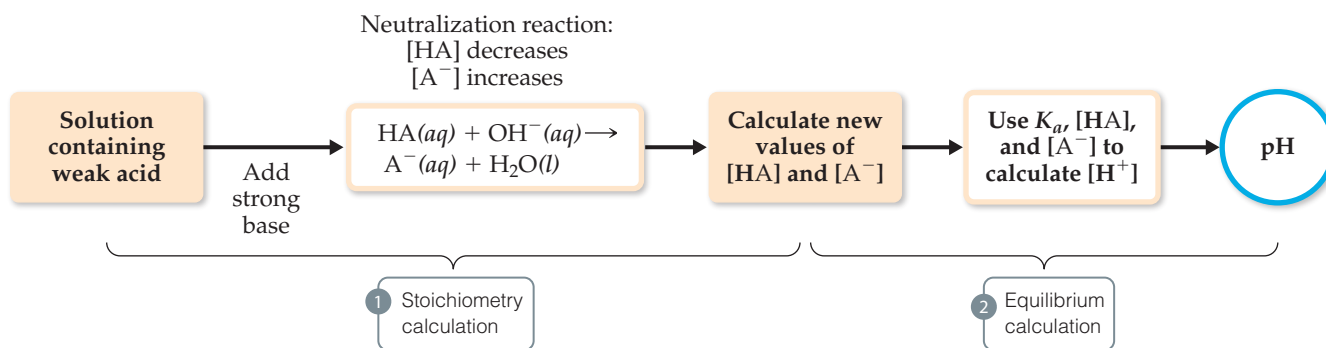
If the acetic acid being titrated here were replaced by hydrochloric acid, would the amount of base needed to reach the equivalence point change? Would the pH at the equivalence point change?



**▲ Figure 17.9 Titration of a weak acid with a strong base.** The pH curve for titration of 50.0 mL of a 0.100 M solution of acetic acid with a 0.100 M solution of  $\text{NaOH}(aq)$ . For clarity, water molecules have been omitted from the molecular art.

Thus, the solution contains a mixture of  $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COO}^-$ . Calculating the pH in this region involves two steps. First, we consider the neutralization reaction between  $\text{CH}_3\text{COOH}$  and  $\text{OH}^-$  to determine  $[\text{CH}_3\text{COOH}]$  and  $[\text{CH}_3\text{COO}^-]$ . 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 17.8.

**3. Equivalence point:** The equivalence point is reached when 50.0 mL of 0.100 M  $\text{NaOH}$  has been added to the 50.0 mL of 0.100 M  $\text{CH}_3\text{COOH}$ . At this point, the  $5.00 \times 10^{-3}$  mol of  $\text{NaOH}$  completely reacts with the  $5.00 \times 10^{-3}$  mol of  $\text{CH}_3\text{COOH}$  to form  $5.00 \times 10^{-3}$  mol of  $\text{CH}_3\text{COONa}$ . The  $\text{Na}^+$  ion of this salt has no significant effect on the pH. The  $\text{CH}_3\text{COO}^-$  ion, however, is a weak base whose reaction with water cannot be neglected, and the pH at the equivalence point is therefore greater than 7. In general, 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.



▲ **Figure 17.10** Procedure for calculating pH when a weak acid is partially neutralized by a strong base.

## Sample Exercise 17.8

### Calculations 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 CH<sub>3</sub>COOH ( $K_a = 1.8 \times 10^{-5}$ ).

#### 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 CH<sub>3</sub>COOH and CH<sub>3</sub>COO<sup>−</sup> present after the neutralization

reaction (the stoichiometry calculation). We then calculate pH using  $K_a$ , [CH<sub>3</sub>COOH], and [CH<sub>3</sub>COO<sup>−</sup>] (the equilibrium calculation).

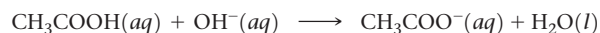
#### Solve

**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  $4.50 \times 10^{-3}$  mol of NaOH consumes  $4.50 \times 10^{-3}$  mol of CH<sub>3</sub>COOH:



Before reaction (mol)	$5.00 \times 10^{-3}$	$4.50 \times 10^{-3}$	0	—
Change (limiting reactant) (mol)	$-4.50 \times 10^{-3}$	$-4.50 \times 10^{-3}$	$+4.50 \times 10^{-3}$	
After reaction (mol)	$0.50 \times 10^{-3}$	0	$4.50 \times 10^{-3}$	—

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 CH<sub>3</sub>COOH and CH<sub>3</sub>COO<sup>−</sup> 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 CH<sub>3</sub>COOH and CH<sub>3</sub>COO<sup>−</sup> must obey the equilibrium expression for CH<sub>3</sub>COOH:

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

Solving for [H<sup>+</sup>] gives:

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

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

Continued

**Comment** We could have solved for pH equally well using the Henderson–Hasselbalch equation in the last step.

► **Practice Exercise**

If you think carefully about what happens during the course of a weak acid–strong base titration, you can learn some very interesting things. For example, let’s look back at Figure 17.9 and pretend

you did not know that acetic acid was the acid being titrated. You can figure out the  $pK_a$  of a weak acid just by thinking about the definition of  $K_a$  and looking at the right place on the titration curve! Which of the following choices is the best way to do this?

(a) At the equivalence point,  $pH = pK_a$ . (b) Halfway to the equivalence point,  $pH = pK_a$ . (c) Before any base is added,  $pH = pK_a$ . (d) At the top of the graph with excess base added,  $pH = pK_a$ .

The procedure for calculating the pH of the solution of a weak base is described in Section 16.6 and is shown in Sample Exercise 17.9.

- 4. After equivalence point (excess base):** In this region,  $[OH^-]$  from the reaction of  $CH_3COO^-$  with water is negligible relative to  $[OH^-]$  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 illustrated in Sample Exercise 17.7(b). Thus, the addition of 51.0 mL of 0.100 M NaOH to 50.0 mL of

## Sample Exercise 17.9

### 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  $CH_3COOH$  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, a conjugate base that can react with water, we expect the pH at the equivalence point to be greater than 7.

**Plan** The initial number of moles of acetic acid equals 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  $[CH_3COO^-]$ .

### Solve

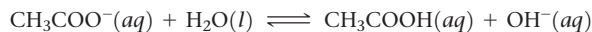
The number of moles of acetic acid in the initial solution is obtained from the volume and molarity of the solution:

$$\begin{aligned}\text{Moles} &= M \times V = (0.100 \text{ mol/L})(0.0500 \text{ L}) \\ &= 5.00 \times 10^{-3} \text{ mol } CH_3COOH\end{aligned}$$

Hence,  $5.00 \times 10^{-3}$  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:

$$[CH_3COO^-] = \frac{5.00 \times 10^{-3} \text{ mol}}{0.1000 \text{ L}} = 0.0500 \text{ M}$$

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:

$$K_b = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]} = \frac{(x)(x)}{0.0500 - x} = 5.6 \times 10^{-10}$$

Making the approximation that  $0.0500 - x \approx 0.0500$ , and then solving for  $x$ , we have:

$$\begin{aligned}x &= [OH^-] = 5.3 \times 10^{-6} \text{ M}, \\ \text{which gives } pOH &= 5.28 \text{ and } pH = 8.72\end{aligned}$$

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

► **Practice Exercise**

Why is pH at the equivalence point larger than 7 when you titrate a weak acid with a strong base? (a) There is excess

strong base at the equivalence point. (b) There is excess weak acid at the equivalence point. (c) The conjugate base that is formed at the equivalence point is a strong base. (d) The conjugate base that is formed at the equivalence point reacts with water. (e) This statement is false: the pH is always 7 at an equivalence point in a pH titration.



either 0.100 M HCl or 0.100 M  $\text{CH}_3\text{COOH}$  yields the same pH, 11.00. Notice by comparing Figures 17.7 and 17.9 that the titration curves for a strong acid and a weak acid are the same after the equivalence point.

In order to further monitor the evolution of pH as a function of added base, we can calculate the pH at the equivalence point.

The titration curve for a weak acid–strong base titration (Figure 17.9) differs from the curve for a strong acid–strong base titration (Figure 17.7) 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 in the rapid-rise portion of the curve near the equivalence point is smaller for the weak acid than for the strong acid.
3. The pH at the equivalence point is above 7.00 for the weak acid titration.

The weaker the acid, the more pronounced these differences become. To illustrate this consider the family of titration curves shown in Figure 17.11. Notice that as the acid becomes weaker (that is, as  $K_a$  becomes smaller), the initial pH increases and the pH change near the equivalence point becomes less marked. Furthermore, the pH at the equivalence point steadily increases as  $K_a$  decreases, because the strength of the conjugate base of the weak acid increases. 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.

pH titration experiments are an excellent way to measure the  $\text{p}K_a$  of a weak acid. Look at Figure 17.11. Notice that for each acid solution, 50 mL of strong base is required to reach the equivalence point. This means, of course, that 50 mL of base is required to convert the HA molecules into  $\text{A}^-$  conjugate base anions. Also notice that halfway to each equivalence point (at 25 mL base added), the pH of the solution is nearly equal to the  $\text{p}K_a$  of the acid. Is this a coincidence? No! Recall that  $K_a = [\text{H}^+][\text{A}^-]/[\text{HA}]$ , where all concentrations are those at equilibrium. Halfway to the equivalence point, half of  $[\text{HA}]$  has been converted to  $[\text{A}^-]$ . In other words,  $[\text{HA}] = [\text{A}^-]$ . Therefore,  $[\text{HA}]/[\text{A}^-] = 1$ . In which case,  $K_a = [\text{H}^+]$ , and therefore  $\text{p}K_a = \text{pH}$ .

It becomes possible, then, to determine the  $\text{p}K_a$  of a weak acid from its pH titration curve. Once you identify the amount of base needed to reach the equivalence point, find the pH on the curve at halfway to the equivalence point. The pH you read off the graph at that point corresponds to the  $\text{p}K_a$  of the weak acid. If the acid's concentration is too low, however, the autoionization of water becomes significant, and this graphical way of measuring  $\text{p}K_a$  is not as accurate.

## Titrating with an Acid–Base Indicator

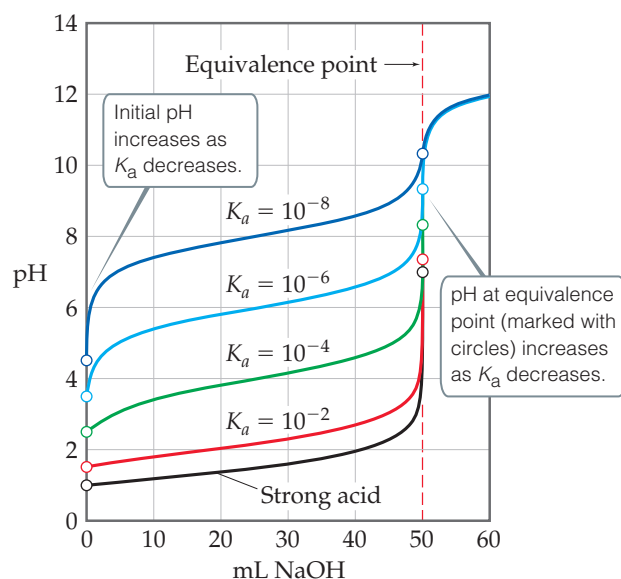
Often in an acid–base titration, an indicator is used rather than a pH meter. An indicator is a compound that changes color in solution over a specific pH range. Optimally, an indicator should change color at the equivalence point in a titration. In practice, however, an indicator need not precisely mark the equivalence point. The pH changes very rapidly near the equivalence point, and in this region one drop of titrant can change the pH by several units. Thus, an indicator beginning and ending its color change anywhere on the rapid-rise portion of the titration curve gives a sufficiently accurate measure of the titrant volume 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 equivalence point that it closely approximates.

Figure 17.12 shows the curve for titration of a strong base (NaOH) with a strong acid (HCl). We see from the vertical part of the curve that the pH changes rapidly



### Go Figure

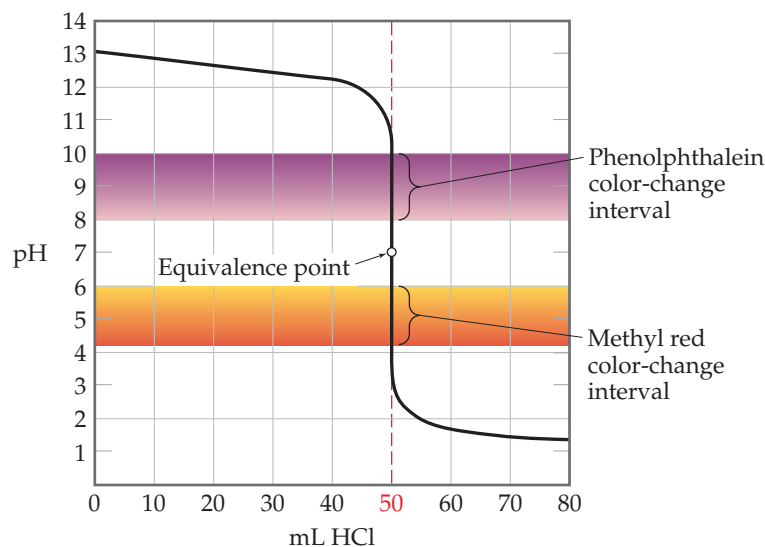
How does the pH at the equivalence point change as the acid being titrated becomes weaker? How does the volume of NaOH(aq) needed to reach the equivalence point change?



▲ **Figure 17.11** A set of curves showing the effect of acid strength on the characteristics of the titration curve when a weak acid is titrated by a strong base. Each curve represents titration of 50.0 mL of 0.10 M acid with 0.10 M NaOH.

### Go Figure

Is methyl red a suitable indicator when you are titrating a strong acid with a strong base? Explain your answer.



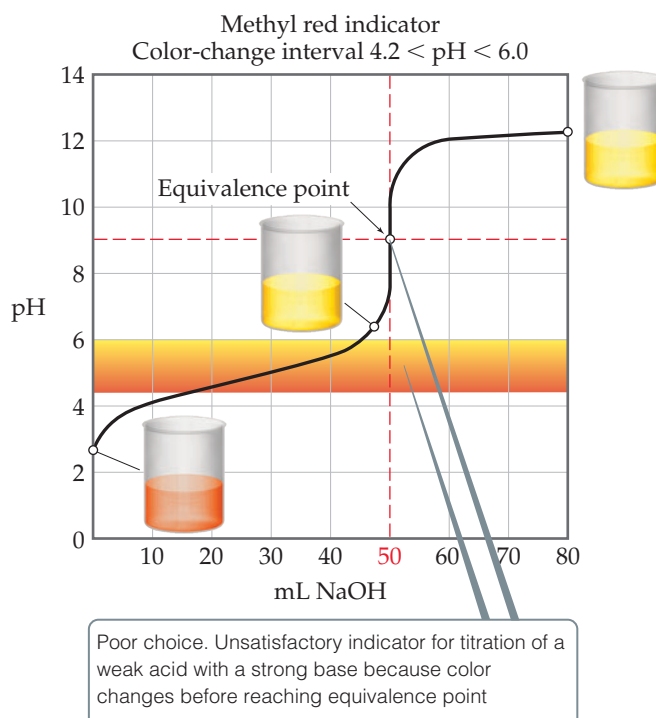
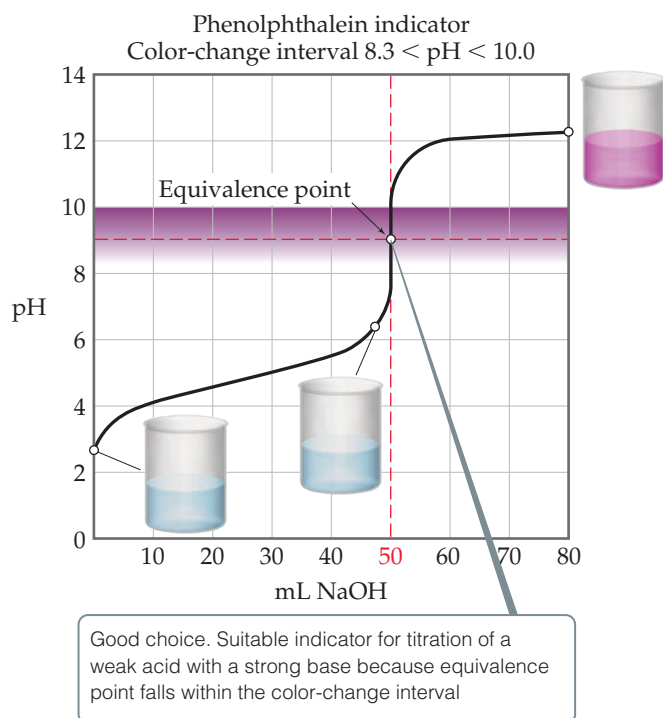
▲ **Figure 17.12** Using color indicators for titration of a strong base with a strong acid. Both phenolphthalein and methyl red change color in the rapid-change portion of the titration curve.

from roughly 11 to 3 near the equivalence point. Consequently, an indicator for this titration can change color anywhere in this range. Most strong acid–strong base titrations are carried out using phenolphthalein as an indicator because it changes color in this range (see Figure 16.7, p. 771). Several other indicators would also be satisfactory, including methyl red, which, as the lower color band in Figure 17.12 shows, changes color in the pH range from about 4.2 to 6.0.

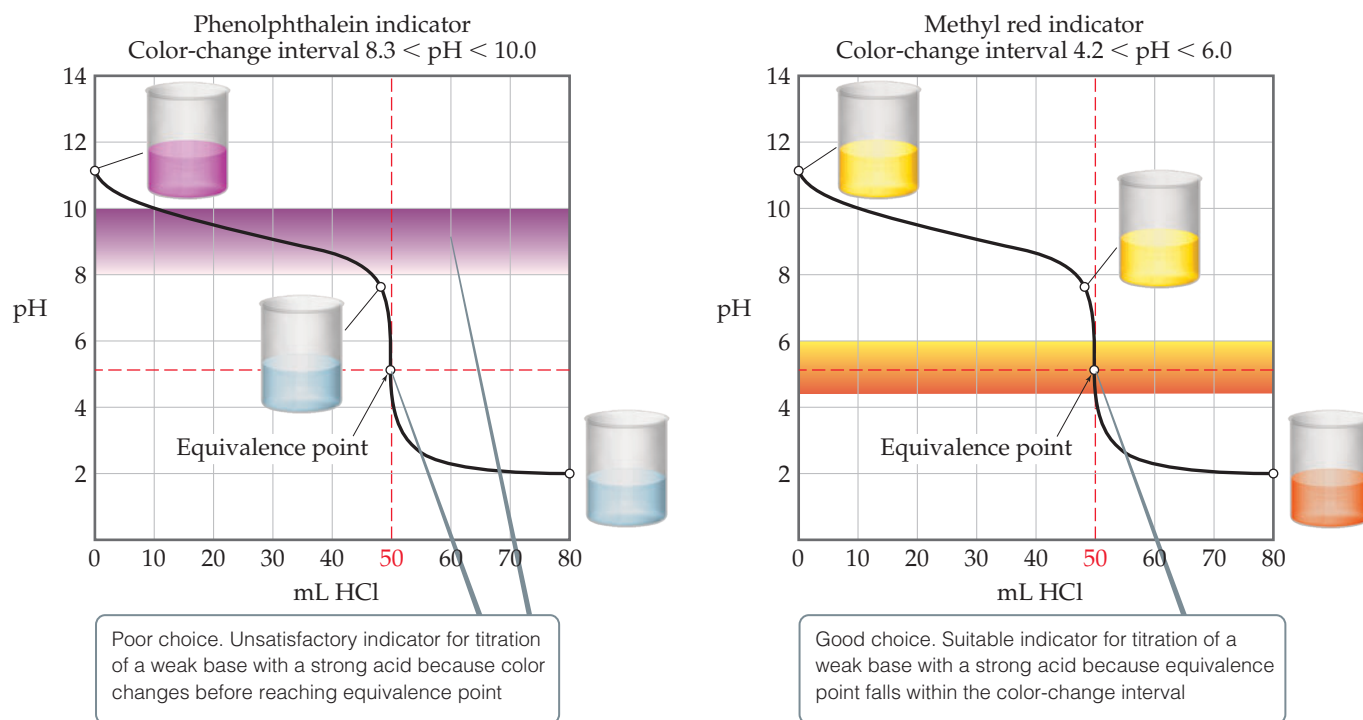
As noted in our discussion of Figure 17.11, because the pH change near the equivalence point becomes smaller as  $K_a$  decreases, the choice of indicator for a weak acid–strong base titration is more critical than it is for titrations where both acid and base are strong. When 0.100 M  $\text{CH}_3\text{COOH}$  ( $K_a = 1.8 \times 10^{-5}$ ) is titrated with 0.100 M NaOH, for example, the pH increases rapidly only over the pH range from about 7 to 11 (Figure 17.13). 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, from 4.2 to 6.0, begins well before the equivalence point is reached.

Titration of a weak base (such as 0.100 M  $\text{NH}_3$ ) with a strong acid solution (such as 0.100 M HCl)

leads to the titration curve shown in Figure 17.14. In this example, the equivalence point occurs at pH 5.28. Thus, methyl red is an ideal indicator, but phenolphthalein would be a poor choice.



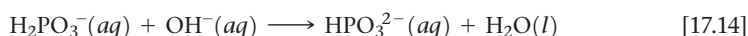
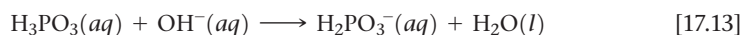
▲ **Figure 17.13** Good and poor indicators for titration of a weak acid with a strong base.



▲ **Figure 17.14** Good and poor indicators for titration of a weak base with a strong acid.

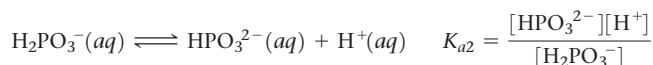
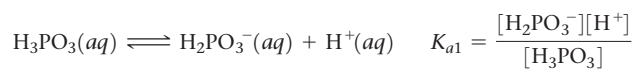
## Titration of Polyprotic Acids

When weak acids contain more than one ionizable H atom, the reaction with  $\text{OH}^-$  occurs in a series of steps. Neutralization of phosphorous acid,  $\text{H}_3\text{PO}_3$ , for example, proceeds in two steps (the third H is bonded to the P and does not ionize):



When the neutralization steps of a polyprotic acid or polybasic base are sufficiently separated, the titration has multiple equivalence points. **Figure 17.15** shows the two equivalence points corresponding to Equations 17.13 and 17.14.

You can use titration data such as that shown in Figure 17.15 to figure out the  $\text{pK}_a$ s of the weak polyprotic acid. For example, let's write the  $K_{a1}$  and  $K_{a2}$  reactions for phosphorous acid:



If we rearrange these equilibrium expressions, you see that we obtain Henderson–Hasselbalch equations:

$$\text{pH} = \text{pK}_{a1} + \log \frac{[\text{H}_2\text{PO}_3^-]}{[\text{H}_3\text{PO}_3]}$$

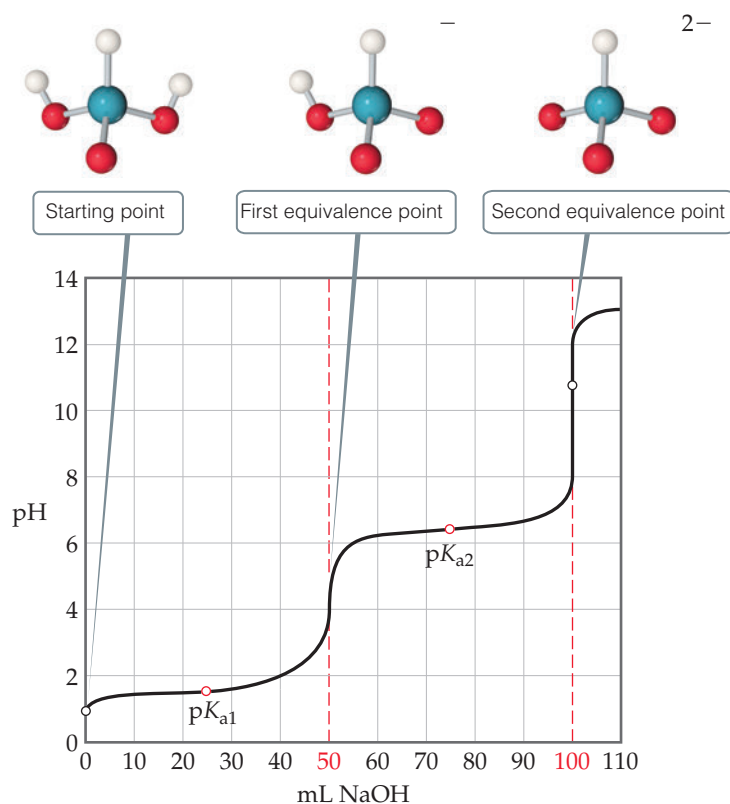
$$\text{pH} = \text{pK}_{a2} + \log \frac{[\text{HPO}_3^{2-}]}{[\text{H}_2\text{PO}_3^-]}$$

Therefore, if the concentrations of each acid and base conjugate pair are identical for each equilibrium,  $\log(1) = 0$  and so  $\text{pH} = \text{pK}_a$ . When does this happen during the titration? At the beginning of the titration, the acid is  $\text{H}_3\text{PO}_3$  initially; at the first equivalence point, it is all converted to  $\text{H}_2\text{PO}_3^-$ . Therefore, halfway to the first equivalence point, half of the  $\text{H}_3\text{PO}_3$  is converted to  $\text{H}_2\text{PO}_3^-$ . Thus, halfway to the equivalence point,



## Go Figure

What is/are the dominant species in solution at pH = 4:  $\text{H}_3\text{PO}_3$ ,  $\text{H}_2\text{PO}_3^-$ ,  $\text{HPO}_3^{2-}$ , and/or  $\text{PO}_3^{3-}$ ? At pH = 11?



▲ **Figure 17.15** Titration curve for a diprotic acid. The curve shows the pH change when 50.0 mL of 0.10 M  $\text{H}_3\text{PO}_3$  is titrated with 0.10 M NaOH.

the concentration of  $\text{H}_3\text{PO}_3$  is equal to that of  $\text{H}_2\text{PO}_3^-$ , and at that point,  $\text{pH} = \text{p}K_{a1}$ . Similar logic is true for the second equilibrium reaction: halfway toward its equivalence point,  $\text{pH} = \text{p}K_{a2}$ .

We can then just look at titration data and estimate the  $\text{p}K_a$ s for the polyprotic acid directly from the titration curve. This procedure is especially useful if you are trying to identify an unknown polyprotic acid. In Figure 17.15, for instance, the first equivalence point occurs for 50 mL NaOH added. Halfway to the equivalence point corresponds to 25 mL NaOH. Because the pH at 25 mL NaOH is about 1.5 we may estimate  $\text{p}K_{a1} = 1.5$  for phosphorous acid. The second equivalence point occurs at 100 mL NaOH added; halfway there (from the first equivalence point) is at 75 mL NaOH added. The graph indicates the pH at 75 mL NaOH added is about 6.5, and we therefore estimate that  $\text{p}K_{a2}$  for phosphorous acid is 6.5. The actual values for the two  $\text{p}K_a$ s are  $\text{p}K_{a1} = 1.3$  and  $\text{p}K_{a2} = 6.7$  (close to our estimates).

## Self-Assessment Exercises

**17.15** A titration involves the addition of a strong acid (0.100 M) to 50.0 mL of a strong base (0.100 M). What is the pH after the addition of 40.0 mL of acid?

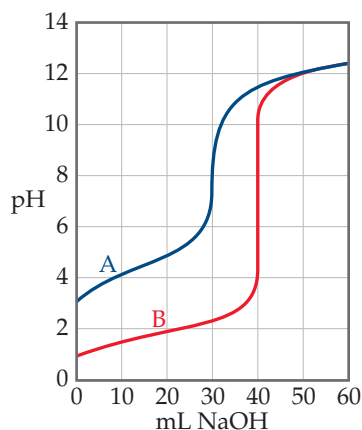
- (a) 13.00
- (b) 12.05
- (c) 11.95

**17.16** Estimate the  $\text{p}K_a$  of the weak base illustrated in figure 17.14.

- (a) 11.0
- (b) 9.4
- (c) 5.2
- (d) 2.0

## Exercises

- 17.17** 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)** 40.0 mL of each acid was titrated with a 0.100 M base. Which acid is more concentrated? **(d)** Estimate the  $pK_a$  of the weak acid.



- 17.18** Determine whether each of the following statements concerning titration of 25.0 mL 1.0 M  $\text{HNO}_3(aq)$  and 25.0 mL 1.0 M  $\text{CH}_3\text{COOH}(aq)$  against 0.100 M solution of NaOH ( $aq$ ) is true or false.
- (a)** The pH at the beginning of the two titrations will be the same.
  - (b)** The titration curves will both be essentially the same after passing the equivalence point.

**(c)** Methyl red would be a suitable indicator for both titrations.

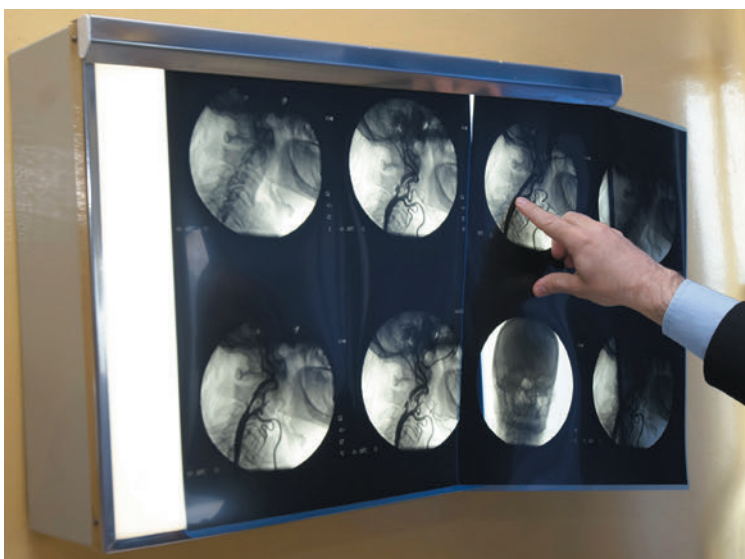
- 17.19** Predict whether the equivalence point of each of the following titrations is below, above, or at pH 7: **(a)** benzoic acid titrated with KOH, **(b)** ammonia titrated with iodic acid, **(c)** hydroxylamine with hydrochloric acid.
- 17.20** Assume that 30.0 mL of a 0.10 M solution of a weak base B that accepts one proton is titrated with a 0.10 M solution of the monoprotic strong acid HA. **(a)** How many moles of HA have been added at the equivalence point? **(b)** What is the predominant form of B at the equivalence point? **(a)** Is the pH 7, less than 7, or more than 7 at the equivalence point? **(d)** Which indicator, phenolphthalein or methyl red, is likely to be the better choice for this titration?
- 17.21** 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  $\text{NH}_3$ , **(c)** 125.0 mL of a solution that contains 1.35 g of NaOH per liter?
- 17.22** A 20.0 mL sample of 0.150 M KOH is titrated with 0.125 M  $\text{HClO}_4$  solution. Calculate the pH after the following volumes of acid have been added: **(a)** 20.0 mL, **(b)** 23.0 mL, **(c)** 24.0 mL, **(d)** 25.0 mL, **(e)** 30.0 mL.
- 17.23** Consider the titration of 30.0 mL of 0.050 M  $\text{NH}_3$  with 0.025 M HCl. Calculate the pH after the following volumes of titrant have been added: **(a)** 0 mL, **(b)** 20.0 mL, **(c)** 59.0 mL, **(d)** 60.0 mL, **(e)** 61.0 mL, **(f)** 65.0 mL.
- 17.24** 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)** chlorous acid ( $\text{HClO}_2$ ), **(c)** benzoic acid ( $\text{C}_6\text{H}_5\text{COOH}$ ).

(q) 9.16

(b) 17.15

### Answers to Self-Assessment Exercises

## 17.4 | Solubility Equilibria



For over one hundred years, X-rays have been used in medical diagnosis and provide a non-invasive way to see inside a patient. While they are useful for highlighting broken bones and displaced joints, they are not so good at imaging soft tissue. A way around this, at least for imaging the gastrointestinal tract, is to use a contrast agent or 'radio opaque'

compound such as barium sulfate. A slurry of barium sulfate in water is swallowed and coats the inside of the upper digestive tract. The barium ions scatter the X-rays and prevent them from passing through the body to the detector on the other side. In this way, the images of the throat, stomach, and small intestine are obtained. Barium ions are toxic to humans; however, the solubility of barium sulfate is so low that it is considered safe to use.

By the end of this section, you should be able to

- Calculate  $K_{sp}$  from molar solubility and molar solubility from  $K_{sp}$ .

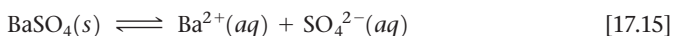
The equilibria we have considered thus far in this chapter have involved acids and bases. Furthermore, they have been homogeneous; that is, all the species have been in the same phase. Through the rest of the chapter, we will consider the equilibria involved in the dissolution or precipitation of ionic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

Dissolution and precipitation occur both within us and around us. Tooth enamel dissolves in acidic solutions, for example, causing tooth decay, and 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  $\text{CaCO}_3$  from groundwater is responsible for the formation of stalactites and stalagmites within limestone caves.

In our earlier discussion of precipitation reactions, we considered general rules for predicting the solubility of common salts in water. These rules give us a qualitative sense of whether a compound has a low or high solubility in water. By considering solubility equilibria, however, we can make quantitative predictions about solubility.

## The Solubility-Product Constant, $K_{sp}$

Recall that a *saturated solution* is one in which the solution is in contact with undissolved solute. Consider, for example, a saturated aqueous solution of  $\text{BaSO}_4$  in contact with solid  $\text{BaSO}_4$ . 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 when dissolved in water, readily establishing the equilibrium



As with any other equilibrium, the extent to which this dissolution reaction occurs is expressed by the magnitude of the 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 expression for the equilibrium between a solid and an aqueous solution of its component ions ( $K_{sp}$ ) is written according to the rules that apply to any other equilibrium expression. Remember, however, that solids do not appear in the equilibrium expressions for heterogeneous equilibrium.

Thus, the solubility-product expression for  $\text{BaSO}_4$ , which is based on Equation 17.15, is

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

## Sample Exercise 17.10

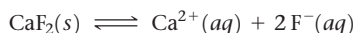
### Writing Solubility-Product ( $K_{sp}$ ) Expressions

Write the expression for the solubility-product constant for  $\text{CaF}_2$ , and look up the corresponding  $K_{sp}$  value in Appendix D.

#### SOLUTION

**Analyze** We are asked to write an equilibrium expression for the process by which  $\text{CaF}_2$  dissolves in water.

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



**Solve** The expression for  $K_{sp}$  is

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

Appendix D gives  $3.9 \times 10^{-11}$  for this  $K_{sp}$ .

#### Practice Exercise

Which of these expressions correctly expresses the solubility-product constant for  $\text{Ag}_3\text{PO}_4$  in water?

- (a)  $[\text{Ag}][\text{PO}_4]$  (b)  $[\text{Ag}^+][\text{PO}_4^{3-}]$  (c)  $[\text{Ag}^+]^3[\text{PO}_4^{3-}]$   
(d)  $[\text{Ag}^+][\text{PO}_4^{3-}]^3$  (e)  $[\text{Ag}^+]^3[\text{PO}_4^{3-}]^3$



The coefficient for each ion in the equilibrium equation also equals its subscript in the compound's chemical formula.

*In general, the solubility product  $K_{sp}$  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.*

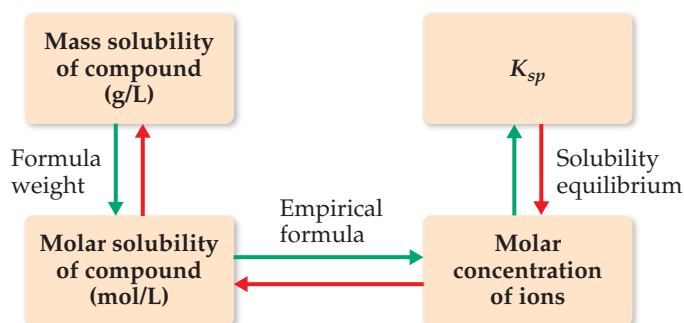
The values of  $K_{sp}$  at 25 °C for many ionic solids are tabulated in Appendix D. The value of  $K_{sp}$  for  $\text{BaSO}_4$  is  $1.1 \times 10^{-10}$ , a very small number indicating that only a very small amount of the solid dissolves in 25 °C water.

## 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. Solubility is often expressed as grams of solute per liter of solution (g/L). *Molar solubility* is the number of moles of solute that dissolve in forming 1 L 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.

The solubility of a substance can change considerably in response to a number of factors. For example, the solubilities of hydroxide salts, like  $\text{Mg}(\text{OH})_2$ , are dependent upon the pH of the solution. The solubility is also affected by concentrations of other ions in solution, especially common ions. In other words, the numeric value of the solubility of a given solute does change as the other species in solution change. In contrast, the solubility-product constant,  $K_{sp}$ , has only one value for a given solute at any specific temperature.\* **Figure 17.16** summarizes the relationships among various expressions of solubility and  $K_{sp}$ .

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 the measured solubility and that calculated from  $K_{sp}$  is usually best for salts whose ions have low charges (1+ and 1−) and do not react with water.



**▲ Figure 17.16** Procedure for converting between solubility and  $K_{sp}$ . Starting from the mass solubility, follow the green arrows to determine  $K_{sp}$ . Starting from  $K_{sp}$ , follow the red arrows to determine either molar solubility or mass solubility.

## Sample Exercise 17.11

### Calculating $K_{sp}$ from Solubility

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

### SOLUTION

**Analyze** We are given the equilibrium concentration of  $\text{Ag}^+$  in a saturated solution of  $\text{Ag}_2\text{CrO}_4$  and asked to determine the value of  $K_{sp}$  for  $\text{Ag}_2\text{CrO}_4$ .

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



$$K_{sp} = [\text{Ag}^+]^2[\text{CrO}_4^{2-}]$$

To calculate  $K_{sp}$ , we need the equilibrium concentrations of  $\text{Ag}^+$  and  $\text{CrO}_4^{2-}$ . We know that at equilibrium  $[\text{Ag}^+] = 1.3 \times 10^{-4} \text{ M}$ . All the  $\text{Ag}^+$  and  $\text{CrO}_4^{2-}$  ions in the solution come from the  $\text{Ag}_2\text{CrO}_4$  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 two  $\text{Ag}^+$  ions in solution for each  $\text{CrO}_4^{2-}$  ion in solution. Consequently, the concentration of  $\text{CrO}_4^{2-}$  is half the concentration of  $\text{Ag}^+$ :

*Continued*

\*This is strictly true only for very dilute solutions, for  $K_{sp}$  values change somewhat when the 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.

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

and  $K_{sp}$  is

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

**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,  $1.2 \times 10^{-12}$ .

### Practice Exercise

You add 10.0 grams of solid copper(II) phosphate,  $\text{Cu}_3(\text{PO}_4)_2$ , to a beaker and then add 100.0 mL of water to the beaker at  $T = 298 \text{ K}$ . The solid does not appear to dissolve. You wait a long time, with occasional stirring and eventually measure the equilibrium concentration of  $\text{Cu}^{2+}(\text{aq})$  in the water to be  $5.01 \times 10^{-8} \text{ M}$ . What is the  $K_{sp}$  of copper(II) phosphate?

- (a)  $5.01 \times 10^{-8}$  (b)  $2.50 \times 10^{-15}$  (c)  $4.20 \times 10^{-15}$   
 (d)  $3.16 \times 10^{-37}$  (e)  $1.40 \times 10^{-37}$

## Sample Exercise 17.12

### Calculating Solubility from $K_{sp}$

The  $K_{sp}$  for  $\text{CaF}_2$  is  $3.9 \times 10^{-11}$  at  $25^\circ\text{C}$ . Assuming equilibrium is established between solid and dissolved  $\text{CaF}_2$ , and that there are no other important equilibria affecting its solubility, calculate the solubility of  $\text{CaF}_2$  in grams per liter.

### SOLUTION

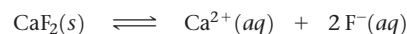
**Analyze** We are given  $K_{sp}$  for  $\text{CaF}_2$  and asked to determine solubility. Recall that the solubility of a substance is the quantity that can dissolve in solvent, whereas the solubility-product constant,  $K_{sp}$ , is an equilibrium constant.

**Plan** To go from  $K_{sp}$  to solubility, we follow the steps indicated by the red arrows in Figure 17.16. We first write the chemical equation

for the dissolution and set up a table of initial and equilibrium concentrations. We then use the equilibrium expression. In this case we know  $K_{sp}$ , and so we solve for the concentrations of the ions in solution. Once we know these concentrations, we use the formula weight to determine solubility in g/L.

### Solve

Assume that initially no salt has dissolved, and then allow  $x \text{ mol/L}$  of  $\text{CaF}_2$  to dissociate completely when equilibrium is achieved:



Initial concentration (M)	—	0	0
Change (M)	—	+ $x$	+ $2x$
Equilibrium concentration (M)	—	$x$	$2x$

The stoichiometry of the equilibrium dictates that  $2x \text{ mol/L}$  of  $\text{F}^{-}$  are produced for each  $x \text{ mol/L}$  of  $\text{CaF}_2$  that dissolve. We now use the expression for  $K_{sp}$  and substitute the equilibrium concentrations to solve for the value of  $x$ :

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

(Remember that  $\sqrt[3]{y} = y^{1/3}$ .) Thus, the molar solubility of  $\text{CaF}_2$  is  $2.1 \times 10^{-4} \text{ mol/L}$ .

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

The mass of  $\text{CaF}_2$  that dissolves in water to form 1 L of solution is:

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

**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 value given in the problem statement,  $3.9 \times 10^{-11}$ .

**Comment** Because  $\text{F}^{-}$  is the anion of a weak acid, you might expect hydrolysis of the ion to affect the solubility of  $\text{CaF}_2$ . The basicity of  $\text{F}^{-}$  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  $0.017 \text{ g/L}$  at  $25^\circ\text{C}$ , in good agreement with our calculation.

### Practice Exercise

Of the five salts listed here, which has the highest concentration of its cation in water? Assume that all salt solutions are saturated and that the ions do not undergo any additional reactions in water.

- (a) lead(II) chromate,  $K_{sp} = 2.8 \times 10^{-13}$   
 (b) cobalt(II) hydroxide,  $K_{sp} = 1.3 \times 10^{-15}$   
 (c) cobalt(II) sulfide,  $K_{sp} = 5 \times 10^{-22}$   
 (d) chromium(III) hydroxide,  $K_{sp} = 1.6 \times 10^{-30}$   
 (e) silver sulfide,  $K_{sp} = 6 \times 10^{-51}$

## A CLOSER LOOK Limitations of Solubility Products

Ion concentrations calculated from  $K_{sp}$  values 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. (“The van’t Hoff Factor”) 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 corrected to account for these interactions.

As an example of the effect of these interactions, consider  $\text{CaCO}_3$  (calcite), whose solubility product,  $4.5 \times 10^{-9}$ , gives a calculated solubility of  $6.7 \times 10^{-5} \text{ mol/L}$ ; correcting for ionic interactions in the solution yields  $7.3 \times 10^{-5} \text{ mol/L}$ . The reported solubility, however, is  $1.4 \times 10^{-4} \text{ mol/L}$ , indicating that there must be 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,  $\text{CaCO}_3$  contains the basic carbonate ion ( $K_b = 1.8 \times 10^{-4}$ ), which reacts with water:



If we consider the effect of ion-ion interactions as well as simultaneous solubility and  $K_b$  equilibria, we calculate a solubility of  $1.4 \times 10^{-4} \text{ mol/L}$ , in agreement with the measured value for calcite.

Finally, we generally assume that ionic compounds dissociate completely when they dissolve, but this assumption is not always valid. When  $\text{MgF}_2$  dissolves, for example, it yields not only  $\text{Mg}^{2+}$  and  $\text{F}^-$  ions but also  $\text{MgF}^+$  ions.

## Self-Assessment Exercise

**17.25** Without doing a calculation, predict which of the following compounds has the greatest molar solubility in water.

(a)  $\text{BaCO}_3$   $K_{sp} = 5.1 \times 10^{-9}$

(b)  $\text{BaSO}_4$   $K_{sp} = 1.1 \times 10^{-10}$

(c)  $\text{PbSO}_4$   $K_{sp} = 6.3 \times 10^{-7}$

## Exercises

**17.26** The solubility of two slightly soluble salts of  $\text{M}^{2+}$ , MA and  $\text{MZ}_2$ , is the same,  $4 \times 10^{-4} \text{ mol/L}$ . (a) Which has the larger numerical value for the solubility product constant? (b) In a saturated solution of each salt in water, which has the higher concentration of  $\text{M}^{2+}$ ? (c) If you added an equal volume of a solution saturated in MA to one saturated in  $\text{MZ}_2$ , what would be the equilibrium concentration of the cation,  $\text{M}^{2+}$ ?

**17.27** (a) True or false: “solubility” and “solubility-product constant” are the same number for a given compound. (b) Write the expression for the solubility-product constant for each

of the following ionic compounds:  $\text{MnCO}_3$ ,  $\text{Hg}(\text{OH})_2$ , and  $\text{Cu}_3(\text{PO}_4)_2$ .

**17.28** (a) The molar solubility of  $\text{PbBr}_2$  at  $25^\circ\text{C}$  is  $1.0 \times 10^{-2} \text{ mol/L}$ . Calculate  $K_{sp}$ . (b) If 0.0490 g of  $\text{AgIO}_3$  dissolves per liter of solution, calculate the solubility-product constant. (c) Using the appropriate  $K_{sp}$  value from Appendix D, calculate the pH of a saturated solution of  $\text{Ca}(\text{OH})_2$ .

**17.29** A 1.00 L solution saturated at  $25^\circ\text{C}$  with lead(II) iodide contains 0.54 g of  $\text{PbI}_2$ . Calculate the solubility-product constant for this salt at  $25^\circ\text{C}$ .

17.25 (c)

Answers to Self-Assessment Exercises

## 17.5 Factors That Affect Solubility



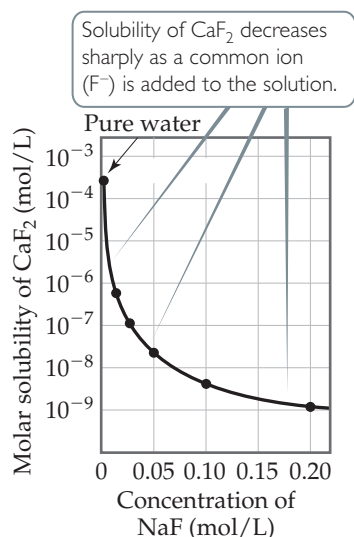
Coral reefs are a striking example of aqueous chemistry at work in nature. Coral reefs are built by tiny animals called stony corals, which secrete a hard calcium carbonate exoskeleton. Over time, the stony corals build up large networks of calcium carbonate upon which a reef is built. The size of such structures can be immense, as illustrated by the Great Barrier Reef.

Stony corals make their exoskeletons from dissolved  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  ions. This process is aided by the fact that the  $\text{CO}_2$  concentration is supersaturated in most parts of the ocean. However, well documented increases in the amount of  $\text{CO}_2$  in the atmosphere threaten to upset the aqueous chemistry that stony corals depend on. As atmospheric  $\text{CO}_2$  levels increase, the amount of  $\text{CO}_2$  dissolved in the ocean also increases. This lowers the pH of the ocean and leads to a decrease in the  $\text{CO}_3^{2-}$  concentration. As a result, it becomes more difficult for stony corals and other important ocean creatures to maintain their exoskeletons. We will take a closer look at the consequences of ocean acidification later in Chapter 18.

By the end of this section, you should be able to

- Calculate the solubility of a substance in the presence of a common ion or at different pH values.

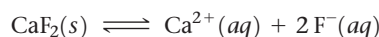
Solubility is affected by temperature and by the presence of other solutes. The presence of an acid, for example, can have a major influence on the solubility of a substance. In Section 17.4, we considered the dissolving of ionic compounds in pure water. In this section, we examine three factors that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



▲ **Figure 17.17 Common-ion effect.** Notice that the  $\text{CaF}_2$  solubility is on a logarithmic scale.

### The Common-Ion Effect

The presence of either  $\text{Ca}^{2+}(aq)$  or  $\text{F}^-(aq)$  in a solution reduces the solubility of  $\text{CaF}_2$ , shifting the equilibrium concentrations to the left:



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

This reduction in solubility is another manifestation of the common-ion effect we looked at in 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*, as **Figure 17.17** shows for  $\text{CaF}_2$ .

### Sample Exercise 17.13

#### Calculating the Effect of a Common Ion on Solubility

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

#### SOLUTION

**Analyze** We are asked to determine the solubility of  $\text{CaF}_2$  in the presence of two strong electrolytes, each containing an ion common to  $\text{CaF}_2$ . In (a) the common ion is  $\text{Ca}^{2+}$ , and  $\text{NO}_3^-$  is a spectator ion. In (b) the common ion is  $\text{F}^-$ , and  $\text{Na}^+$  is a spectator ion.

**Plan** Because the slightly soluble compound is  $\text{CaF}_2$ , we need to use  $K_{sp}$  for this compound, which Appendix D gives as  $3.9 \times 10^{-11}$ . 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 decreases in the presence of common ions. We use our standard equilibrium techniques of starting with the equation for  $\text{CaF}_2$  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  $\text{CaF}_2$ .

**Solve**

- (a) The initial concentration of  $\text{Ca}^{2+}$  is  $0.010\text{ M}$  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 Concentration (M)	—	0.010	0
Change (M)	—	+ $x$	+ $2x$
Equilibrium Concentration (M)	—	$(0.010 + x)$	$2x$

Substituting into the solubility-product expression gives:

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

If we assume that  $x$  is small compared to  $0.010$ , we have:

$$3.9 \times 10^{-11} = (0.010)(2x)^2$$

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

$$x^2 = \frac{3.9 \times 10^{-11}}{4(0.010)} = 9.8 \times 10^{-10}$$

$$x = \sqrt{9.8 \times 10^{-10}} = 3.1 \times 10^{-5}\text{ M}$$

- (b) The common ion is  $\text{F}^{-}$ , and at equilibrium we have:

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

Assuming that  $2x$  is much smaller than  $0.010\text{ M}$  (that is,  $0.010 + 2x \approx 0.010$ ), we have:

$$3.9 \times 10^{-11} = (x)(0.010 + 2x)^2 \approx x(0.010)^2$$

Thus,  $3.9 \times 10^{-7}\text{ mol}$  of solid  $\text{CaF}_2$  should dissolve per liter of  $0.010\text{ M NaF}$  solution.

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

**Comment** The molar solubility of  $\text{CaF}_2$  in water is  $2.1 \times 10^{-4}\text{ M}$  (Sample Exercise 17.12). By comparison, our calculations here give a  $\text{CaF}_2$  solubility of  $3.1 \times 10^{-5}\text{ M}$  in the presence of  $0.010\text{ M Ca}^{2+}$  and  $3.9 \times 10^{-7}\text{ M}$  in the presence of  $0.010\text{ M F}^{-}$  ion. Thus, the addition of either  $\text{Ca}^{2+}$  or  $\text{F}^{-}$  to a solution of  $\text{CaF}_2$  decreases the solubility. However, the effect of  $\text{F}^{-}$  on the solubility is more pronounced than that of  $\text{Ca}^{2+}$  because  $[\text{F}^{-}]$  appears to the second power in the  $K_{sp}$  expression for  $\text{CaF}_2$ , whereas  $[\text{Ca}^{2+}]$  appears to the first power.

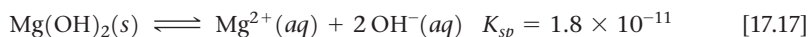
**Practice Exercise**

Consider a saturated solution of the salt  $\text{MA}_3$ , in which M is a metal cation with a  $3+$  charge and A is an anion with a  $1-$  charge, in water at  $298\text{ K}$ . Which of the following will affect the  $K_{sp}$  of  $\text{MA}_3$  in water?

(a) The addition of more  $\text{M}^{3+}$  to the solution. (b) The addition of more  $\text{A}^{-}$  to the solution. (c) Diluting the solution. (d) Raising the temperature of the solution. (e) More than one of the above factors.

## Solubility and pH

The solubility of almost any ionic compound is affected if the solution is made sufficiently acidic or basic. The effects are noticeable, however, only when one (or both) ions in the compound is 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. Let's look at  $\text{Mg}(\text{OH})_2$ , for which the solubility equilibrium is



A saturated solution of  $\text{Mg}(\text{OH})_2$  has a calculated pH of 10.52, and its  $\text{Mg}^{2+}$  concentration is  $1.7 \times 10^{-4}\text{ M}$ . Now suppose that solid  $\text{Mg}(\text{OH})_2$  is equilibrated with a solution buffered at pH 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, the  $\text{Mg}(\text{OH})_2$  dissolves until  $[\text{Mg}^{2+}] = 0.18\text{ M}$ . It is apparent that  $\text{Mg}(\text{OH})_2$  is much more soluble in this solution.

If  $[\text{OH}^-]$  were reduced further by making the solution even more acidic, the  $\text{Mg}^{2+}$  concentration would have to increase to maintain the equilibrium condition. Thus, a sample of  $\text{Mg}(\text{OH})_2(\text{s})$  dissolves completely if sufficient acid is added, as we saw in Figure 4.7 (page 190).

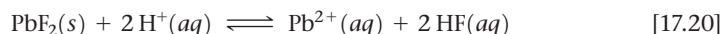
As we have seen, the solubility of  $\text{Mg}(\text{OH})_2$  greatly increases as the acidity of the solution increases. Based on this observation we can make the following generalization:

*In general, the solubility of a compound containing a basic anion (that is, the anion of a weak acid) increases as the solution becomes more acidic.*

The solubility of  $\text{PbF}_2$  increases as the solution becomes more acidic, too, because  $\text{F}^-$  is a base (it is the conjugate base of the weak acid  $\text{HF}$ ). As a result, the solubility equilibrium of  $\text{PbF}_2$  is shifted to the right as the concentration of  $\text{F}^-$  is reduced by protonation to form  $\text{HF}$ . Thus, the solution process can be understood in terms of two consecutive reactions:

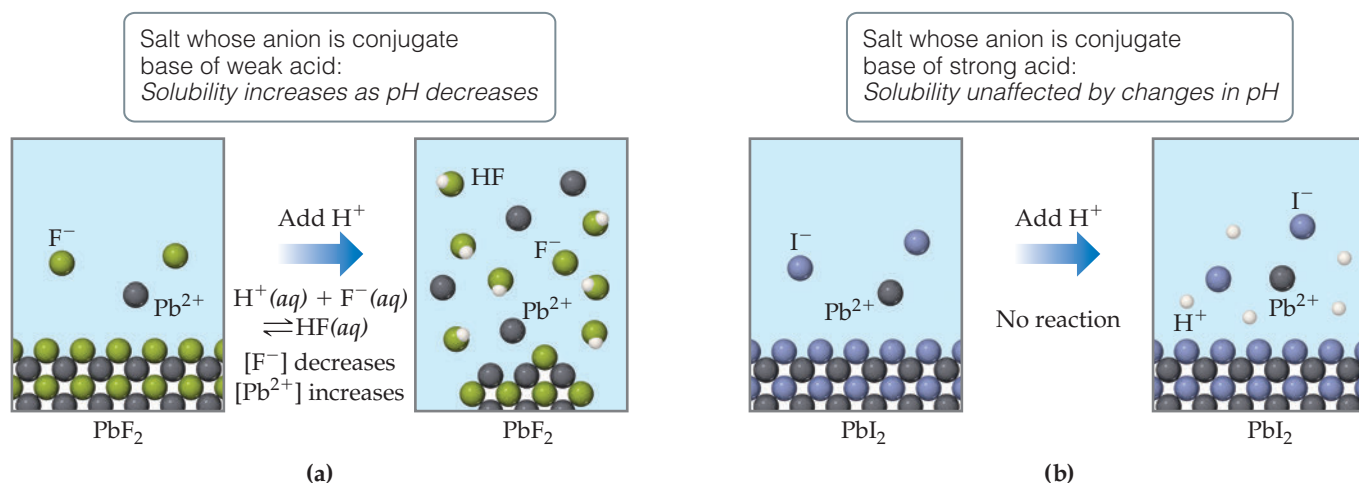


The equation for the overall process is



The processes responsible for the increase in solubility of  $\text{PbF}_2$  in acidic solution are illustrated in Figure 17.18(a).

Other salts that contain basic anions, such as  $\text{CO}_3^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{CN}^-$ , or  $\text{S}^{2-}$ , 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. The solubility of salts with anions of negligible basicity (the anions of strong acids), such as  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ , and  $\text{NO}_3^-$ , is unaffected by pH changes, as shown in Figure 17.18(b).



▲ **Figure 17.18** Response of two ionic compounds to addition of a strong acid. (a) The solubility of  $\text{PbF}_2$  increases upon addition of acid. (b) The solubility of  $\text{PbI}_2$  is not affected by the addition of acid. The water molecules and the anion of the strong acid have been omitted for clarity.



## Sample Exercise 17.14

### Predicting the Effect of Acid on Solubility

Which of these substances are more soluble in acidic solution than in basic solution:

- (a)  $\text{Ni}(\text{OH})_2(s)$ , (b)  $\text{CaCO}_3(s)$ , (c)  $\text{BaF}_2(s)$ , (d)  $\text{AgCl}(s)$ ?

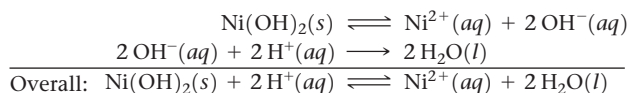
### SOLUTION

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

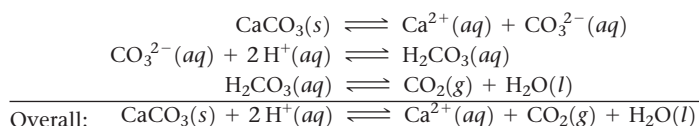
**Plan** We will identify ionic compounds that dissociate to produce a basic anion, as these are especially soluble in acid solution.

#### Solve

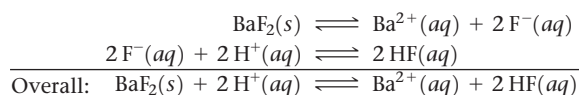
- (a)  $\text{Ni}(\text{OH})_2(s)$  is more soluble in acidic solution because of the basicity of  $\text{OH}^-$ ; the  $\text{H}^+$  reacts with the  $\text{OH}^-$  ion, forming water:



- (b) Similarly,  $\text{CaCO}_3(s)$  dissolves in acid solutions because  $\text{CO}_3^{2-}$  is a basic anion:  
The reaction between  $\text{CO}_3^{2-}$  and  $\text{H}^+$  occurs in steps, with  $\text{HCO}_3^-$  forming first and  $\text{H}_2\text{CO}_3$  forming in appreciable amounts only when  $[\text{H}^+]$  is sufficiently high.



- (c) The solubility of  $\text{BaF}_2$  is enhanced by lowering the pH because  $\text{F}^-$  is a basic anion:



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

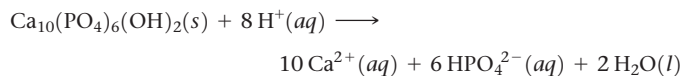
#### Practice Exercise

Which of the following actions will increase the solubility of  $\text{AgBr}$  in water?

- (a) increasing the pH      (b) decreasing the pH  
(c) adding  $\text{NaBr}$       (d) adding  $\text{NaNO}_3$   
(e) none of the above

## CHEMISTRY AND LIFE Tooth Decay and Fluoridation

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

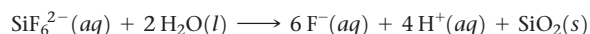


The  $\text{Ca}^{2+}$  and  $\text{HPO}_4^{2-}$  ions diffuse out of the enamel and are washed away by saliva. The acids that attack the hydroxyapatite are formed by the action of bacteria on sugars and other carbohydrates present in the plaque adhering to the teeth.

Fluoride ion, which is added to municipal water systems and toothpastes, can react with hydroxyapatite to form fluoroapatite,  $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ . This mineral, in which  $\text{F}^-$  has replaced  $\text{OH}^-$ , is much

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

The usual concentration of  $\text{F}^-$  in municipal water systems is 1 mg/L (1 ppm). The compound added may be  $\text{NaF}$  or  $\text{Na}_2\text{SiF}_6$ . The silicon-fluorine anion reacts with water to release fluoride ions:

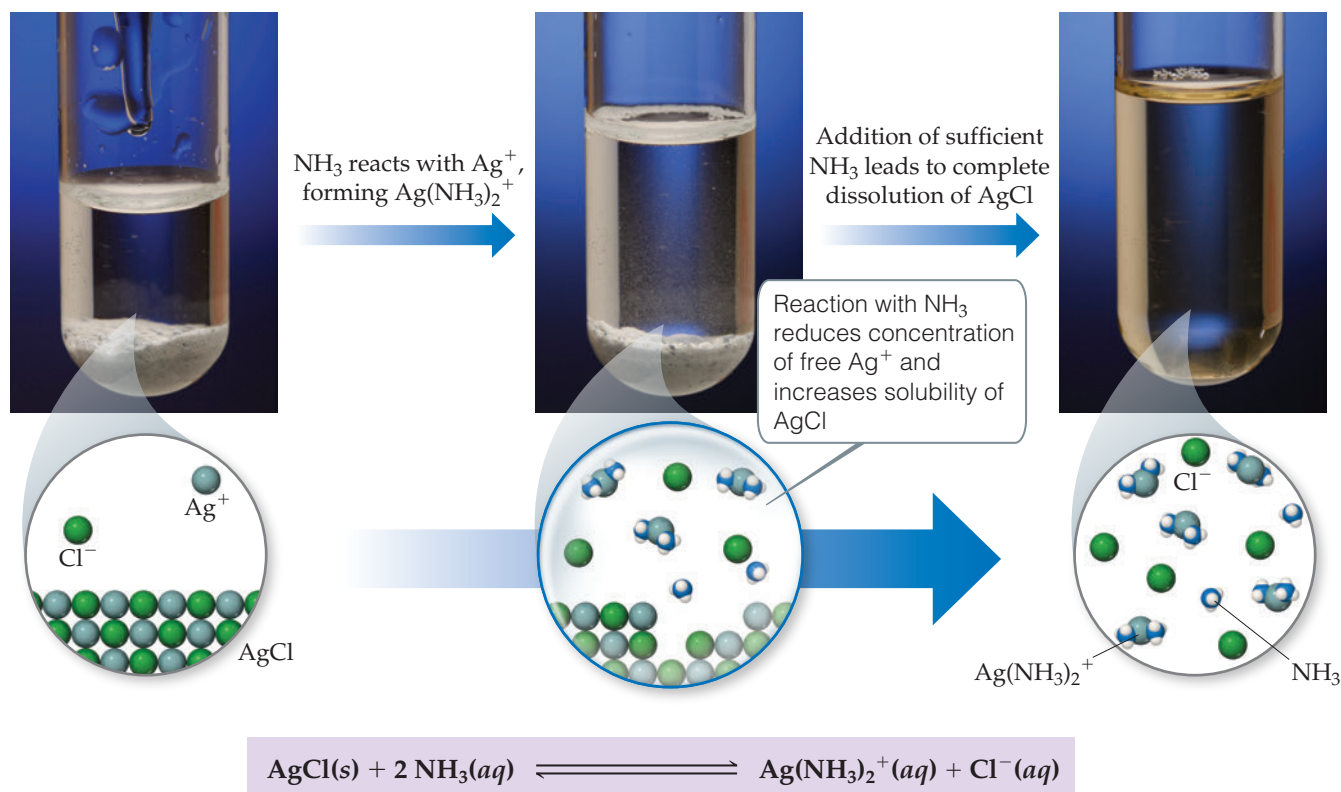


Many toothpastes now sold in the United States contain fluoride compounds, usually at the level of 0.1% fluoride by mass. The most common compounds in toothpastes are sodium fluoride ( $\text{NaF}$ ), sodium monofluorophosphate ( $\text{Na}_2\text{PO}_3\text{F}$ ), and stannous fluoride ( $\text{SnF}_2$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

**Related Exercises:** 17.110, 17.128

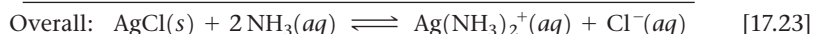
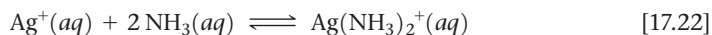
## Formation of Complex Ions

A characteristic property of metal ions is their ability to act as Lewis acids toward water molecules, which act as Lewis bases. Lewis bases other than water can also interact with metal ions, particularly transition-metal ions. Such interactions can dramatically affect the solubility of a metal salt. For example,  $\text{AgCl}$  ( $K_{sp} = 1.8 \times 10^{-10}$ ) dissolves in the



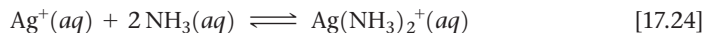
▲ **Figure 17.19** Concentrated NH<sub>3</sub>(aq) dissolves AgCl(s), which otherwise has very low solubility in water.

presence of aqueous ammonia because Ag<sup>+</sup> interacts with the Lewis base NH<sub>3</sub>, as shown in **Figure 17.19**. This process can be viewed as the sum of two reactions:



The presence of NH<sub>3</sub> drives the reaction, the dissolution of AgCl, to the right as Ag<sup>+</sup>(aq) is consumed to form Ag(NH<sub>3</sub>)<sub>2</sub><sup>+</sup>, which is a very soluble species.

For a Lewis base such as NH<sub>3</sub> to increase the solubility of a metal salt, the base must be able to interact more strongly with the metal ion than water does. In other words, the NH<sub>3</sub> must displace solvating H<sub>2</sub>O molecules in order to form [Ag(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup>:



An assembly of a metal ion and the Lewis bases bonded to it, such as Ag(NH<sub>3</sub>)<sub>2</sub><sup>+</sup>, is called a **complex ion**. Complex ions are very soluble in water. 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 Equation 17.24 is

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

Note that 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**.

The general rule is that the solubility of metal salts increases in the presence of suitable Lewis bases, such as NH<sub>3</sub>, CN<sup>-</sup>, or OH<sup>-</sup>, provided the metal forms a complex with the base. The ability of metal ions to form complexes is an extremely important aspect of their chemistry.

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

Complex Ion	$K_f$	Chemical Equation
$\text{Ag}(\text{NH}_3)_2^+$	$1.7 \times 10^7$	$\text{Ag}^+(aq) + 2 \text{NH}_3(aq) \rightleftharpoons \text{Ag}(\text{NH}_3)_2^+(aq)$
$\text{Ag}(\text{CN})_2^-$	$1 \times 10^{21}$	$\text{Ag}^+(aq) + 2 \text{CN}^-(aq) \rightleftharpoons \text{Ag}(\text{CN})_2^-(aq)$
$\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$	$2.9 \times 10^{13}$	$\text{Ag}^+(aq) + 2 \text{S}_2\text{O}_3^{2-}(aq) \rightleftharpoons \text{Ag}(\text{S}_2\text{O}_3)_2^{3-}(aq)$
$\text{Al}(\text{OH})_4^-$	$1.1 \times 10^{33}$	$\text{Al}^{3+}(aq) + 4 \text{OH}^-(aq) \rightleftharpoons \text{Al}(\text{OH})_4^-(aq)$
$\text{CdBr}_4^{2-}$	$5 \times 10^3$	$\text{Cd}^{2+}(aq) + 4 \text{Br}^-(aq) \rightleftharpoons \text{CdBr}_4^{2-}(aq)$
$\text{Cr}(\text{OH})_4^-$	$8 \times 10^{29}$	$\text{Cr}^{3+}(aq) + 4 \text{OH}^-(aq) \rightleftharpoons \text{Cr}(\text{OH})_4^-(aq)$
$\text{Co}(\text{SCN})_4^{2-}$	$1 \times 10^3$	$\text{Co}^{2+}(aq) + 4 \text{SCN}^-(aq) \rightleftharpoons \text{Co}(\text{SCN})_4^{2-}(aq)$
$\text{Cu}(\text{NH}_3)_4^{2+}$	$5 \times 10^{12}$	$\text{Cu}^{2+}(aq) + 4 \text{NH}_3(aq) \rightleftharpoons \text{Cu}(\text{NH}_3)_4^{2+}(aq)$
$\text{Cu}(\text{CN})_4^{2-}$	$1 \times 10^{25}$	$\text{Cu}^{2+}(aq) + 4 \text{CN}^-(aq) \rightleftharpoons \text{Cu}(\text{CN})_4^{2-}(aq)$
$\text{Ni}(\text{NH}_3)_6^{2+}$	$1.2 \times 10^9$	$\text{Ni}^{2+}(aq) + 6 \text{NH}_3(aq) \rightleftharpoons \text{Ni}(\text{NH}_3)_6^{2+}(aq)$
$\text{Fe}(\text{CN})_6^{4-}$	$1 \times 10^{35}$	$\text{Fe}^{2+}(aq) + 6 \text{CN}^-(aq) \rightleftharpoons \text{Fe}(\text{CN})_6^{4-}(aq)$
$\text{Fe}(\text{CN})_6^{3-}$	$1 \times 10^{42}$	$\text{Fe}^{3+}(aq) + 6 \text{CN}^-(aq) \rightleftharpoons \text{Fe}(\text{CN})_6^{3-}(aq)$
$\text{Zn}(\text{OH})_4^{2-}$	$4.6 \times 10^{17}$	$\text{Zn}^{2+}(aq) + 4 \text{OH}^-(aq) \rightleftharpoons \text{Zn}(\text{OH})_4^{2-}(aq)$

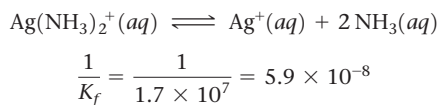
**Sample Exercise 17.15****Evaluating an Equilibrium Involving a Complex Ion**

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

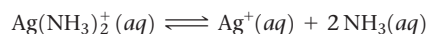
**SOLUTION**

**Analyze** Addition of  $\text{NH}_3(aq)$  to  $\text{Ag}^+(aq)$  forms  $\text{Ag}(\text{NH}_3)_2^+(aq)$ , as shown in Equation 17.22. We are asked to determine what concentration of  $\text{Ag}^+(aq)$  remains uncombined when the  $\text{NH}_3$  concentration is brought to 0.20 *M* in a solution originally 0.010 *M* in  $\text{AgNO}_3$ .

**Plan** We assume that the  $\text{AgNO}_3$  is completely dissociated, giving 0.010 *M*  $\text{Ag}^+$ . Because  $K_f$  for the formation of  $\text{Ag}(\text{NH}_3)_2^+$  is quite large, we assume that essentially all the  $\text{Ag}^+$  is 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 need to reverse Equation 17.22 and make the corresponding change to the equilibrium constant:



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



Initial ( <i>M</i> )	0.010	0	—
Change ( <i>M</i> )	− <i>x</i>	+ <i>x</i>	—
Equilibrium ( <i>M</i> )	(0.010 − <i>x</i> )	<i>x</i>	0.20

Because  $[\text{Ag}^+]$  is very small, we can assume *x* is small compared to 0.010. Substituting these values into the equilibrium expression for the dissociation of  $\text{Ag}(\text{NH}_3)_2^+$ , we obtain

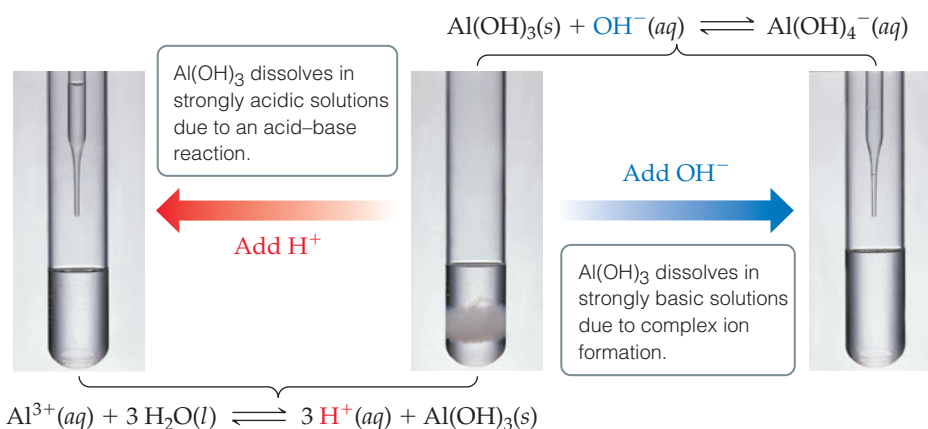
$$\frac{[\text{Ag}^+][\text{NH}_3]^2}{[\text{Ag}(\text{NH}_3)_2^+]} = \frac{(x)(0.20)^2}{0.010} = 5.9 \times 10^{-8}$$

$$x = 1.5 \times 10^{-8} \text{ M} = [\text{Ag}^+]$$

Formation of the  $\text{Ag}(\text{NH}_3)_2^+$  complex drastically reduces the concentration of free  $\text{Ag}^+$  ion in solution.

**Practice Exercise**

You have an aqueous solution of chromium(III) nitrate that you titrate with an aqueous solution of sodium hydroxide. After a certain amount of titrant has been added, you observe a precipitate forming. You add more sodium hydroxide solution and the precipitate dissolves, leaving a solution again. What has happened? **(a)** The precipitate was sodium hydroxide, which redissolved in the larger volume. **(b)** The precipitate was chromium hydroxide, which dissolved once more solution was added, forming  $\text{Cr}^{3+}(aq)$ . **(c)** The precipitate was chromium hydroxide, which then reacted with more hydroxide to produce a soluble complex ion,  $\text{Cr}(\text{OH})_4^-(aq)$ . **(d)** The precipitate was sodium nitrate, which reacted with more nitrate to produce the soluble complex ion  $\text{Na}(\text{NO}_3)_2^-(aq)$ .



▲ **Figure 17.20 Amphoterism.** Some metal oxides and hydroxides, such as  $\text{Al}(\text{OH})_3$ , are amphoteric, which means they dissolve in both strongly acidic and strongly basic solutions.

## Amphoterism

Some metal oxides and hydroxides that are relatively insoluble in water dissolve in strongly acidic and strongly basic solutions. These substances, called **amphoteric oxides** and **amphoteric hydroxides**,\* are soluble in strong acids and bases because they themselves are capable of behaving as either an acid or base. Examples of amphoteric substances include the oxides and hydroxides of  $\text{Al}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Sn}^{2+}$ .

Like other metal oxides and hydroxides, amphoteric species dissolve in acidic solutions because their anions,  $\text{O}^{2-}$  or  $\text{OH}^{-}$ , react with acids. What makes amphoteric oxides and hydroxides special, though, is that they also dissolve in strongly basic solutions. This behavior results from the formation of complex anions containing several (typically four) hydroxides bound to the metal ion (**Figure 17.20**):



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 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 hydrated  $\text{Al}_2\text{O}_3$  contaminated with  $\text{Fe}_2\text{O}_3$ . When bauxite is added to a strongly basic solution, the  $\text{Al}_2\text{O}_3$  dissolves because the aluminum forms complex ions, such as  $\text{Al}(\text{OH})_4^{-}$ . The  $\text{Fe}_2\text{O}_3$  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.

\*Notice that the term *amphoteric* is applied to the behavior of insoluble oxides and hydroxides that dissolve in acidic or basic solutions. The similar term *amphiprotic* (Section 16.1) relates more generally to any molecule or ion that can either gain or lose a proton.

## A CLOSER LOOK Lead Contamination in Drinking Water

Access to clean drinking water is something most people in the industrialized world take for granted. Unfortunately, there are rare instances in which tap water is not safe to drink, as illustrated by the discovery in 2015 of elevated levels of lead in the municipal water supply of Flint, a city in Michigan State, USA.

Lead is detrimental to many organs in the human body, but the brain and central nervous system are particularly sensitive to its presence. In the brain,  $\text{Pb}^{2+}$  ions interfere with cell communication and growth by mimicking  $\text{Ca}^{2+}$  ions. One of the most serious side effects of lead poisoning occurs in young children, where it leads to cognitive impairment. Although lead compounds were once used in a variety of applications—as a gasoline additive, in pigments, shotgun pellets, glass, and water pipes—our daily exposure to lead dropped dramatically once governmental agencies started regulating its use in the 1970s. According to the National Health and Nutrition Examination Survey, the mean concentration of lead in the blood for an average U.S. resident dropped from 150 ppb in 1976 to 16 ppb by 2002, nearly an order-of-magnitude decrease.

The regulatory limit set by the U.S. Environmental Protection Agency (EPA) for lead in drinking water is 15 parts per billion (ppb). According to EPA regulations, utilities serving more than 50,000 people must monitor the level of lead in their water and take corrective action if more than 10% of the homes sampled exceed the 15 ppb limit. Tests performed on samples collected in September 2015 by researchers from Virginia Tech found that in 10% of the 252 Flint homes tested the lead concentration exceeded 25 ppb, and in several homes the concentration exceeded 100 ppb. At the same time, a local pediatrician analyzed the results of infant blood tests and found that the percentage of children with elevated concentrations of lead in their bloodstream ( $>50$  ppb) had doubled from 2.4% in the 2013 to 4.9% in 2015.

The troubles began in April 2014 when the city began using the nearby Flint River as the natural source of its municipal water. Prior to that, Flint obtained water from Detroit, where water taken from Lake Huron was treated before piping it to Flint. The source of the lead was not the Flint River itself, but corrosion from lead pipes that are present in the underground water distribution network. Why did the change in water supply dramatically increase the leaching of lead from the old pipes? Many factors were at play, but basically they all came down to solubility considerations.

When water is properly treated, a passivation layer of insoluble lead salts builds up on the inner surface of the lead pipes (Figure 17.21).

This layer prevents corrosion that would otherwise allow lead to be oxidized and dissolve into the water as  $\text{Pb}^{2+}$  ions. The water treatment facility in Detroit was adding phosphate ions,  $\text{PO}_4^{3-}$ , to their water to inhibit corrosion, whereas the people managing water treatment in Flint elected not to do so. The presence of  $\text{PO}_4^{3-}$  ions promotes the formation of highly insoluble phosphate salts on the inner surface of the pipes that helps prevent corrosion.

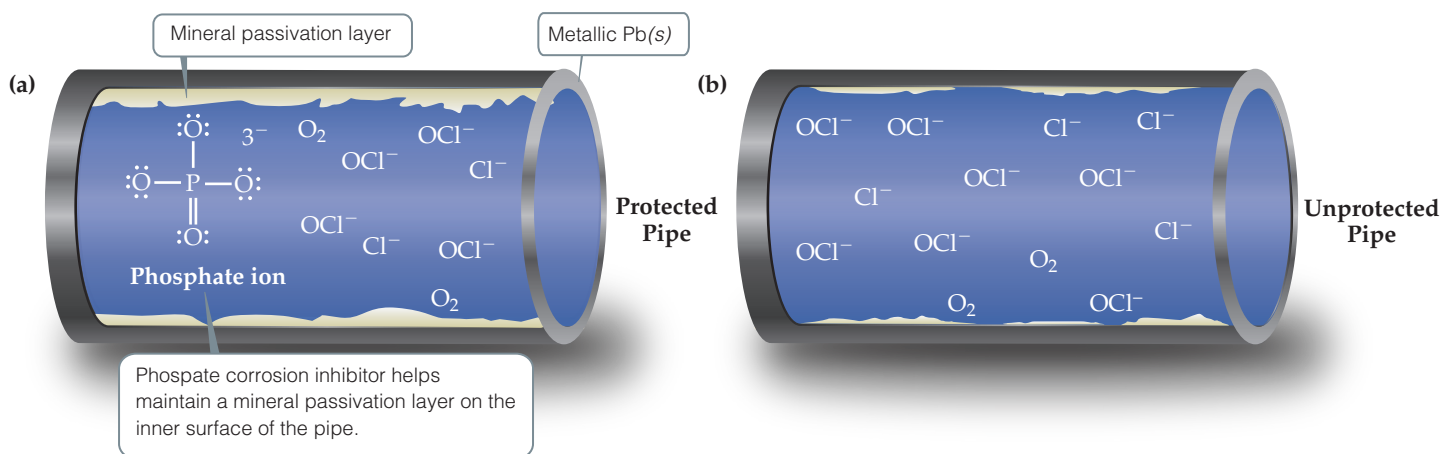
Another factor that appears to have contributed to the problem is a drop in the pH of the water, from 8.0 in December 2014 to 7.3 in August 2015. Because the insoluble lead salts that form the passivating layer, like  $\text{Pb}_3(\text{PO}_4)_2$ ,  $\text{PbHSO}_4$ , and  $\text{PbCO}_3$ , contain anions that can act as weak bases, anything that makes the water more acidic increases their solubility.

Another contributing factor was the presence of high levels of chloride ions. The treated water from Detroit had chloride levels of about 11 ppm, whereas the treated Flint water had chloride levels of 85 ppm in August 2015. While  $\text{PbCl}_2$  is fairly insoluble ( $K_{\text{sp}} = 1.7 \times 10^{-5}$ ), high concentrations of chloride ions can lead to the formation of soluble complex ions such as  $\text{PbCl}_3^-$  and  $\text{PbCl}_4^{2-}$ . The increased chloride levels were due in part to the addition of  $\text{FeCl}_3$ , which was used to help coagulate and filter out unwanted organic matter that was leading to problems with *E. coli* contamination. Chloride ions are also produced when unwanted organic matter is oxidized by hypochlorite ions, which are added to kill bacteria. Run-off containing chloride salts used to treat icy roads in the winter may have also contributed.

In the face of mounting evidence that the lead in Flint's drinking water was at unsafe levels, in October of 2015 the city switched back to water piped in from Detroit. Over a period of many months, the circulation of properly treated water should restore the passivating layers inside the pipes. However, cleanup costs are expected to be in excess of \$120 million and possibly much more, a large sum compared to the estimated \$50,000 per year that it would have cost to treat the water with phosphates. More importantly, the damage done to people who drank the contaminated water, especially children, cannot be undone.

Although the use of lead in plumbing has been banned in the United States since 1986, it is estimated that millions of kilometers of buried lead pipe are still in use in America's cities. Vigilance by water treatment facilities and environmental protection agencies is needed to avoid a repeat of the tragedy in Flint.

**Related Exercises:** 17.107, 17.111



▲ **Figure 17.21** Protected and unprotected lead pipes. (a) A lead pipe that has a protective passivation layer, and (b) a lead pipe where the lack of a phosphate corrosion inhibitor causes the passivation layer to dissolve and fall off, exposing the lead to oxidizing agents such as  $\text{O}_2$  and  $\text{OCl}^-$ .

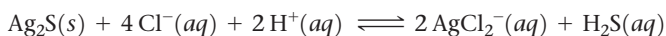


## Self-Assessment Exercises

- 17.30** Which of the following actions will increase the solubility of  $\text{Mg}(\text{OH})_2$  at  $25^\circ\text{C}$ ?  
 (a) Adding dilute  $\text{HCl}(\text{aq})$   
 (b) Adding dilute  $\text{MgCl}_2(\text{aq})$   
 (c) Adding dilute  $\text{NaOH}(\text{aq})$
- 17.31** What is the molar solubility of  $\text{AgCl}$  in  $0.10\text{ M HCl}$  at  $25^\circ\text{C}$  given  $K_{\text{sp}} = 1.80 \times 10^{-10}$  at this temperature.  
 (a)  $1.80 \times 10^{-10}\text{ M}$   
 (b)  $1.80 \times 10^{-9}\text{ M}$   
 (c)  $1.34 \times 10^{-5}\text{ M}$

## Exercises

- 17.32** Calculate the solubility of  $\text{LaF}_3$  in grams per liter in (a) pure water, (b)  $0.010\text{ M KF}$  solution, (c)  $0.050\text{ M LaCl}_3$  solution.
- 17.33** Consider a beaker containing a saturated solution of  $\text{PbI}_2$  in equilibrium with undissolved  $\text{PbI}_2(\text{s})$ . Now solid  $\text{KI}$  is added to this solution. (a) Will the amount of solid  $\text{PbI}_2$  at the bottom of the beaker increase, decrease, or remain the same? (b) Will the concentration of  $\text{Pb}^{2+}$  ions in solution increase or decrease? (c) Will the concentration of  $\text{I}^-$  ions in solution increase or decrease?
- 17.34** Calculate the molar solubility of  $\text{Ni}(\text{OH})_2$  when buffered at pH (a) 8.0, (b) 10.0, (c) 12.0.
- 17.35** Which of the following salts will be substantially more soluble in an  $\text{HNO}_3$  solution than in pure water: (a)  $\text{BaSO}_4$ , (b)  $\text{CuS}$ , (c)  $\text{Cd}(\text{OH})_2$ , (d)  $\text{PbF}_2$ , (e)  $\text{Cu}(\text{NO}_3)_2$ ?
- 17.36** From the value of  $K_f$  listed in Table 17.1, calculate the concentration of  $\text{NH}_3$  required to just dissolve  $0.020\text{ mol}$  of  $\text{NiC}_2\text{O}_4$  ( $K_{\text{sp}} = 4 \times 10^{-10}$ ) in  $1.00\text{ L}$  of solution? (Hint: You can neglect the hydrolysis of  $\text{C}_2\text{O}_4^{2-}$  because the solution will be quite basic.)
- 17.37** Using the value of  $K_{\text{sp}}$  for  $\text{Ag}_2\text{S}$ ,  $K_{a1}$  and  $K_{a2}$  for  $\text{H}_2\text{S}$ , and  $K_f = 1.1 \times 10^5$  for  $\text{AgCl}_2^-$ , calculate the equilibrium constant for the following reaction:



17.30 (a) 17.31 (b)

### Answers to Self-Assessment Exercises

## 17.6 | Precipitation and Separation of Ions



One of the first steps in many commercial water treatment plants is to add either aluminum sulfate or iron(III) chloride. This results in the precipitation of hydroxide salts of  $\text{Al}^{3+}$  or  $\text{Fe}^{3+}$  and flocculation of other ions present in the water. The water is then filtered and disinfected and in some countries a source of fluoride ion added as part of public health policy.



In this section, we examine the precipitation and separation of ions, by the end of which, you should be able to

- Understand how to separate cations based on their solubility.

Equilibrium can be achieved starting with the substances on either side of a chemical equation. For example, the equilibrium that exists between  $\text{BaSO}_4(s)$ ,  $\text{Ba}^{2+}(aq)$ , and  $\text{SO}_4^{2-}(aq)$  (Equation 17.15), can be achieved by starting either with  $\text{BaSO}_4(s)$  or with solutions containing  $\text{Ba}^{2+}$  and  $\text{SO}_4^{2-}$ . If we mix, say, a  $\text{BaCl}_2$  aqueous solution with a  $\text{Na}_2\text{SO}_4$  aqueous solution,  $\text{BaSO}_4$  might precipitate out. How can we predict whether a precipitate will form under various conditions?

Recall that we used the reaction quotient  $Q$  in Section 15.4 to determine the direction in which a reaction must proceed to reach equilibrium. The form of  $Q$  is the same as the equilibrium expression for a reaction, but instead of only equilibrium concentrations, you can use whatever concentrations are being considered. The direction in which a reaction proceeds to reach equilibrium depends on the relationship between  $Q$  and  $K$  for the reaction. If  $Q < K$ , the product concentrations are too low and reactant concentrations are too high relative to the equilibrium concentrations, and so the reaction will proceed to the right (toward products) to achieve equilibrium. If  $Q > K$ , product concentrations are too high and reactant concentrations are too low, and so the reaction will proceed to the left to achieve equilibrium. If  $Q = K$ , the reaction is at equilibrium.

For solubility-product equilibria, the relationship between  $Q$  and  $K_{sp}$  is exactly like that for other equilibria. For  $K_{sp}$  reactions, products are always the soluble ions, and the reactant is always the solid.

Therefore, for solubility equilibria,

- If  $Q = K_{sp}$ , the system is at equilibrium, which means the solution is saturated; this is the highest concentration the solution can have without precipitating.
- If  $Q < K_{sp}$ , the reaction will proceed to the right, toward the soluble ions; no precipitate will form.
- If  $Q > K_{sp}$ , the reaction will proceed to the left, toward the solid; precipitate will form.

For the case of the barium sulfate solution, then we would calculate  $Q = [\text{Ba}^{2+}][\text{SO}_4^{2-}]$ , and compare this quantity to the  $K_{sp}$  for barium sulfate.



## Sample Exercise 17.16

### Predicting Whether a Precipitate Forms

Does 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  $5.0 \times 10^{-3} M \text{Na}_2\text{SO}_4$ ?

### SOLUTION

**Analyze** The problem asks us to determine whether a precipitate forms when two salt solutions are combined.

**Plan** We should determine the concentrations of all ions just after the solutions are mixed and compare the value of  $Q$  with  $K_{sp}$  for any potentially insoluble product. The possible metathesis

products are  $\text{PbSO}_4$  and  $\text{NaNO}_3$ . Like all sodium salts  $\text{NaNO}_3$  is soluble, but  $\text{PbSO}_4$  has a  $K_{sp}$  of  $6.3 \times 10^{-7}$  (Appendix D) and will precipitate if the  $\text{Pb}^{2+}$  and  $\text{SO}_4^{2-}$  concentrations are high enough for  $Q$  to exceed  $K_{sp}$ .

### Solve

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

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

The concentration of  $\text{Pb}^{2+}$  in the 0.50 L mixture is therefore:

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

*Continued*

The number of moles of  $\text{SO}_4^{2-}$  in 0.40 L of  $5.0 \times 10^{-3} \text{ M Na}_2\text{SO}_4$  is:

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

Therefore:

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

and:

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

Because  $Q > K_{sp}$ ,  $\text{PbSO}_4$  precipitates.

### Practice Exercise

An insoluble salt MA has a  $K_{sp}$  of  $1.0 \times 10^{-16}$ . Two solutions,  $\text{MNO}_3$  and  $\text{NaA}$  are mixed, to yield a final solution that is

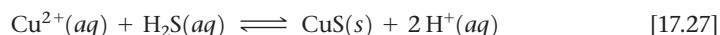
$1.0 \times 10^{-8} \text{ M}$  in  $\text{M}^+(aq)$  and  $1.00 \times 10^{-7} \text{ M}$  in  $\text{A}^-(aq)$ . Will a precipitate form?

(a) Yes (b) No

## Selective Precipitation of Ions

Ions can be separated from each other based on the solubilities of their salts. Consider a solution containing both  $\text{Ag}^+$  and  $\text{Cu}^{2+}$ . If  $\text{HCl}$  is added to the solution,  $\text{AgCl}$  ( $K_{sp} = 1.8 \times 10^{-10}$ ) precipitates, while  $\text{Cu}^{2+}$  remains in solution because  $\text{CuCl}_2$  is soluble. Separation of ions in an aqueous solution by using a reagent that forms a precipitate with one or more (but not all) of the ions is called *selective precipitation*.

Sulfide ion is often used to separate metal ions because the solubilities of sulfide salts span a wide range and depend greatly on solution pH. For example,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  can be separated by bubbling  $\text{H}_2\text{S}$  gas through an acidified solution containing these two cations. Because  $\text{CuS}$  ( $K_{sp} = 6 \times 10^{-37}$ ) is less soluble than  $\text{ZnS}$  ( $K_{sp} = 2 \times 10^{-25}$ ),  $\text{CuS}$  precipitates from an acidified solution ( $\text{pH} \approx 1$ ) while  $\text{ZnS}$  does not (Figure 17.22):



The  $\text{CuS}$  can be separated from the  $\text{Zn}^{2+}$  solution by filtration. The separated  $\text{CuS}$  can then be dissolved by raising the concentration of  $\text{H}^+$  even further, shifting the equilibrium concentrations of the compounds in Equation 17.27 to the left.

## Qualitative Analysis for Metallic Elements

We turn our attention to 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



### Sample Exercise 17.17

#### Selective Precipitation

A solution contains  $1.0 \times 10^{-2} \text{ M Ag}^+(aq)$  and  $2.0 \times 10^{-2} \text{ M Pb}^{2+}(aq)$ . When  $\text{Cl}^-(aq)$  is added, both  $\text{AgCl}$  ( $K_{sp} = 1.8 \times 10^{-10}$ ) and  $\text{PbCl}_2$  ( $K_{sp} = 1.7 \times 10^{-5}$ ) can precipitate. What concentration of  $\text{Cl}^-(aq)$  is necessary to begin the precipitation of each salt? Which salt precipitates first?

#### SOLUTION

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

**Plan** We are given  $K_{sp}$  values for the two precipitates. Using these and the metal ion concentrations, we can calculate what  $\text{Cl}^-(aq)$  concentration is necessary to precipitate each salt. The salt requiring the lower  $\text{Cl}^-(aq)$  ion concentration precipitates first.

**Solve** For  $\text{AgCl}$  we have  $K_{sp} = [\text{Ag}^+][\text{Cl}^-] = 1.8 \times 10^{-10}$ .

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

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

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

Any  $\text{Cl}^-(aq)$  in excess of this very small concentration will cause  $\text{AgCl}$  to precipitate from solution. Proceeding similarly for  $\text{PbCl}_2$ , we have

$$K_{sp} = [\text{Pb}^{2+}][\text{Cl}^-]^2 = 1.7 \times 10^{-5}$$

$$(2.0 \times 10^{-2})[\text{Cl}^-]^2 = 1.7 \times 10^{-5}$$

$$[\text{Cl}^-]^2 = \frac{1.7 \times 10^{-5}}{2.0 \times 10^{-2}} = 8.5 \times 10^{-4}$$

$$[\text{Cl}^-] = \sqrt{8.5 \times 10^{-4}} = 2.9 \times 10^{-2} M$$

Thus, a concentration of  $\text{Cl}^-(aq)$  in excess of  $2.9 \times 10^{-2} M$  causes  $\text{PbCl}_2$  to precipitate.

Comparing the  $\text{Cl}^-(aq)$  concentration required to precipitate each salt, we see that as  $\text{Cl}^-(aq)$  is added,  $\text{AgCl}$  precipitates first because it requires a much smaller concentration of  $\text{Cl}^-$ .

Thus,  $\text{Ag}^+(aq)$  can be separated from  $\text{Pb}^{2+}(aq)$  by slowly adding  $\text{Cl}^-(aq)$  so that the chloride ion concentration remains between  $1.8 \times 10^{-8} M$  and  $2.9 \times 10^{-2} M$ .

**Comment** Precipitation of  $\text{AgCl}$  will keep the  $\text{Cl}^-(aq)$  concentration low until the number of moles of  $\text{Cl}^-(aq)$  added exceeds the number of moles of  $\text{Ag}^+(aq)$  in the solution. Once past this point,  $[\text{Cl}^-]$  rises sharply and  $\text{PbCl}_2$  will soon begin to precipitate.

### Practice Exercise

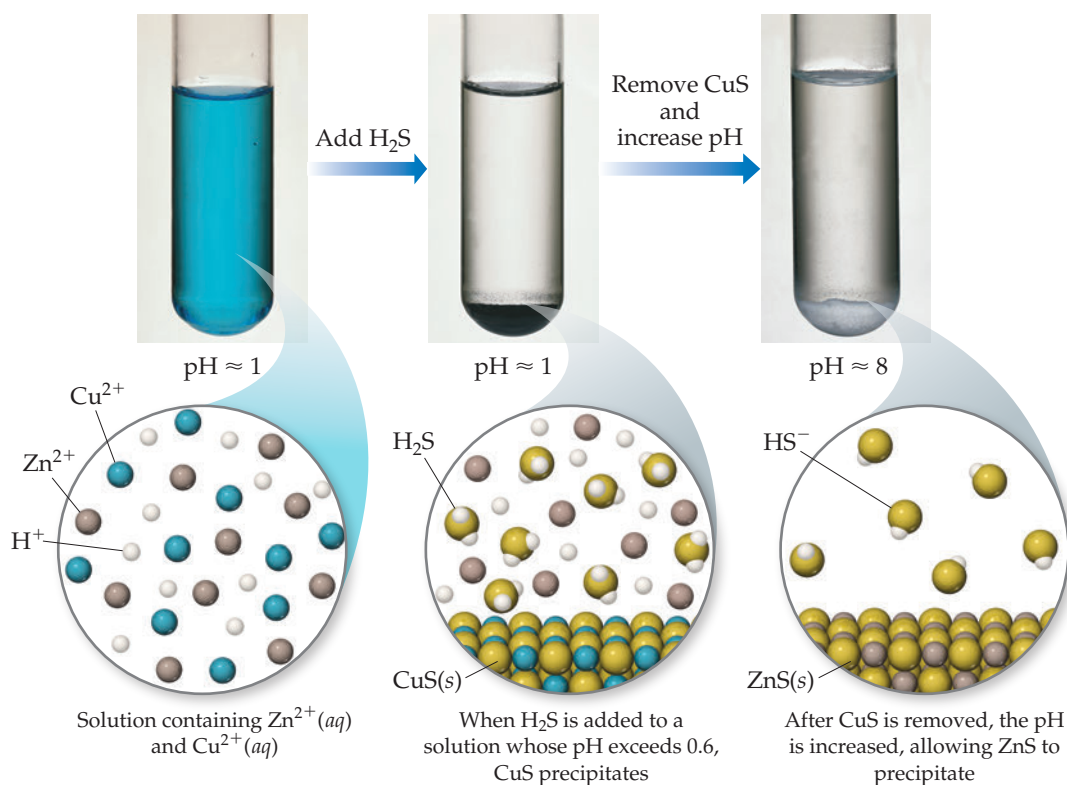
Under what conditions does an ionic compound precipitate from a solution of the constituent ions?

(a) always (b) when  $Q = K_{sp}$  (c) when  $Q$  exceeds  $K_{sp}$  (d) when  $Q$  is less than  $K_{sp}$  (e) never, if it is very soluble



### Go Figure

Why is the sulfide reagent  $\text{HS}^-$  in the third test tube and not  $\text{H}_2\text{S}$ ?



▲ **Figure 17.22** Selective precipitation. In this example,  $\text{Cu}^{2+}$  ions are separated from  $\text{Zn}^{2+}$  ions.

metals in a sample by what were called *wet chemical methods*. For example, an ore sample that might contain several metallic elements was dissolved in a concentrated acid solution that 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 relative to some threshold, whereas **quantitative analysis** determines how much of a given substance is present. Even though wet methods of qualitative analysis have become less important in the chemical industry, they are frequently used in general chemistry laboratory programs 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 ions in

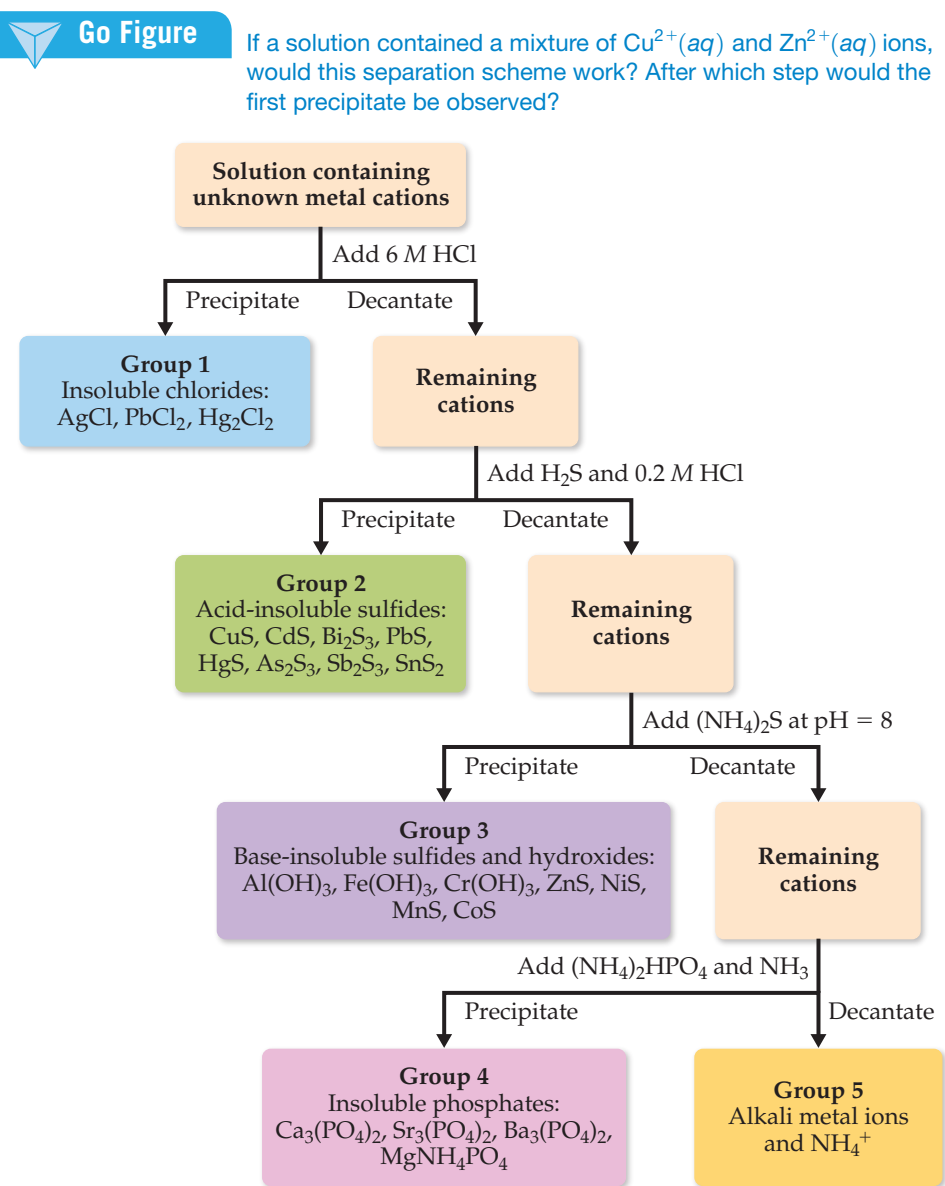
each group are separated by selectively dissolving members in the group. (3) The ions are identified by means of specific tests.

A scheme in general use divides the common cations into five groups (Figure 17.23). The order in which reagents are added is important in this scheme. The most selective separations—those that involve the smallest number of ions—are carried out first. The reactions 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 look at each of these five groups of cations, briefly examining the logic used in this qualitative analysis scheme.

**Group 1. Insoluble chlorides:** Of the common metal ions, only  $\text{Ag}^+(\text{aq})$ ,  $\text{Hg}_2^{2+}(\text{aq})$ , and  $\text{Pb}^{2+}(\text{aq})$  form insoluble chlorides. When HCl is added to a mixture of cations, therefore, only AgCl,  $\text{Hg}_2\text{Cl}_2$ , and  $\text{PbCl}_2$  precipitate, leaving the other cations in solution. The absence of a precipitate indicates that the starting solution contains no  $\text{Ag}^+(\text{aq})$ ,  $\text{Hg}_2^{2+}(\text{aq})$ , or  $\text{Pb}^{2+}(\text{aq})$ .

**Group 2. Acid-insoluble sulfides:** After any insoluble chlorides have been removed, the remaining solution, now acidic from HCl treatment, is treated with  $\text{H}_2\text{S}$ . Since



▲ Figure 17.23 Qualitative analysis. A flowchart showing a common scheme for identifying cations.

$\text{H}_2\text{S}$  is a weak acid compared to  $\text{HCl}$ , its role here is to act as a source for small amounts of sulfide. Only the most insoluble metal sulfides— $\text{CuS}$ ,  $\text{Bi}_2\text{S}_3$ ,  $\text{CdS}$ ,  $\text{PbS}$ ,  $\text{HgS}$ ,  $\text{As}_2\text{S}_3$ ,  $\text{Sb}_2\text{S}_3$ , and  $\text{SnS}_2$ —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,  $\text{ZnS}$  or  $\text{NiS}$ —remain in solution.

**Group 3. Base-insoluble sulfides and hydroxides:** After the solution is filtered to remove any acid-insoluble sulfides, it is made slightly basic, and  $(\text{NH}_4)_2\text{S}$  is added. In basic solutions the concentration of  $\text{S}^{2-}(\text{aq})$  is higher than in acidic solutions. Under these conditions, the ion products for many of the more soluble sulfides exceed their  $K_{sp}$  values and thus precipitation occurs. The metal ions precipitated at this stage are  $\text{Al}^{3+}(\text{aq})$ ,  $\text{Cr}^{3+}(\text{aq})$ ,  $\text{Fe}^{3+}(\text{aq})$ ,  $\text{Zn}^{2+}(\text{aq})$ ,  $\text{Ni}^{2+}(\text{aq})$ ,  $\text{Co}^{2+}(\text{aq})$ , and  $\text{Mn}^{2+}(\text{aq})$ . (The  $\text{Al}^{3+}(\text{aq})$ ,  $\text{Fe}^{3+}(\text{aq})$ , and  $\text{Cr}^{3+}(\text{aq})$  ions do not form insoluble sulfides; instead they precipitate as insoluble hydroxides, as Figure 17.23 shows.)

**Group 4. Insoluble phosphates:** At this point, the solution contains only metal ions from Groups 1 and 2 of the periodic table. Adding  $(\text{NH}_4)_2\text{HPO}_4$  to a basic solution precipitates the Group 2 elements  $\text{Mg}^{2+}(\text{aq})$ ,  $\text{Ca}^{2+}(\text{aq})$ ,  $\text{Sr}^{2+}(\text{aq})$ , and  $\text{Ba}^{2+}(\text{aq})$  because these metals form insoluble phosphates.

**Group 5. The alkali metal ions and  $\text{NH}_4^+(\text{aq})$ :** The ions that remain after removing the insoluble phosphates are tested for individually. A flame test can be used to determine the presence of  $\text{K}^+(\text{aq})$ , for example, because the flame turns a characteristic violet color if  $\text{K}^+(\text{aq})$  is present (Figure 7.22).

## Self-Assessment Exercise

- 17.38** In the analysis of metal ions by the precipitation of insoluble sulfides, why is it important to perform the test at pH 2 before pH 8?
- (a) Performing the test first at pH 8 will precipitate all metal sulfides that are insoluble up to this pH including those only precipitated at pH 2.
- (b) It is more convenient to increase pH from 2 to 8 rather than decrease pH from 8 to 2.
- (c) Cations from Group 2 of Figure 17.23 can react with those of Group 3 of Figure 17.23 and need to be removed as soon as possible.

## Exercises

- 17.39** (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  $\text{AgIO}_3$  precipitate when 20 mL of 0.010 M  $\text{AgIO}_3$  is mixed with 10 mL of 0.015 M  $\text{NaIO}_3$ ? ( $K_{sp}$  of  $\text{AgIO}_3$  is  $3.1 \times 10^{-8}$ .)
- 17.40** Suppose that a 10 mL sample of a solution is to be tested for  $\text{I}^-$  ion by addition of 1 drop (0.2 mL) of 0.10 M  $\text{Pb}(\text{NO}_3)_2$ . What is the minimum number of grams of  $\text{I}^-$  that must be present for  $\text{PbI}_2(\text{s})$  to form?
- 17.41** A solution of  $\text{Na}_2\text{SO}_4$  is added dropwise to a solution that is 0.010 M in  $\text{Ba}^{2+}(\text{aq})$  and 0.010 M in  $\text{Sr}^{2+}(\text{aq})$ . (a) What concentration of  $\text{SO}_4^{2-}$  is necessary to begin precipitation? (Neglect volume changes.  $\text{BaSO}_4$ :  $K_{sp} = 1.1 \times 10^{-10}$ ,  $\text{SrSO}_4$ :  $K_{sp} = 3.2 \times 10^{-7}$ .) (b) Which cation precipitates first? (c) What is the concentration of  $\text{SO}_4^{2-}(\text{aq})$  when the second cation begins to precipitate?
- 17.42** A 1.0 M  $\text{Na}_2\text{SO}_4$  solution is slowly added to 10.0 mL of a solution that is 0.20 M in  $\text{Ca}^{2+}$  and 0.30 M in  $\text{Ag}^+$ . (a) Which compound will precipitate first:  $\text{CaSO}_4$  ( $K_{sp} = 2.4 \times 10^{-5}$ ) or  $\text{Ag}_2\text{SO}_4$  ( $K_{sp} = 1.5 \times 10^{-5}$ )? (b) How much  $\text{Na}_2\text{SO}_4$  solution must be added to initiate the precipitation?
- 17.43** An unknown solid is entirely soluble in water. On addition of dilute  $\text{HCl}$ , a precipitate forms. After the precipitate is filtered off, the pH is adjusted to about 1 and  $\text{H}_2\text{S}$  is bubbled in; a precipitate again forms. After filtering off this precipitate, the pH is adjusted to 8 and  $\text{H}_2\text{S}$  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 (see Figure 7.22). Based on these observations, which of the following compounds might be present, which are definitely present, and which are definitely absent:  $\text{CdS}$ ,  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{HgO}$ ,  $\text{ZnSO}_4$ ,  $\text{Cd}(\text{NO}_3)_2$ , and  $\text{Na}_2\text{SO}_4$ ?
- 17.44** Suggest how the cations in each of the following solution mixtures can be separated: (a)  $\text{Na}^+$  and  $\text{Cd}^{2+}$ , (b)  $\text{Cu}^{2+}$  and  $\text{Mg}^{2+}$ , (c)  $\text{Pb}^{2+}$  and  $\text{Al}^{3+}$ , (d)  $\text{Ag}^+$  and  $\text{Hg}^{2+}$ .
- 17.45** (a) Precipitation of the Group 4 cations of Figure 17.23 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.



## Sample Integrative Exercise

### Putting Concepts Together

A sample of 1.25 L of HCl gas at 21 °C and 96.3 kPa is bubbled through 0.500 L of 0.150 *M* NH<sub>3</sub> 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

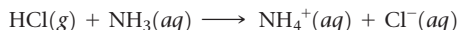
The number of moles of HCl gas is calculated from the ideal gas law:

$$n = \frac{PV}{RT} = \frac{(96.3 \text{ kPa})(1.25 \text{ L})}{(8.314 \text{ L}\cdot\text{kPa}/\text{mol}\cdot\text{K})(294 \text{ K})} = 0.0492 \text{ mol HCl}$$

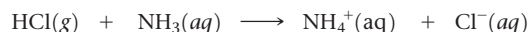
The number of moles of NH<sub>3</sub> in the solution is given by the product of the volume of the solution and its concentration:

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

The acid HCl and base NH<sub>3</sub> react, transferring a proton from HCl to NH<sub>3</sub>, producing NH<sub>4</sub><sup>+</sup> and Cl<sup>−</sup> 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. Because you can assume this neutralization reaction proceeds as far toward the product side as possible, this is a limiting reactant problem.



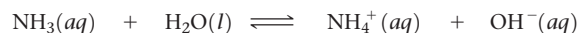
Before reaction (mol)	0.0492	0.0750	0	0
Change (limiting reactant) (mol)	−0.0492	−0.0492	+0.0492	+0.0492
After reaction (mol)	0	0.0258	0.0492	0.0492

Thus, the reaction produces a solution containing a mixture of NH<sub>3</sub>, NH<sub>4</sub><sup>+</sup>, and Cl<sup>−</sup>. The NH<sub>3</sub> is a weak base ( $K_b = 1.8 \times 10^{-5}$ ), NH<sub>4</sub><sup>+</sup> is its conjugate acid, and Cl<sup>−</sup> is neither acidic nor basic. Consequently, the pH depends on [NH<sub>3</sub>] and [NH<sub>4</sub><sup>+</sup>]:

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

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

We can calculate the pH using either  $K_b$  for NH<sub>3</sub> or  $K_a$  for NH<sub>4</sub><sup>+</sup>. Using the  $K_b$  expression, we have:



Initial (M)	0.0516	—	0.0984	0
Change (M)	− <i>x</i>	—	+ <i>x</i>	+ <i>x</i>
Equilibrium (M)	(0.0516 − <i>x</i> )	—	(0.0984 + <i>x</i> )	<i>x</i>

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

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

$$\text{Hence, pOH} = -\log(9.4 \times 10^{-6}) = 5.03$$

$$\text{and pH} = 14.00 - \text{pOH} = 14.00 - 5.03 = 8.97.$$

## Chapter Summary and Key Terms

**THE COMMON ION EFFECT (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 (the **common-ion effect**).

**BUFFERS (SECTION 17.2)** A particularly important type of acid–base mixture is that of a weak conjugate acid–base pair that functions as a **buffered solution (buffer)**. 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 range. The optimal pH of a buffer is equal to  $pK_a$  (or  $pK_b$ ) of the acid (or base) used to prepare the buffer. The relationship between pH,  $pK_a$ , and the concentrations of an acid and its conjugate base can be expressed by the **Henderson–Hasselbalch equation**. It is important to realize that the Henderson–Hasselbalch equation is an approximation, and more detailed calculations may need to be performed to obtain equilibrium concentrations.

**ACID–BASE TITRATIONS (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**. 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 such a titration  $pH = 7$ . 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 as for a strong acid–strong base titration, nor will the pH equal 7 at the equivalence point in these cases. Instead, what determines the pH at the equivalence point is the conjugate base or acid salt solution that results from the neutralization reaction. For this reason, it is important to choose an indicator whose color change is near the pH at the equivalence point for titrations involving either weak acids or weak bases. It is possible to calculate the pH at any point of the titration curve by first considering the effects of the acid–base reaction on solution concentrations and then examining equilibria involving the remaining solute species.

**SOLUBILITY EQUILIBRIA (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  $K_{sp}$ .

**FACTORS THAT AFFECT SOLUBILITY (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.

**PRECIPITATION AND SEPARATION OF IONS (SECTION 17.6)** Comparison of the reaction quotient,  $Q$ , 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  $Q > K_{sp}$ . If two salts have sufficiently different solubilities, selective precipitation can be used to precipitate one ion while leaving the other in solution, effectively separating the two ions.

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.

## Learning Outcomes After studying this chapter, you should be able to:

- Describe the common-ion effect. (Section 17.1)  
*Related Exercises:* 17.2, 17.58
- Explain how a buffer functions and calculate the pH of a buffered solution. (Section 17.2) *Related Exercises:* 17.8, 17.61
- Calculate the pH of a buffer after the addition of small amounts of a strong acid or a strong base. (Section 17.2)  
*Related Exercises:* 17.12, 17.65
- Calculate the appropriate quantities of compounds to make a buffer at a given pH. (Section 17.2) *Related Exercises:* 17.14, 17.67
- Calculate the pH at any point for an acid–base titration curve. (Section 17.3) *Related Exercises:* 17.23, 17.74
- Estimate the  $pK_a$  for monoprotic or polyprotic acids from their titration curves. (Section 17.3) *Related Exercises:* 17.17, 17.68
- Given either  $K_{sp}$ , molar solubility, or mass solubility for a substance, calculate the other two quantities. (Section 17.4)  
*Related Exercises:* 17.26, 17.28, 17.76, 17.78
- Qualitatively predict, and quantitatively calculate, the molar solubility of a substance in the presence of a common ion or at different pH values. (Section 17.5)  
*Related Exercises:* 17.29, 17.35, 17.37, 17.79, 17.83, 17.85
- Qualitatively predict whether a precipitate will form when solutions are mixed, and quantitatively calculate the ion concentrations required to initiate precipitation. (Section 17.6)  
*Related Exercises:* 17.39, 17.41, 17.86, 17.88
- Explain the effect of complex-ion formation on solubility. (Section 17.6) *Related Exercises:* 17.36, 17.84
- Predict how to separate and identify cations based on their solubility characteristics. (Section 17.6)  
*Related Exercises:* 17.44, 17.91

## Key Equations

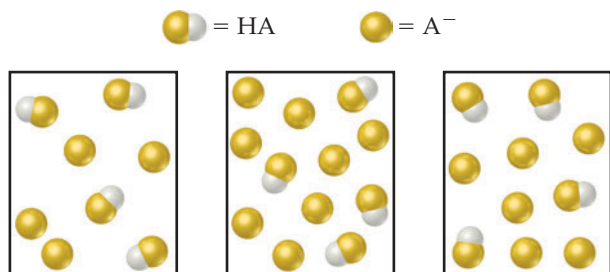
$$pH = pK_a + \log \frac{[\text{base}]}{[\text{acid}]} \quad [17.9]$$

The Henderson–Hasselbalch equation, used to estimate the pH of a buffer from the concentrations of a conjugate acid–base pair

## Exercises

## Visualizing Concepts

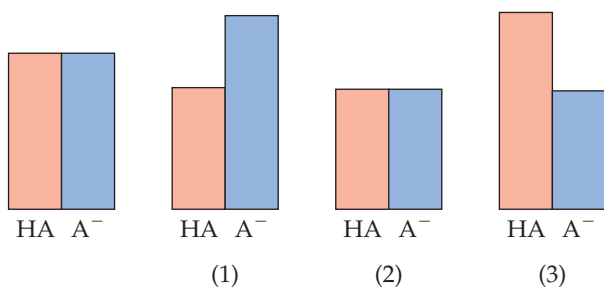
- 17.46** The following boxes represent aqueous solutions containing a weak acid, HA, and its conjugate base,  $A^-$ . Water molecules, hydronium ions, and cations are not shown. Which solution has the highest pH? Explain. [Section 17.1]



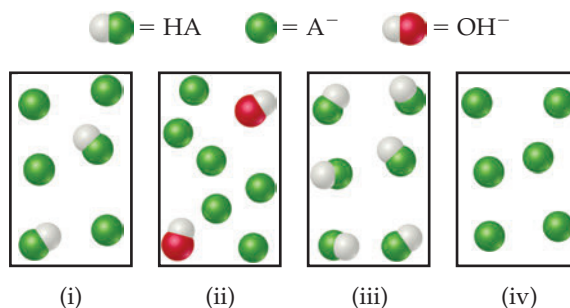
- 17.47** The beaker on the right contains 0.1 M acetic acid solution with methyl orange as an indicator. The beaker on the left contains a mixture of 0.1 M acetic acid and 0.1 M sodium acetate with methyl orange. (a) Using Figures 16.8 and 16.9, which solution has a higher pH? (b) Which solution is better able to maintain its pH when small amounts of NaOH are added? Explain. [Sections 17.1 and 17.2]



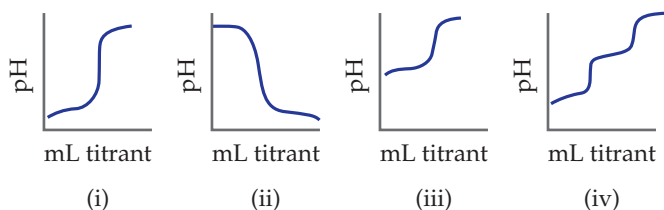
- 17.48** A buffer contains a weak acid, HA, and its conjugate base. The weak acid has a  $pK_a$  of 4.5, and the buffer has a pH of 4.7. Without doing a calculation, state which of these possibilities are correct at pH 4.7. (a)  $[HA] > [A^-]$ , (b)  $[HA] = [A^-]$ , or (c)  $[HA] < [A^-]$ .
- 17.49** The following diagram represents a buffer composed of equal concentrations of a weak acid, HA, and its conjugate base,  $A^-$ . 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]



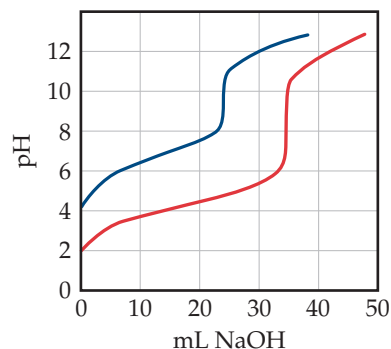
- 17.50** The following figure represents solutions at various stages of the titration of a weak acid, HA, with NaOH. (The  $Na^+$  ions and water molecules have been omitted for clarity.) To which of the following regions of the titration curve does each drawing correspond: (a) before addition of NaOH,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



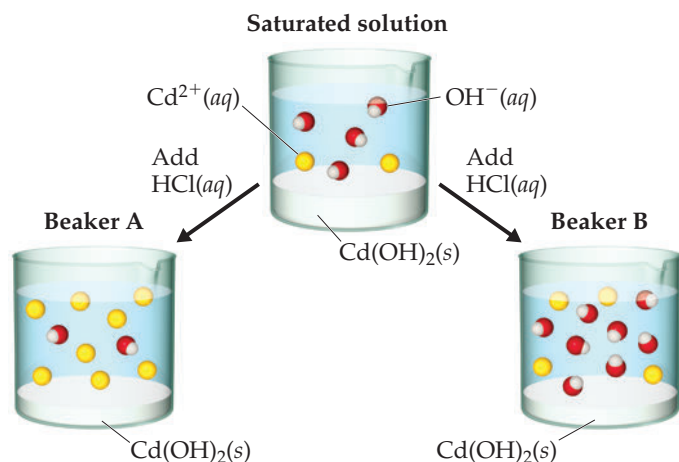
- 17.51** Match the following descriptions of titration curves with the diagrams: (a) strong acid added to strong base, (b) strong base added to weak acid, (c) strong base added to strong acid, (d) strong base added to polyprotic acid. [Section 17.3]



- 17.52** 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 larger  $K_a$ ? [Section 17.3]

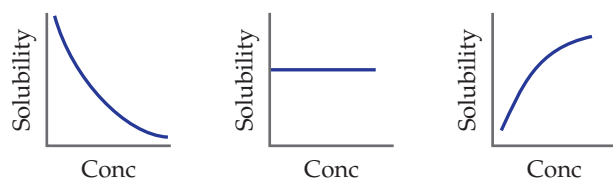


- 17.53** A saturated solution of  $Cd(OH)_2$  is shown in the middle beaker. If hydrochloric acid solution is added, the solubility of  $Cd(OH)_2$  will increase, causing additional solid to

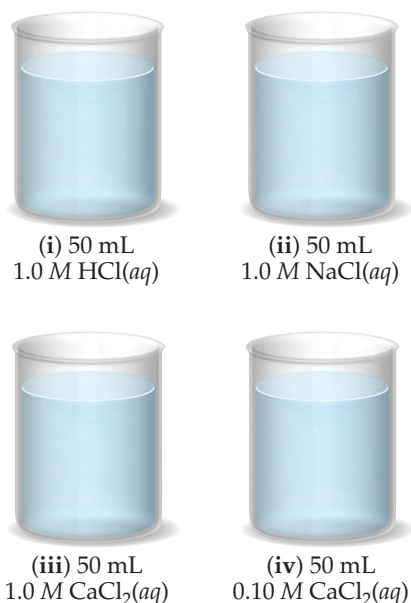


dissolve. Which of the two choices, Beaker A or Beaker B, accurately represents the solution after equilibrium is reestablished? (The water molecules and  $\text{Cl}^{-}$  ions are omitted for clarity.) [Sections 17.4 and 17.5]

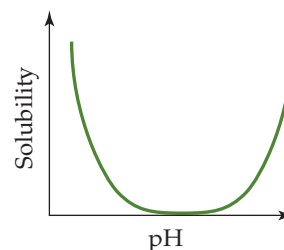
- 17.54** The following graphs represent the behavior of  $\text{BaCO}_3$  under different circumstances. In each case, the vertical axis indicates the solubility of the  $\text{BaCO}_3$  and the horizontal axis represents the concentration of some other reagent. (a) Which graph represents what happens to the solubility of  $\text{BaCO}_3$  as  $\text{HNO}_3$  is added? (b) Which graph represents what happens to the  $\text{BaCO}_3$  solubility as  $\text{Na}_2\text{CO}_3$  is added? (c) Which represents what happens to the  $\text{BaCO}_3$  solubility as  $\text{NaNO}_3$  is added? [Section 17.5]



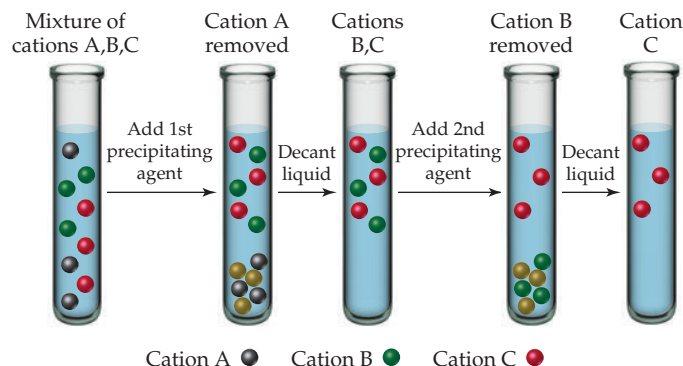
- 17.55**  $\text{Ca}(\text{OH})_2$  has a  $K_{sp}$  of  $6.5 \times 10^{-6}$ . (a) If 0.370 g of  $\text{Ca}(\text{OH})_2$  is added to 500 mL of water and the mixture is allowed to come to equilibrium, will the solution be saturated? (b) If 50 mL of the solution from part (a) is added to each of the beakers shown here, in which beakers, if any, will a precipitate form? In those cases where a precipitate forms, what is its identity? [Section 17.6]



- 17.56** This graph shows the solubility of a salt as a function of pH. Which of the following choices explain the shape of this graph? (a) None; this behavior is not possible. (b) A soluble salt reacts with acid to form a precipitate, and additional acid reacts with this product to dissolve it. (c) A soluble salt forms an insoluble hydroxide, then additional base reacts with this product to dissolve it. (d) The solubility of the salt increases with pH, then decreases because of the heat generated from the neutralization reactions. [Section 17.5]



- 17.57** Three cations,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Ag}^{+}$ , are separated using two different precipitating agents. Based on Figure 17.23, 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 17.6]



### The Common-Ion Effect (Section 17.1)

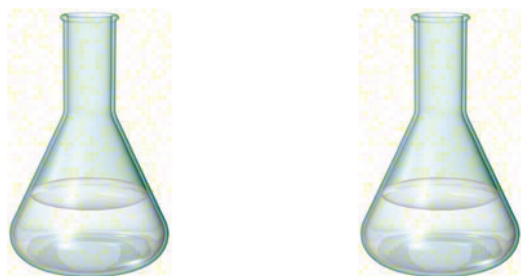
- 17.58** Which of these statements about the common-ion effect is most correct? (a) The solubility of a salt  $\text{MA}$  is decreased in a solution that already contains either  $\text{M}^{+}$  or  $\text{A}^{-}$ . (b) Common ions alter the equilibrium constant for the reaction of an ionic solid with water. (c) The common-ion effect does not apply to unusual ions like  $\text{SO}_3^{2-}$ . (d) The solubility of a salt  $\text{MA}$  is affected equally by the addition of either  $\text{A}^{-}$  or a noncommon ion.
- 17.59** Use information from Appendix D to calculate the pH of (a) a solution that is 0.070 M in potassium propanoate ( $\text{C}_2\text{H}_5\text{COOK}$  or  $\text{KC}_2\text{H}_5\text{O}_2$ ) and 0.085 M in propanoic acid ( $\text{C}_2\text{H}_5\text{COOH}$  or  $\text{HC}_2\text{H}_5\text{O}_2$ ); (b) a solution that is 0.085 M in trimethylamine,  $(\text{CH}_3)_3\text{N}$ , and 0.10 M in trimethylammonium chloride,  $(\text{CH}_3)_3\text{NCl}$ ; (c) a solution that is made by mixing 25.0 mL of 0.20 M acetic acid and 25.0 mL of 0.25 M sodium acetate.
- 17.60** (a) Calculate the percent ionization of 0.0085 M butanoic acid ( $K_a = 1.5 \times 10^{-5}$ ). (b) Calculate the percent ionization of 0.0085 M butanoic acid in a solution containing 0.075 M sodium butanoate.

## Buffers (Section 17.2)

- 17.61** Which of the following solutions is a buffer? (a) 0.20 M formic acid ( $\text{HCOOH}$ ), (b) 0.20 M formic acid ( $\text{HCOOH}$ ) and 0.20 M sodium formate ( $\text{HCOONa}$ ), (c) 0.20 M nitric acid ( $\text{HNO}_3$ ) and 0.20 M sodium nitrate ( $\text{NaNO}_3$ ), (d) both b and c, (e) all of a, b, and c.
- 17.62** (a) Calculate the pH of a buffer that is 0.150 M in lactic acid and 0.120 M in sodium lactate. (b) Calculate the pH of a buffer formed by mixing 75 mL of 0.150 M lactic acid with 25 mL of 0.120 M sodium lactate.
- 17.63** A buffer is prepared by adding 15.0 g of sodium acetate ( $\text{CH}_3\text{COONa}$ ) to 500 mL of a 0.100 M acetic acid ( $\text{CH}_3\text{COOH}$ ) solution. (a) Determine the pH of the 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.
- 17.64** You are asked to prepare a pH = 2.50 buffer solution starting from 1.50 L of a 0.75 M solution of hydrofluoric acid ( $\text{HF}$ ) and any amount you need of sodium fluoride ( $\text{NaF}$ ). (a) What is the pH of the hydrofluoric acid solution prior to adding sodium fluoride? (b) How many grams of sodium fluoride should be added to prepare the buffer solution? Neglect the small volume change that occurs when the sodium fluoride is added.
- 17.65** A buffer contains 0.20 mol of acetic acid and 0.25 mol of sodium acetate in 2.50 L. (a) What is the pH of this buffer? (b) What is the pH of the buffer after the addition of 0.05 mol of  $\text{NaOH}$ ? (c) What is the pH of the buffer after the addition of 0.05 mol of  $\text{HCl}$ ?
- 17.66** (a) What is the ratio of  $\text{HCO}_3^-$  to  $\text{H}_2\text{CO}_3$  in blood of pH 7.4? (b) What is the ratio of  $\text{HCO}_3^-$  to  $\text{H}_2\text{CO}_3$  in an exhausted marathon runner whose blood pH is 7.1?
- 17.67** You have to prepare a pH = 2.50 buffer, and you have the following 0.20 M solutions available:  $\text{HCOOH}$ ,  $\text{CH}_3\text{COOH}$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{KCH}_3\text{COO}$ ,  $\text{KHCOO}$ , and  $\text{KH}_2\text{PO}_4$ . Which solutions would you use? How many liters of each solution would you use to make approximately 2 L of the buffer?

## Acid–Base Titrations (Section 17.3)

- 17.68** Compare the titration of a strong, monoprotic acid with a strong base to the titration of a weak, monoprotic acid with a strong base. Assume the strong and weak acid solutions initially have the same concentrations. Indicate whether the following statements are true or false. (a) More base is required to reach the equivalence point for the strong acid than the weak acid. (b) The pH at the beginning of the titration is lower for the weak acid than the strong acid. (c) The pH at the equivalence point is 7 no matter which acid is titrated.
- 17.69** The samples of nitric and acetic acids shown here are both titrated with a 0.100 M solution of  $\text{NaOH}(aq)$ .

25.0 mL of 1.0 M  $\text{HNO}_3(aq)$     25.0 mL of 1.0 M  $\text{CH}_3\text{COOH}(aq)$ 

Determine whether each of the following statements concerning these titrations is true or false.

- (a) A larger volume of  $\text{NaOH}(aq)$  is needed to reach the equivalence point in the titration of  $\text{HNO}_3$ .
- (b) The pH at the equivalence point in the  $\text{HNO}_3$  titration will be lower than the pH at the equivalence point in the  $\text{CH}_3\text{COOH}$  titration.
- (c) Phenolphthalein would be a suitable indicator for both titrations.
- 17.70** Predict whether the equivalence point of each of the following titrations is below, above, or at pH 7: (a)  $\text{NaHCO}_3$  titrated with  $\text{NaOH}$ , (b)  $\text{NH}_3$  titrated with  $\text{HCl}$ , (c)  $\text{KOH}$  titrated with  $\text{HBr}$ .
- 17.71** As shown in Figure 16.7, the indicator thymol blue has two color changes. Which color change will generally be more suitable for the titration of a weak acid with a strong base?
- 17.72** How many milliliters of 0.0750 M  $\text{KOH}$  are required to titrate each of the following solutions to the equivalence point: (a) 30.0 mL of 0.0900 M  $\text{HCOOH}$ , (b) 45.0 mL of 0.0750 M  $\text{HNO}_3$ , (c) 50.0 mL of a solution that contains 3.00 g of  $\text{HBr}$  per liter?
- 17.73** A 10.0 mL sample of 0.250 M  $\text{HNO}_3$  solution is titrated with 0.100 M  $\text{KOH}$  solution. Calculate the pH of the solution after the following volumes of base have been added: (a) 20.0 mL, (b) 24.9 mL, (c) 25.0 mL, (d) 25.1 mL, (e) 30.0 mL.
- 17.74** A 10.0 mL sample of 0.250 M acetic acid ( $\text{CH}_3\text{COOH}$ ) is titrated with 0.100 M  $\text{KOH}$  solution. Calculate the pH after the following volumes of base have been added: (a) 0 mL, (b) 12.5 mL, (c) 24.5 mL, (d) 25.0 mL, (e) 25.5 mL, (f) 30.0 mL.
- 17.75** Calculate the pH at the equivalence point for titrating 0.200 M solutions of each of the following bases with 0.200 M  $\text{HBr}$ : (a) sodium hydroxide ( $\text{NaOH}$ ), (b) hydroxylamine ( $\text{NH}_2\text{OH}$ ), (c) aniline ( $\text{C}_6\text{H}_5\text{NH}_2$ ).

## Solubility Equilibria and Factors Affecting Solubility (Sections 17.4 and 17.5)

- 17.76** For each statement, indicate whether it is true or false.
- (a) The solubility of a slightly soluble salt can be expressed in units of moles per liter.
- (b) The solubility product of a slightly soluble salt is simply the square of the solubility.
- (c) The solubility of a slightly soluble salt is independent of the presence of a common ion.
- (d) The solubility product of a slightly soluble salt is independent of the presence of a common ion.
- 17.77** Write the expression for the solubility-product constant for each of the following ionic compounds:  $\text{BaCrO}_4$ ,  $\text{CuS}$ ,  $\text{PbCl}_2$  and  $\text{LaF}_3$ .
- 17.78** (a) If the molar solubility of  $\text{CaF}_2$  at 35 °C is  $1.24 \times 10^{-3}$  mol/L, what is  $K_{sp}$  at this temperature? (b) It is found that  $1.1 \times 10^{-2}$  g  $\text{SrF}_2$  dissolves per 100 mL of aqueous solution at 25 °C. Calculate the solubility product for  $\text{SrF}_2$ . (c) The  $K_{sp}$  of  $\text{Ba}(\text{IO}_3)_2$  at 25 °C is  $6.0 \times 10^{-10}$ . What is the molar solubility of  $\text{Ba}(\text{IO}_3)_2$ ?
- 17.79** A 1.50 L solution saturated at 25 °C with cobalt carbonate ( $\text{CoCO}_3$ ) contains 2.71 mg of  $\text{CoCO}_3$ . Calculate the solubility-product constant for this salt at 25 °C.
- 17.80** Using Appendix D, calculate the molar solubility of  $\text{AgI}$  in (a) pure water, (b) 0.15 M  $\text{KI}$  solution, (c)  $5.0 \times 10^{-2}$  M  $\text{AgNO}_3$  solution.
- 17.81** Consider a beaker containing a saturated solution of  $\text{CaF}_2$  in equilibrium with undissolved  $\text{CaF}_2(s)$ . Solid  $\text{CaCl}_2$  is then added to the solution. (a) Will the amount of solid  $\text{CaF}_2$  at the bottom of the beaker increase, decrease, or



remain the same? (b) Will the concentration of  $\text{Ca}^{2+}$  ions in solution increase or decrease? (c) Will the concentration of  $\text{F}^-$  ions in solution increase or decrease?

- 17.82** Calculate the solubility of  $\text{Mn}(\text{OH})_2$  in grams per liter when buffered at pH (a) 7.0, (b) 9.5, (c) 11.8.
- 17.83** For each of the following slightly soluble salts, write the net ionic equation, if any, for reaction with a strong acid: (a)  $\text{MnS}$ , (b)  $\text{PbF}_2$ , (c)  $\text{AuCl}_3$ , (d)  $\text{Hg}_2\text{C}_2\text{O}_4$ , (e)  $\text{CuBr}$ .
- 17.84** From the value of  $K_f$  listed in Table 17.1, calculate the concentration of  $\text{Cu}^{2+}(\text{aq})$  and  $\text{Cu}(\text{NH}_3)_4^{2+}$  that are present at equilibrium after dissolving 5.00 g  $\text{CuCl}_2$  in 1.00 L of 0.10 M  $\text{NH}_3(\text{aq})$ .
- 17.85** Use values of  $K_{sp}$  for  $\text{AgI}$  and  $K_f$  for  $\text{Ag}(\text{CN})_2^-$  to (a) calculate the molar solubility of  $\text{AgI}$  in pure water, (b) calculate the equilibrium constant for the reaction  $\text{AgI}(\text{s}) + 2 \text{CN}^-(\text{aq}) \rightleftharpoons \text{Ag}(\text{CN})_2^-(\text{aq}) + \text{I}^-(\text{aq})$ , (c) determine the molar solubility of  $\text{AgI}$  in a 0.100 M  $\text{NaCN}$  solution.

### Precipitation and Separation of Ions (Section 17.6)

- 17.86** (a) Will  $\text{Ca}(\text{OH})_2$  precipitate from solution if the pH of a 0.050 M solution of  $\text{CaCl}_2$  is adjusted to 8.0? (b) Will  $\text{Ag}_2\text{SO}_4$  precipitate when 100 mL of 0.050 M  $\text{AgNO}_3$  is mixed with 10 mL of  $5.0 \times 10^{-2}$  M  $\text{Na}_2\text{SO}_4$  solution?
- 17.87** Calculate the minimum pH needed to precipitate  $\text{Mn}(\text{OH})_2$  so completely that the concentration of  $\text{Mn}^{2+}(\text{aq})$  is less than  $1 \mu\text{g}$  per liter [1 part per billion (ppb)].

- 17.88** A solution contains  $1.0 \times 10^{-4}$   $\text{Ca}^{2+}(\text{aq})$  and  $1.0 \times 10^{-4}$   $\text{La}^{3+}(\text{aq})$ . If  $\text{NaF}$  is added, will  $\text{CaF}_2$  ( $K_{sp} = 3.9 \times 10^{-11}$ ) or  $\text{LaF}_3$  ( $K_{sp} = 2 \times 10^{-19}$ ) precipitate first? Specify the concentration of  $\text{F}^-(\text{aq})$  needed to begin precipitation.
- 17.89** A solution contains three anions with the following concentrations: 0.20 M  $\text{CrO}_4^{2-}$ , 0.10 M  $\text{CO}_3^{2-}$ , and 0.010 M  $\text{Cl}^-$ . If a dilute  $\text{AgNO}_3$  solution is slowly added to the solution, what is the first compound to precipitate:  $\text{Ag}_2\text{CrO}_4$  ( $K_{sp} = 1.2 \times 10^{-12}$ ),  $\text{Ag}_2\text{CO}_3$  ( $K_{sp} = 8.1 \times 10^{-12}$ ), or  $\text{AgCl}$  ( $K_{sp} = 1.8 \times 10^{-10}$ )?
- 17.90** A solution containing several metal ions is treated with dilute  $\text{HCl}$ ; no precipitate forms. The pH is adjusted to about 1, and  $\text{H}_2\text{S}$  is bubbled through. Again, no precipitate forms. The pH of the solution is then adjusted to about 8. Again,  $\text{H}_2\text{S}$  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 of these metal cations are either possibly present or definitely absent:  $\text{Al}^{3+}$ ,  $\text{Na}^+$ ,  $\text{Ag}^+$ ,  $\text{Mg}^{2+}$ ?
- 17.91** In the course of various qualitative analysis procedures, the following mixtures are encountered: (a)  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$ , (b)  $\text{Cr}(\text{OH})_3$  and  $\text{Fe}(\text{OH})_3$ , (c)  $\text{Mg}^{2+}$  and  $\text{K}^+$ , (d)  $\text{Ag}^+$  and  $\text{Mn}^{2+}$ . Suggest how each mixture might be separated.
- 17.92** A student who is in a great hurry to finish his laboratory work decides that his qualitative analysis unknown contains a metal ion from Group 4 of Figure 17.23. 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?

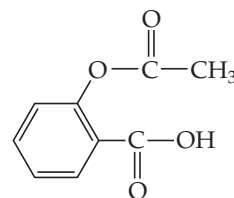
## Additional Exercises

- 17.93** Derive an equation similar to the Henderson–Hasselbalch equation relating the pOH of a buffer to the  $\text{p}K_b$  of its base component.
- 17.94** Rainwater is acidic because  $\text{CO}_2(\text{g})$  dissolves in the water, creating carbonic acid,  $\text{H}_2\text{CO}_3$ . If the rainwater is too acidic, it will react with limestone and seashells (which are principally made of calcium carbonate,  $\text{CaCO}_3$ ). Calculate the concentrations of carbonic acid, bicarbonate ion ( $\text{HCO}_3^-$ ) and carbonate ion ( $\text{CO}_3^{2-}$ ) that are in a raindrop that has a pH of 5.60, assuming that the sum of all three species in the raindrop is  $1.0 \times 10^{-5}$  M.
- 17.95** Furoic acid ( $\text{HC}_5\text{H}_3\text{O}_3$ ) has a  $K_a$  value of  $6.76 \times 10^{-4}$  at 25 °C. Calculate the pH at 25 °C of (a) a solution formed by adding 30.0 g of furoic acid and 25.0 g of sodium furoate ( $\text{NaC}_5\text{H}_3\text{O}_3$ ) to enough water to form 0.300 L of solution, (b) a solution formed by mixing 20.0 mL of 0.200 M  $\text{HC}_5\text{H}_3\text{O}_3$  and 30.0 mL of 0.250 M  $\text{NaC}_5\text{H}_3\text{O}_3$  and diluting the total volume to 125 mL, (c) a solution prepared by adding 25.0 mL of 1.00 M  $\text{NaOH}$  solution to 100.0 mL of 0.100 M  $\text{HC}_5\text{H}_3\text{O}_3$ .
- 17.96** 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  $\text{p}K_a$  for bromocresol green?
- 17.97** 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 chemical equation and equilibrium expression for the reaction between HA and B. (b) If  $K_a$  for HA is  $8.0 \times 10^{-5}$ , 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?
- 17.98** Two buffers are prepared by adding an equal number of moles of methanoic acid ( $\text{HCOOH}$ ) and sodium methanoate ( $\text{HCOONa}$ ) to enough water to make 1.00 L of solution. Buffer A is prepared using 1.00 mole each of methanoic acid and sodium methanoate. Buffer B is prepared by using 0.010 mol of each. (a) Calculate the pH of each buffer. (b) Which buffer will have the greater buffer capacity? (c) Calculate the change in pH for each buffer upon the addition of 1.0 mL of 1.00 M  $\text{HCl}$ . (d) Calculate the change in pH for each buffer upon the addition of 10 mL of 1.00 M  $\text{HCl}$ .
- 17.99** A biochemist needs 750 mL of an acetic acid–sodium acetate buffer with pH 4.50. Solid sodium acetate ( $\text{CH}_3\text{COONa}$ ) and glacial acetic acid ( $\text{CH}_3\text{COOH}$ ) are available. Glacial acetic acid is 99%  $\text{CH}_3\text{COOH}$  by mass and has a density of 1.05 g/mL. If the buffer is to be 0.15 M in  $\text{CH}_3\text{COOH}$ , how many grams of  $\text{CH}_3\text{COONa}$  and how many milliliters of glacial acetic acid must be used?
- 17.100** 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  $\text{NaOH}$ . The acid required 30.0 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?
- 17.101** A sample of 500 mg of an unknown monoprotic acid was dissolved in 50.0 mL of water and titrated with 0.200 M  $\text{KOH}$ . The acid required 20.60 mL of base to reach the equivalence point. (a) What is the molar mass of the acid? (b) After 10.30 mL of base had been added in the titration, the pH was found to be 4.20. What is the  $\text{p}K_a$  for the unknown acid?

- 17.102** Mathematically prove 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.
- 17.103** A weak monoprotic acid is titrated with 0.100 M NaOH. It requires 25.0 mL of the NaOH solution to reach the equivalence point. After 12.5 mL of base is added, the pH of the solution is 4.16. Estimate the  $pK_a$  of the weak acid.
- 17.104** What is the pH of a solution made by mixing 0.40 mol NaOH, 0.25 mol  $\text{Na}_2\text{HPO}_4$ , and 0.30 mol  $\text{H}_3\text{PO}_4$  with water and diluting to 2.00 L?
- 17.105** Suppose you want to do a physiological experiment that calls for a pH 6.50 buffer. You find that the organism with which you are working is not sensitive to the weak acid  $\text{H}_2\text{A}$  ( $K_{a1} = 2 \times 10^{-2}$ ;  $K_{a2} = 5.0 \times 10^{-7}$ ) 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.)
- 17.106** 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?
- 17.107** Lead(II) carbonate,  $\text{PbCO}_3$ , is one of the components of the passivating layer that forms inside lead pipes. (a) If the  $K_{sp}$  for  $\text{PbCO}_3$  is  $7.4 \times 10^{-14}$  what is the molarity of  $\text{Pb}^{2+}$  in a saturated solution of lead(II) carbonate? (b) What is the concentration in ppb of  $\text{Pb}^{2+}$  ions in a saturated solution? (c) Will the solubility of  $\text{PbCO}_3$  increase or decrease as the pH is lowered? (d) The EPA threshold for acceptable levels of lead ions in water is 15 ppb. Does a saturated solution of lead(II) carbonate produce a solution that exceeds the EPA limit?
- 17.108** For each pair of compounds, use  $K_{sp}$  values to determine which has the greater molar solubility: (a)  $\text{CdS}$  or  $\text{CuS}$ , (b)  $\text{PbCO}_3$  or  $\text{BaCrO}_4$ , (c)  $\text{Ni}(\text{OH})_2$  or  $\text{NiCO}_3$ , (d)  $\text{AgI}$  or  $\text{Ag}_2\text{SO}_4$ .
- 17.109** The solubility of  $\text{CaCO}_3$  is pH dependent. (a) Calculate the molar solubility of  $\text{CaCO}_3$  ( $K_{sp} = 4.5 \times 10^{-9}$ ) neglecting the acid-base character of the carbonate ion. (b) Use the  $K_b$  expression for the  $\text{CO}_3^{2-}$  ion to determine the equilibrium constant for the reaction
- $$\text{CaCO}_3(s) + \text{H}_2\text{O}(l) \rightleftharpoons \text{Ca}^{2+}(aq) + \text{HCO}_3^-(aq) + \text{OH}^-(aq)$$
- (c) If we assume that the only sources of  $\text{Ca}^{2+}$ ,  $\text{HCO}_3^-$ , and  $\text{OH}^-$  ions are from the dissolution of  $\text{CaCO}_3$ , what is the molar solubility of  $\text{CaCO}_3$  using the equilibrium expression from part (b)? (d) What is the molar solubility of  $\text{CaCO}_3$  at the pH of the ocean (8.3)? (e) If the pH is buffered at 7.5, what is the molar solubility of  $\text{CaCO}_3$ ?
- 17.110** Tooth enamel is composed of hydroxyapatite, whose simplest formula is  $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ , and whose corresponding  $K_{sp} = 6.8 \times 10^{-27}$ . As discussed in the Chemistry and Life box on page 845, fluoride in fluorinated water or in toothpaste reacts with hydroxyapatite to form fluoroapatite,  $\text{Ca}_5(\text{PO}_4)_3\text{F}$ , 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.
- 17.111** Salts containing the phosphate ion are added to municipal water supplies to prevent the corrosion of lead pipes. (a) Based on the  $pK_a$  values for phosphoric acid ( $pK_{a1} = 7.5 \times 10^{-3}$ ,  $pK_{a2} = 6.2 \times 10^{-8}$ ,  $pK_{a3} = 4.2 \times 10^{-13}$ ) what is the  $K_b$  value for the  $\text{PO}_4^{3-}$  ion? (b) What is the pH of a  $1 \times 10^{-3}$  M solution of  $\text{Na}_3\text{PO}_4$  (you can ignore the formation of  $\text{H}_2\text{PO}_4^-$  and  $\text{H}_3\text{PO}_4$ )?
- 17.112** Calculate the solubility of  $\text{Fe}(\text{OH})_2$  in 0.50 M  $\text{NH}_4\text{Cl}$ .
- 17.113** The solubility-product constant for barium permanganate,  $\text{Ba}(\text{MnO}_4)_2$ , is  $2.5 \times 10^{-10}$ . Assume that solid  $\text{Ba}(\text{MnO}_4)_2$  is in equilibrium with a solution of  $\text{KMnO}_4$ . What concentration of  $\text{KMnO}_4$  is required to establish a concentration of  $2.0 \times 10^{-8}$  M for the  $\text{Ba}^{2+}$  ion in solution?
- 17.114** Calculate the ratio of  $[\text{Ca}^{2+}]$  to  $[\text{Fe}^{2+}]$  in a lake in which the water is in equilibrium with deposits of both  $\text{CaCO}_3$  and  $\text{FeCO}_3$ . Assume that the water is slightly basic and that the hydrolysis of the carbonate ion can therefore be ignored.
- 17.115** The solubility product constants of  $\text{PbSO}_4$  and  $\text{SrSO}_4$  are  $6.3 \times 10^{-7}$  and  $3.2 \times 10^{-7}$ , respectively. What are the values of  $[\text{SO}_4^{2-}]$ ,  $[\text{Pb}^{2+}]$ , and  $[\text{Sr}^{2+}]$  in a solution at equilibrium with both substances?
- 17.116** A buffer of what pH is needed to give a  $\text{Mg}^{2+}$  concentration of  $3.0 \times 10^{-2}$  M in equilibrium with solid magnesium oxalate?
- 17.117** The value of  $K_{sp}$  for  $\text{Mg}_3(\text{AsO}_4)_2$  is  $2.1 \times 10^{-20}$ . The  $\text{AsO}_4^{3-}$  ion is derived from the weak acid  $\text{H}_3\text{AsO}_4$  ( $pK_{a1} = 2.22$ ;  $pK_{a2} = 6.98$ ;  $pK_{a3} = 11.50$ ). (a) Calculate the molar solubility of  $\text{Mg}_3(\text{AsO}_4)_2$  in water. (b) Calculate the pH of a saturated solution of  $\text{Mg}_3(\text{AsO}_4)_2$  in water.
- 17.118** The solubility product for  $\text{Zn}(\text{OH})_2$  is  $3.0 \times 10^{-16}$ . The formation constant for the hydroxo complex,  $\text{Zn}(\text{OH})_4^{2-}$ , is  $4.6 \times 10^{17}$ . What concentration of  $\text{OH}^-$  is required to dissolve 0.015 mol of  $\text{Zn}(\text{OH})_2$  in a liter of solution?
- 17.119** The value of  $K_{sp}$  for  $\text{Cd}(\text{OH})_2$  is  $2.5 \times 10^{-14}$ . (a) What is the molar solubility of  $\text{Cd}(\text{OH})_2$ ? (b) The solubility of  $\text{Cd}(\text{OH})_2$  can be increased through formation of the complex ion  $\text{CdBr}_4^{2-}$  ( $K_f = 5 \times 10^3$ ). If solid  $\text{Cd}(\text{OH})_2$  is added to a NaBr solution, what is the initial concentration of NaBr needed to increase the molar solubility of  $\text{Cd}(\text{OH})_2$  to  $1.0 \times 10^{-3}$  mol/L?

## Integrative Exercises

- 17.120** (a) Write the net ionic equation for the reaction that occurs when a solution of nitric acid ( $\text{HNO}_3$ ) is mixed with a solution of potassium propionate ( $\text{KC}_2\text{H}_5\text{CO}_2$ ). (b) Calculate the equilibrium constant for this reaction. (c) Calculate the equilibrium concentrations of  $\text{K}^+$ ,  $\text{H}^+$ ,  $\text{NO}_3^-$ ,  $\text{C}_2\text{H}_5\text{COO}^-$  and  $\text{C}_2\text{H}_5\text{COOH}$  when 100.0 mL of 0.30 M  $\text{HNO}_3$  is mixed with 100.0 mL of 0.30 M  $\text{KC}_2\text{H}_5\text{CO}_2$ .
- 17.121** (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 molar mass 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.
- 17.122** A sample of 7.5 L of  $\text{NH}_3$  gas at 22 °C and 98 kPa is bubbled into a 0.50 L solution of 0.40 M HCl. Assuming that all the  $\text{NH}_3$  dissolves and that the volume of the solution remains 0.50 L, calculate the pH of the resulting solution.
- 17.123** Aspirin has the structural formula





At body temperature ( $37^{\circ}\text{C}$ ),  $K_a$  for aspirin equals  $3 \times 10^{-5}$ . 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?

- 17.124** What is the pH at  $25^{\circ}\text{C}$  of water saturated with  $\text{CO}_2$  at a partial pressure of 111.5 kPa? The Henry's law constant for  $\text{CO}_2$  at  $25^{\circ}\text{C}$  is  $3.1 \times 10^{-4} \text{ mol/L kPa}$ .
- 17.125** 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. Suggest a reason for any differences you find between your value and the one in Appendix D.
- 17.126** The osmotic pressure of a saturated solution of lead(II) sulfate ( $\text{PbSO}_4$ ) at  $25^{\circ}\text{C}$  is 3.93 kPa. What is the solubility product of this salt at  $25^{\circ}\text{C}$ ?
- 17.127** A concentration of 10–100 parts per billion (by mass) of  $\text{Ag}^+$  is an effective disinfectant in swimming pools. However, if the concentration exceeds this range, the  $\text{Ag}^+$  can cause adverse health effects. One way to maintain an appropriate concentration of  $\text{Ag}^+$  is to add a slightly soluble salt to the pool. Using  $K_{sp}$  values from Appendix D, calculate the equilibrium concentration of  $\text{Ag}^+$  in parts per billion that would exist in equilibrium with (a)  $\text{AgCl}$ , (b)  $\text{AgBr}$ , (c)  $\text{AgI}$ .
- 17.128** Fluoridation of drinking water is employed in many places to aid in the prevention of tooth decay. Typically, the  $\text{F}^-$

ion concentration is adjusted to about 1 ppm. Some water supplies are also “hard”; that is, they contain certain cations such as  $\text{Ca}^{2+}$  that interfere with the action of soap. Consider a case where the concentration of  $\text{Ca}^{2+}$  is 8 ppm. Could a precipitate of  $\text{CaF}_2$  form under these conditions? (Make any necessary approximations.)

- 17.129** Baking soda (sodium bicarbonate,  $\text{NaHCO}_3$ ) reacts with acids in foods to form carbonic acid ( $\text{H}_2\text{CO}_3$ ), which in turn decomposes to water and carbon dioxide gas. In a cake batter, the  $\text{CO}_2(\text{g})$  forms bubbles and causes the cake to rise. (a) A rule of thumb in baking is that 1/2 teaspoon of baking soda is neutralized by one cup of sour milk. The acid component in sour milk is lactic acid,  $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$ . Write the chemical equation for this neutralization reaction. (b) The density of baking soda is  $2.16 \text{ g/cm}^3$ . Calculate the concentration of lactic acid in one cup of sour milk (assuming the rule of thumb applies), in units of mol/L. (One cup = 236.6 mL = 48 teaspoons). (c) If 1/2 teaspoon of baking soda is indeed completely neutralized by the lactic acid in sour milk, calculate the volume of carbon dioxide gas that would be produced at a pressure of 101.3 kPa, in an oven set to  $177^{\circ}\text{C}$ .
- 17.130** In nonaqueous solvents, it is possible to react HF to create  $\text{H}_2\text{F}^+$ . Which of these statements follows from this observation? (a) HF can act like a strong acid in nonaqueous solvents, (b) HF can act like a base in nonaqueous solvents, (c) HF is thermodynamically unstable, (d) There is an acid in the nonaqueous medium that is a stronger acid than HF.

## Design an Experiment

You are cleaning up an old chemistry lab and find a glass bottle labeled “6.00 M NaOH.” The bottle looks like it holds about 5 mL of solution. However, it is possible that sodium hydroxide, over a long period of time, has reacted with glass ( $\text{SiO}_2$ ). It is also possible that the bottle was not well sealed, and some water evaporated.

Design an experiment to determine the concentration of the NaOH, using a very small amount from the bottle (less than 1 mL). Consider that you have unlimited water available, a stock solution of 2.00 M HCl, and any pH indicators you need. Also consider that your equipment only allows you to measure volumes to the nearest mL.