

In the strictly scientific sense of the word, insolubility does not exist, and even those substances characterized by the most obstinate resistance to the solvent action of water may properly be designated as extraordinarily difficult of solution, not as insoluble.

—OTTO N. WITT (1853–1915)

CHAPTER

# 18

## Aqueous Ionic Equilibrium

We have already seen the importance of aqueous solutions, first in Chapters 5, 14, and 16, and most recently in Chapter 17 on acids and bases. We now turn our attention to two additional topics involving aqueous solutions: buffers (solutions that resist pH change) and solubility equilibria (the extent to which slightly soluble ionic compounds dissolve in water). Buffers are tremendously important in biology because nearly all physiological processes must occur within a narrow pH range. Solubility equilibria are related to the solubility rules that we discussed in Chapter 5. In this chapter, we find a more complicated picture: solids that we considered insoluble under the simple “solubility rules” are actually better described as being only very slightly soluble, as the chapter-opening quotation from Otto Witt suggests. Solubility equilibria are important in predicting not only solubility, but also precipitation reactions that might occur when aqueous solutions are mixed.



Antifreeze is a dangerous poison that affects the blood's ability to carry oxygen.

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## 18.1 The Danger of Antifreeze

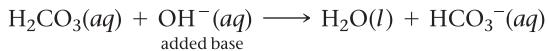
Every year, thousands of dogs and cats die from consuming a common household product: improperly stored or leaked antifreeze. Most types of auto antifreeze are aqueous solutions of ethylene glycol:



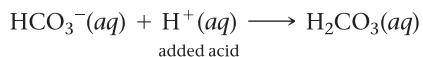
Some brands of antifreeze use propylene glycol, which is less toxic than ethylene glycol.

Ethylene glycol has a somewhat sweet taste that can attract curious dogs and cats—and sometimes even young children, who are also vulnerable to this toxic compound. The first stage of ethylene glycol poisoning is a state resembling drunkenness. Because the compound is an alcohol, it affects the brain much as an alcoholic beverage would. Once ethylene glycol starts to be metabolized, however, a second and more deadly stage commences.

In the liver, ethylene glycol is oxidized to glycolic acid ( $\text{HOCH}_2\text{COOH}$ ), which enters the bloodstream. The acidity of blood is critically important and tightly regulated because many proteins only function in a narrow pH range. In human blood, for example, pH is held between 7.36 and 7.42. This nearly constant blood pH is maintained by *buffers*. We discuss buffers more carefully later in this chapter, but for now know that a buffer is a chemical system that resists pH changes by neutralizing added acid or base. An important buffer in blood is a mixture of carbonic acid ( $\text{H}_2\text{CO}_3$ ) and the bicarbonate ion ( $\text{HCO}_3^-$ ). The carbonic acid neutralizes added base:



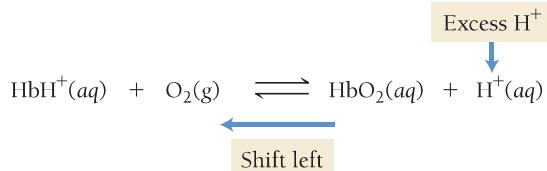
The bicarbonate ion neutralizes added acid:



In this way, the carbonic acid and bicarbonate ion buffering system keeps blood pH nearly constant.

When the glycolic acid generated by antifreeze consumption first enters the bloodstream, the acid's tendency to lower blood pH is countered by the buffering action of the bicarbonate ion. However, if the quantities of consumed antifreeze are large enough, the glycolic acid overwhelms the capacity of the buffer (we discuss buffer capacity in Section 18.3), causing blood pH to drop to dangerously low levels.

Low blood pH results in *acidosis*, a condition in which the acid affects the equilibrium between hemoglobin (Hb) and oxygen:



The excess acid causes the equilibrium to shift to the left, reducing the blood's ability to carry oxygen. At this point, the cat or dog may begin hyperventilating in an effort to overcome the acidic blood's lowered oxygen-carrying capacity. If no treatment is administered, the animal will eventually go into a coma and die.

One treatment for ethylene glycol poisoning is the administration of ethyl alcohol (the alcohol found in alcoholic beverages). The two molecules are similar enough that the liver enzyme that catalyzes the metabolism of ethylene glycol also acts on ethyl alcohol, but the enzyme has a higher affinity for ethyl alcohol than for ethylene glycol. Consequently, the enzyme preferentially metabolizes ethyl alcohol, allowing the unmetabolized ethylene glycol to escape through the urine. If administered early, this treatment can save the life of a dog or cat that has consumed ethylene glycol.

## WATCH NOW!

### KEY CONCEPT VIDEO 18.2A



## 18.2

### Buffers: Solutions That Resist pH Change

Most solutions significantly change pH when an acid or base is added to them. As we have just learned, however, a **buffer** resists pH change by neutralizing added acid or added base. A buffer contains either:

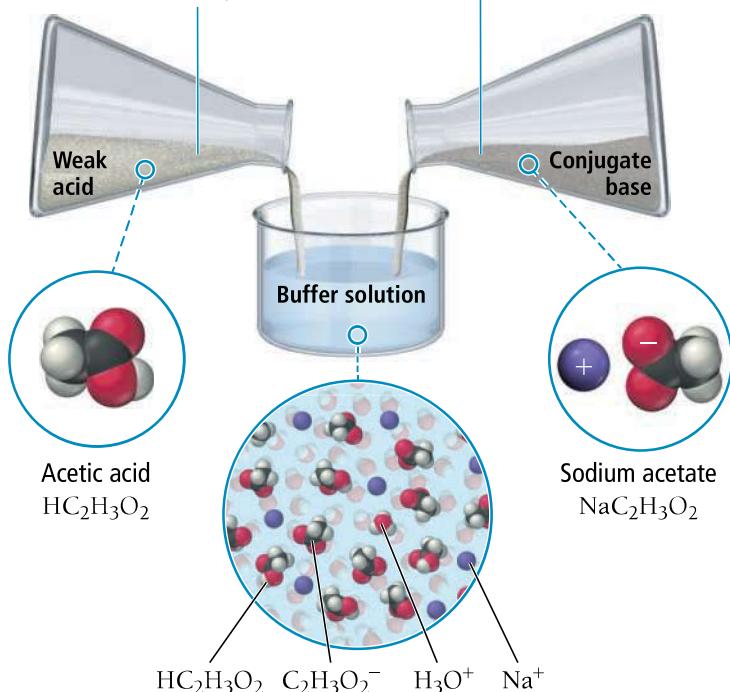
1. significant amounts of a weak acid and its conjugate base or
2. significant amounts of a weak base and its conjugate acid.

For example, the buffer in blood is composed of carbonic acid ( $\text{H}_2\text{CO}_3$ ) and its conjugate base, the bicarbonate ion ( $\text{HCO}_3^-$ ). When additional base is added to a buffer, the weak acid reacts with the base, neutralizing it. When additional acid is added to a buffer, the conjugate base reacts with the acid, neutralizing it. In this way, a buffer can maintain a nearly constant pH.

### Formation of a Buffer

A buffer typically consists of a weak acid (which can neutralize added base)...

...and its conjugate base (which can neutralize added acid).



◀ FIGURE 18.1 A Buffer Solution

A weak acid by itself, even though it partially ionizes to form some of its conjugate base, does not contain sufficient base to be a buffer. Similarly, a weak base by itself, even though it partially ionizes water to form some of its conjugate acid, does not contain sufficient acid to be a buffer. *A buffer must contain significant amounts of both a weak acid and its conjugate base (or vice versa).* Consider the simple buffer made by dissolving acetic acid ( $\text{HC}_2\text{H}_3\text{O}_2$ ) and sodium acetate ( $\text{NaC}_2\text{H}_3\text{O}_2$ ) in water (Figure 18.1▲).

Suppose, on one hand, that we add a strong base, such as  $\text{NaOH}$ , to this solution. The acetic acid neutralizes the base:



As long as the amount of added  $\text{NaOH}$  is less than the amount of  $\text{HC}_2\text{H}_3\text{O}_2$  in solution, the buffer neutralizes the added  $\text{NaOH}$  and the resulting pH change is small.

Suppose, on the other hand, that we add a strong acid, such as  $\text{HCl}$ , to the solution. In this case, the conjugate base,  $\text{NaC}_2\text{H}_3\text{O}_2$ , neutralizes the added  $\text{HCl}$ :



As long as the amount of added  $\text{HCl}$  is less than the amount of  $\text{NaC}_2\text{H}_3\text{O}_2$  in solution, the buffer neutralizes the added  $\text{HCl}$  and the resulting pH change is small.

#### Summarizing Buffer Characteristics:

- Buffers resist pH change.
- A buffer contains significant amounts of either (1) a weak acid and its conjugate base, or (2) a weak base and its conjugate acid.
- The acid neutralizes added base.
- The base neutralizes added acid.

### BUFFERS Which solution is a buffer?

- a solution that is 0.100 M in  $\text{HNO}_2$  and 0.100 M in  $\text{HCl}$
- a solution that is 0.100 M in  $\text{HNO}_3$  and 0.100 M in  $\text{NaNO}_3$
- a solution that is 0.100 M in  $\text{HNO}_2$  and 0.100 M in  $\text{NaCl}$
- a solution that is 0.100 M in  $\text{HNO}_2$  and 0.100 M in  $\text{NaNO}_2$

$\text{C}_2\text{H}_3\text{O}_2^-$  is the conjugate base of  $\text{HC}_2\text{H}_3\text{O}_2$ .

18.1  
Cc  
Conceptual Connection

ANSWER NOW!



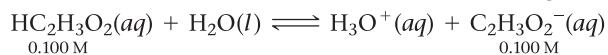
**WATCH NOW!****KEY CONCEPT VIDEO 18.2B**

 Finding pH and pH Changes in Buffer Solutions

Le Châtelier's principle is discussed in Section 16.9.

**Calculating the pH of a Buffer Solution**

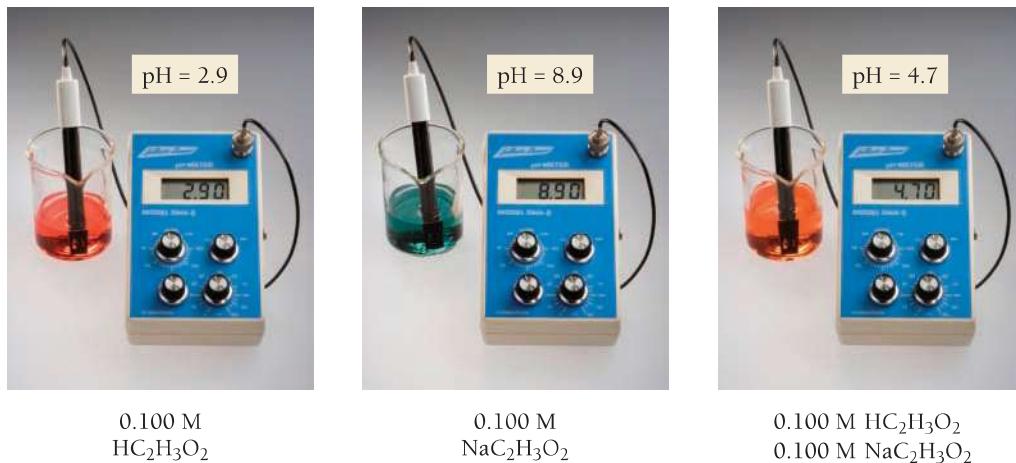
In Chapter 17, we discussed how to calculate the pH of a solution containing either a weak acid or its conjugate base, but not both. How do we calculate the pH of a buffer—a solution containing both? Consider a solution that initially contains  $\text{HC}_2\text{H}_3\text{O}_2$  and  $\text{NaC}_2\text{H}_3\text{O}_2$ , each at a concentration of 0.100 M. The acetic acid ionizes according to the reaction:



However, the ionization of  $\text{HC}_2\text{H}_3\text{O}_2$  in the solution is suppressed compared to its ionization in a solution that does not initially contain any  $\text{C}_2\text{H}_3\text{O}_2^-$ , because the presence of  $\text{C}_2\text{H}_3\text{O}_2^-$  shifts the equilibrium to the left (as we would expect from Le Châtelier's principle). In other words, the presence of the  $\text{C}_2\text{H}_3\text{O}_2^-(aq)$  ion causes the acid to ionize even less than it normally would (Figure 18.2▼), resulting in a less acidic solution (higher pH). This effect is known as the **common ion effect**, so named because the solution contains two substances ( $\text{HC}_2\text{H}_3\text{O}_2$  and  $\text{NaC}_2\text{H}_3\text{O}_2$ ) that share a common ion ( $\text{C}_2\text{H}_3\text{O}_2^-$ ). To find the pH of a buffer solution containing common ions, we work an equilibrium problem in which the initial concentrations include both the acid and its conjugate base, as shown in Example 18.1.

**► FIGURE 18.2** The Common Ion Effect

The pH of a 0.100 M acetic acid solution is 2.9. The pH of a 0.100 M sodium acetate solution is 8.9. The pH of a solution that is 0.100 M in acetic acid and 0.100 M in sodium acetate is 4.7.

**EXAMPLE 18.1** Calculating the pH of a Buffer Solution

Calculate the pH of a buffer solution that is 0.100 M in  $\text{HC}_2\text{H}_3\text{O}_2$  and 0.100 M in  $\text{NaC}_2\text{H}_3\text{O}_2$ .

**SOLUTION**

1. Write the balanced equation for the ionization of the acid and use it as a guide to prepare an ICE table showing the given concentrations of the acid and its conjugate base as the initial concentrations. Leave room in the table for the changes in concentrations and for the equilibrium concentrations.

2. Represent the change in the concentration of  $\text{H}_3\text{O}^+$  with the variable  $x$ . Express the changes in the concentrations of the other reactants and products in terms of  $x$ .



	[ $\text{HC}_2\text{H}_3\text{O}_2$ ]	[ $\text{H}_3\text{O}^+$ ]	[ $\text{C}_2\text{H}_3\text{O}_2^-$ ]
Initial	0.100	≈ 0.00	0.100
Change			
Equil			



	[ $\text{HC}_2\text{H}_3\text{O}_2$ ]	[ $\text{H}_3\text{O}^+$ ]	[ $\text{C}_2\text{H}_3\text{O}_2^-$ ]
Initial	0.100	≈ 0.00	0.100
Change	- $x$	+ $x$	+ $x$
Equil			

3. Sum each column to determine the equilibrium concentrations in terms of the initial concentrations and the variable  $x$ .

	$\text{HC}_2\text{H}_3\text{O}_2(aq)$	$\text{H}_2\text{O}(l)$	$\text{H}_3\text{O}^+(aq)$	$\text{C}_2\text{H}_3\text{O}_2^-(aq)$
Initial	0.100		$\approx 0.00$	0.100
Change	$-x$		$+x$	$+x$
Equil	$0.100 - x$		$x$	$0.100 + x$

4. Substitute the expressions for the equilibrium concentrations (from step 3) into the expression for the acid ionization constant.

In most cases, you can make the approximation that  $x$  is small. (See Sections 16.8 and 17.6 to review the  $x$  is small approximation.)

Substitute the value of the acid ionization constant (from Table 17.5) into the  $K_a$  expression and solve for  $x$ .

Confirm that  $x$  is small by calculating the ratio of  $x$  and the number it was subtracted from in the approximation. The ratio should be less than 0.05 (5%).

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]}$$

$$= \frac{x(0.100 + x)}{0.100 - x} \quad (x \text{ is small})$$

$$1.8 \times 10^{-5} = \frac{x(0.100)}{0.100}$$

$$x = 1.8 \times 10^{-5}$$

$$\frac{1.8 \times 10^{-5}}{0.100} \times 100\% = 0.018\%$$

Therefore the approximation is valid.

5. Determine the  $\text{H}_3\text{O}^+$  concentration from the calculated value of  $x$  and substitute into the pH equation to find pH.

$$[\text{H}_3\text{O}^+] = x = 1.8 \times 10^{-5} \text{ M}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+]$$

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

$$= 4.74$$

**FOR PRACTICE 18.1** Calculate the pH of a buffer solution that is 0.200 M in  $\text{HC}_2\text{H}_3\text{O}_2$  and 0.100 M in  $\text{NaC}_2\text{H}_3\text{O}_2$ .

**FOR MORE PRACTICE 18.1** Calculate the pH of the buffer that results from mixing 60.0 mL of 0.250 M  $\text{HCHO}_2$  and 15.0 mL of 0.500 M  $\text{NaCHO}_2$ .

## The Henderson–Hasselbalch Equation

We can derive an equation that relates the pH of a buffer solution to the initial concentration of the buffer components, thus simplifying the calculation of the pH of a buffer solution. Consider a buffer containing the generic weak acid HA and its conjugate base  $\text{A}^-$ . The acid ionizes as follows:



We derive an expression for the concentration of  $\text{H}_3\text{O}^+$  from the acid ionization equilibrium expression by solving the expression for  $[\text{H}_3\text{O}^+]$ :

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

$$[\text{H}_3\text{O}^+] = K_a \frac{[\text{HA}]}{[\text{A}^-]} \quad [18.1]$$

If we make the same  $x$  is small approximation that we make for weak acid or weak base equilibrium problems, we can consider the equilibrium concentrations of HA and  $\text{A}^-$  to be essentially identical to the initial concentrations of HA and  $\text{A}^-$  (see step 4 of Example 18.1). Therefore, to determine  $[\text{H}_3\text{O}^+]$  for any buffer solution, we multiply  $K_a$  by the ratio of the

Recall that the variable  $x$  in a weak acid equilibrium problem represents the change in the initial acid concentration. The  $x$  is small approximation is valid because so little of the weak acid ionizes compared to its initial concentration.

concentrations of the acid and the conjugate base. To find the  $[H_3O^+]$  of the buffer in Example 18.1 (a solution that is 0.100 M in  $HC_2H_3O_2$  and 0.100 M in  $NaC_2H_3O_2$ ), we substitute the concentrations of  $HC_2H_3O_2$  and  $C_2H_3O_2^-$  into Equation 18.1:

$$\begin{aligned}[H_3O^+] &= K_a \frac{[HC_2H_3O_2]}{[C_2H_3O_2^-]} \\ &= K_a \frac{0.100}{0.100} \\ &= K_a\end{aligned}$$

In this buffer solution, as in any in which the acid and conjugate base concentrations are equal,  $[H_3O^+]$  is equal to  $K_a$ .

We can derive an equation for the pH of a buffer by taking the negative logarithm of both sides of Equation 18.1:

$$\begin{aligned}[H_3O^+] &= K_a \frac{[HA]}{[A^-]} \\ -\log[H_3O^+] &= -\log\left(K_a \frac{[HA]}{[A^-]}\right) \\ -\log[H_3O^+] &= -\log K_a - \log \frac{[HA]}{[A^-]}\end{aligned}\quad [18.2]$$

We can rearrange Equation 18.2 to get:

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

Since  $pH = -\log[H_3O^+]$  and since  $pK_a = -\log K_a$ , we obtain the result:

$$pH = pK_a + \log \frac{[A^-]}{[HA]}$$

Since  $A^-$  is a weak base and HA is a weak acid, we can generalize the equation:

$$pH = pK_a + \log \frac{[\text{base}]}{[\text{acid}]}\quad [18.3]$$

Note that, as expected, the pH of a buffer increases with an increase in the amount of base relative to the amount of acid.

where the base is the conjugate base of the acid or the acid is the conjugate acid of the base. This equation, known as the **Henderson–Hasselbalch equation**, allows us to quickly calculate the pH of a buffer solution from the initial concentrations of the buffer components *as long as the x is small approximation is valid*. In Example 18.2, we show how to find the pH of a buffer in two ways: in the left column we solve a common ion effect equilibrium problem using a method similar to the one we used in Example 18.1; in the right column we use the Henderson–Hasselbalch equation.

#### WATCH NOW!

#### INTERACTIVE WORKED EXAMPLE 18.2

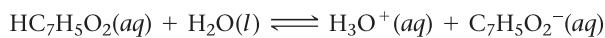
### Calculating the pH of a Buffer Solution as an Equilibrium Problem and with the Henderson–Hasselbalch Equation

#### EXAMPLE 18.2

Calculate the pH of a buffer solution that is 0.050 M in benzoic acid ( $HC_7H_5O_2$ ) and 0.150 M in sodium benzoate ( $NaC_7H_5O_2$ ). For benzoic acid,  $K_a = 6.5 \times 10^{-5}$ .

#### SOLUTION

Equilibrium Approach	Henderson–Hasselbalch Approach
Write the balanced equation for the ionization of the acid and use it as a guide to prepare an ICE table.	To find the pH of this solution, determine which component is the acid and which is the base and substitute their concentrations into the Henderson–Hasselbalch equation to calculate pH.



	[HC <sub>7</sub> H <sub>5</sub> O <sub>2</sub> ]	[H <sub>3</sub> O <sup>+</sup> ]	[C <sub>7</sub> H <sub>5</sub> O <sub>2</sub> <sup>-</sup> ]
Initial	0.050	≈ 0.00	0.150
Change	-x	+x	+x
Equil	0.050 - x	x	0.150 + x

Substitute the expressions for the equilibrium concentrations into the expression for the acid ionization constant. Make the  $x$  is small approximation and solve for  $x$ .

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{C}_7\text{H}_5\text{O}_2^-]}{[\text{HC}_7\text{H}_5\text{O}_2]}$$

$$= \frac{x(0.150 + x)}{0.050 - x} \quad (\text{x is small})$$

$$6.5 \times 10^{-5} = \frac{x(0.150)}{0.050}$$

$$x = 2.2 \times 10^{-5}$$

Since [H<sub>3</sub>O<sup>+</sup>] =  $x$ , we calculate pH as follows:

$$\begin{aligned} \text{pH} &= -\log[\text{H}_3\text{O}^+] \\ &= -\log(2.2 \times 10^{-5}) \\ &= 4.66 \end{aligned}$$

Confirm that the  $x$  is small approximation is valid by calculating the ratio of  $x$  to the number it was subtracted from in the approximation. The ratio should be less than 0.05 (5%). (See Sections 16.8 and 17.6 to review the  $x$  is small approximation.)

$$\frac{2.2 \times 10^{-5}}{0.050} \times 100\% = 0.044\%$$

The approximation is valid.

HC<sub>7</sub>H<sub>5</sub>O<sub>2</sub> is the acid and NaC<sub>7</sub>H<sub>5</sub>O<sub>2</sub> is the base. Therefore, we calculate the pH as follows:

$$\begin{aligned} \text{pH} &= \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]} \\ &= -\log(6.5 \times 10^{-5}) + \log \frac{0.150}{0.050} \\ &= 4.187 + 0.477 \\ &= 4.66 \end{aligned}$$

Confirm that the  $x$  is small approximation is valid by calculating the [H<sub>3</sub>O<sup>+</sup>] from the pH. Since [H<sub>3</sub>O<sup>+</sup>] is formed by ionization of the acid, the calculated [H<sub>3</sub>O<sup>+</sup>] has to be less than 0.05 (or 5%) of the initial concentration of the acid in order for the  $x$  is small approximation to be valid.

$$\begin{aligned} \text{pH} &= 4.66 = -\log [\text{H}_3\text{O}^+] \\ [\text{H}_3\text{O}^+] &= 10^{-4.66} = 2.2 \times 10^{-5} \text{ M} \\ \frac{2.2 \times 10^{-5}}{0.050} \times 100\% &= 0.044\% \end{aligned}$$

The approximation is valid.

**FOR PRACTICE 18.2** Calculate the pH of a buffer solution that is 0.250 M in HCN and 0.170 M in KCN. For HCN,  $K_a = 4.9 \times 10^{-10}$  ( $\text{p}K_a = 9.31$ ). Use both the equilibrium approach and the Henderson–Hasselbalch approach.

You may be wondering how to decide whether to use the equilibrium approach or the Henderson–Hasselbalch equation when calculating the pH of buffer solutions. The answer depends on the specific problem. In cases where you can make the  $x$  is small approximation, the Henderson–Hasselbalch equation is adequate. However, as you can see from Example 18.2, checking the  $x$  is small approximation is not as convenient with the Henderson–Hasselbalch equation (because the approximation is implicit). Thus, the equilibrium approach, though lengthier, gives you a better sense of the important quantities in the problem and the nature of the approximation.

When first working buffer problems, use the equilibrium approach until you get a good sense for when the  $x$  is small approximation is adequate. Then you can switch to the more streamlined approach in cases where the approximation applies (and only in those cases). In general, remember that the  $x$  is small approximation applies to problems in which both of the following are true: (a) the initial concentrations of acids (and/or bases) are not too dilute; and (b) the equilibrium constant is fairly small. Although the exact values depend on the details of the problem, for many buffer problems this means that the initial concentrations of acids and conjugate bases should be at least 10<sup>2</sup>–10<sup>3</sup> times greater than the equilibrium constant (depending on the required accuracy).

ANSWER NOW!



## 18.2 Cc Conceptual Connection

**pH OF BUFFER SOLUTIONS** A buffer contains the weak acid HA and its conjugate base  $A^-$ . The weak acid has a  $pK_a$  of 4.82 and the buffer has a pH of 4.25. Which statement is true of the relative concentrations of the weak acid and conjugate base in the buffer?

- (a)  $[HA] > [A^-]$       (b)  $[HA] < [A^-]$       (c)  $[HA] = [A^-]$

### Calculating pH Changes in a Buffer Solution

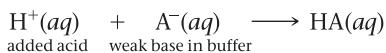
When we add acid or base to a buffer, the buffer resists a pH change. Nonetheless, the pH does change by a small amount. Calculating the pH change requires breaking up the problem into two parts:

- The stoichiometry calculation** in which we calculate how the addition changes the relative amounts of acid and conjugate base.
- The equilibrium calculation** in which we calculate the pH based on the new amounts of acid and conjugate base.

We demonstrate this calculation with a 1.0-L buffer solution that is 0.100 M in the generic acid HA and 0.100 M in its conjugate base  $A^-$ . Since the concentrations of the weak acid and the conjugate base are equal, the pH of the buffer is equal to  $pK_a$ . Let's calculate the pH of the solution after we add 0.025 mol of strong acid ( $H^+$ ) (assuming that the change in volume from adding the acid is negligible).

### The Stoichiometry Calculation

As the added acid is neutralized, it converts a stoichiometric amount of the base into its conjugate acid through the neutralization reaction (Figure 18.3a▶, on p. 796):



Neutralizing 0.025 mol of the strong acid ( $H^+$ ) requires 0.025 mol of the weak base ( $A^-$ ). Consequently, the amount of  $A^-$  decreases by 0.025 mol, and the amount of HA increases by 0.025 mol (because of the 1:1:1 stoichiometry of the neutralization reaction). We can track these changes in tabular form as follows:

	$H^+(aq)$	+	$A^-(aq)$	$\longrightarrow$	$HA(aq)$
<b>Before addition</b>	$\approx 0.00 \text{ mol}$		$0.100 \text{ mol}$		$0.100 \text{ mol}$
<b>Addition</b>	$+0.025 \text{ mol}$		—	—	—
<b>After addition</b>	$\approx 0.00 \text{ mol}$		$0.075 \text{ mol}$		$0.125 \text{ mol}$

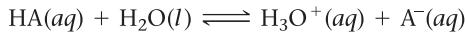
It is best to work with amounts in moles instead of concentrations when tracking these changes, as explained later in this chapter.

Notice that this table is not an ICE table. This table simply tracks the stoichiometric changes that occur during the neutralization of the added acid. We write  $\approx 0.00 \text{ mol}$  for the amount of  $H^+$  because the amount is so small compared to the amounts of  $A^-$  and HA. (Remember that weak acids ionize only to a small extent and that the presence of the common ion further suppresses the ionization.) The amount of  $H^+$ , of course, is not exactly zero, as we can see by completing the equilibrium part of the calculation.

### The Equilibrium Calculation

We have just seen that adding a small amount of acid to a buffer is equivalent to changing the initial concentrations of the acid and conjugate base present in the buffer (in this case, since the volume is 1.0 L,  $[HA]$  increased from 0.100 M to 0.125 M and  $[A^-]$  decreased from 0.100 M to 0.075 M). Knowing these new initial concentrations, we can calculate the new pH in the same way that we calculate the pH of any buffer: either by working a full equilibrium problem or by using the Henderson–Hasselbalch equation (see Examples 18.1 and 18.2).

In this case, we work the full equilibrium problem. We begin by writing the balanced equation for the ionization of the acid and using it as a guide to prepare an ICE table. The initial concentrations for the ICE table are those that we calculated in the stoichiometry part of the calculation:



	[HA]	[H <sub>3</sub> O <sup>+</sup> ]	[A <sup>-</sup> ]	
Initial	0.125	≈ 0.00	0.075	From stoichiometry calculation
Change	-x	+x	+x	
Equil	0.125 - x	x	0.075 + x	

We then substitute the expressions for the equilibrium concentrations into the expression for the acid ionization constant. As long as  $K_a$  is sufficiently small relative to the initial concentrations, we can make the  $x$  is small approximation and solve for  $x$ , which is equal to [H<sub>3</sub>O<sup>+</sup>]:

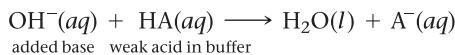
$$\begin{aligned} K_a &= \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \\ &= \frac{x(0.075 + x)}{0.125 - x} \quad (x \text{ is small}) \\ K_a &= \frac{x(0.075)}{0.125} \\ x &= [\text{H}_3\text{O}^+] = K_a \frac{0.125}{0.075} \end{aligned}$$

Once we calculate [H<sub>3</sub>O<sup>+</sup>], we can calculate the pH with the equation  $\text{pH} = -\log[\text{H}_3\text{O}^+]$ .

Notice that, since the expression for  $x$  contains a ratio of concentrations [HA]/[A<sup>-</sup>], the amounts of acid and base in moles may be substituted in place of concentration because, in a single buffer solution, the volume is the same for both the acid and the base. Therefore, the volumes cancel:

$$[\text{HA}]/[\text{A}^-] = \frac{\frac{n_{\text{HA}}}{V}}{\frac{n_{\text{A}^-}}{V}} = n_{\text{HA}}/n_{\text{A}^-}$$

The effect of adding a small amount of strong base to the buffer is exactly the opposite of adding acid. The added base converts a stoichiometric amount of the acid into its conjugate base through the neutralization reaction (Figure 18.3b►):



If we add 0.025 mol of OH<sup>-</sup>, the amount of A<sup>-</sup> goes up by 0.025 mol and the amount of HA goes down by 0.025 mol, as shown in the following table:

	OH <sup>-</sup> (aq)	+	HA(aq)	→	H <sub>2</sub> O(l)	+	A <sup>-</sup> (aq)
Before addition	≈ 0.00 mol		0.100 mol				0.100 mol
Addition	+0.025 mol		—				—
After addition	≈ 0.00 mol		0.075 mol				0.125 mol

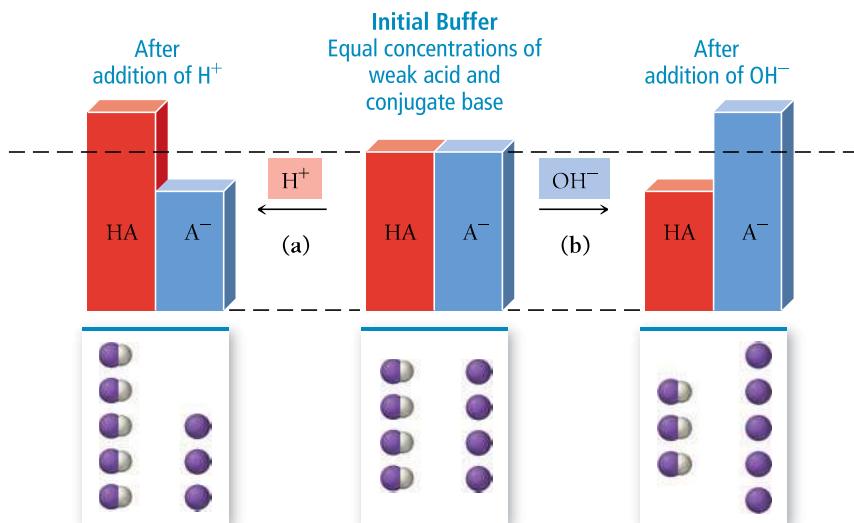
**When you calculate the pH of a buffer after adding small amounts of acid or base, remember the following:**

- Adding a small amount of strong acid to a buffer converts a stoichiometric amount of the base to the conjugate acid and decreases the pH of the buffer (adding acid decreases pH just as we would expect).
- Adding a small amount of strong base to a buffer converts a stoichiometric amount of the acid to the conjugate base and increases the pH of the buffer (adding base increases pH just as we would expect).

The easiest way to remember these changes is relatively simple: adding acid creates more acid; adding base creates more base.

**► FIGURE 18.3 Buffering**

**Action** (a) When a strong acid is added to a buffer, a stoichiometric amount of the weak base is converted to the conjugate acid. (b) When a strong base is added to a buffer, a stoichiometric amount of the weak acid is converted to the conjugate base.

**Action of a Buffer****HOW TO: Calculate pH Changes in a Buffer Solution after Adding Small Amounts of Strong Acid or Strong Base**

- 1. Stoichiometry Calculation** Use the stoichiometry of the neutralization equation to calculate the changes in the amounts (in moles) of the buffer components upon addition of the acid or base.
- 2. Equilibrium Calculation** Use the new amounts of buffer components to work an equilibrium problem to find pH. (For most buffers, this can also be done with the Henderson–Hasselbalch equation.)

Example 18.3 and the For Practice Problems that follow apply this procedure.

**ANSWER NOW!**
**18.3**  
**Cc**  
 Conceptual Connection
**EXAMPLE 18.3****Calculating the pH Change in a Buffer Solution after the Addition of a Small Amount of Strong Acid or Base**

A 1.0-L buffer solution contains 0.100 mol  $\text{HC}_2\text{H}_3\text{O}_2$  and 0.100 mol  $\text{NaC}_2\text{H}_3\text{O}_2$ . The value of  $K_a$  for  $\text{HC}_2\text{H}_3\text{O}_2$  is  $1.8 \times 10^{-5}$ . Because the initial amounts of acid and conjugate base are equal, the pH of the buffer is equal to  $\text{p}K_a = -\log(1.8 \times 10^{-5}) = 4.74$ . Calculate the new pH after adding 0.010 mol of solid NaOH to the buffer. For comparison, calculate the pH after adding 0.010 mol of solid NaOH to 1.0 L of pure water. (Ignore any small changes in volume that might occur upon addition of the base.)

**SOLUTION**

- 1. Stoichiometry Calculation** The addition of the base converts a stoichiometric amount of acid to the conjugate base (adding base creates more base). Write an equation showing the neutralization reaction and then set up a table to track the changes.

**WATCH NOW!****INTERACTIVE WORKED EXAMPLE 18.3**

$\text{OH}^-(aq) + \text{HC}_2\text{H}_3\text{O}_2(aq) \longrightarrow \text{H}_2\text{O}(l) + \text{C}_2\text{H}_3\text{O}_2^-(aq)$			
Before addition	$\approx 0.00 \text{ mol}$	0.100 mol	0.100 mol
Addition	0.010 mol	—	—
After addition	$\approx 0.00 \text{ mol}$	0.090 mol	0.110 mol

- 2. Equilibrium Calculation** Write the balanced equation for the ionization of the acid and use it as a guide to prepare an ICE table. Use the amounts of acid and conjugate base from part I as the initial amounts of acid and conjugate base in the ICE table.

	$\text{HC}_2\text{H}_3\text{O}_2(aq)$	$\text{H}_2\text{O}(l)$	$\text{H}_3\text{O}^+(aq)$	$\text{C}_2\text{H}_3\text{O}_2^-(aq)$
Initial	0.090		$\approx 0.00$	0.110
Change	$-x$		$+x$	$+x$
Equil	$0.090 - x$		$x$	$0.110 + x$

Substitute the expressions for the equilibrium concentrations of acid and conjugate base into the expression for the acid ionization constant. Make the  $x$  is small approximation and solve for  $x$ . Calculate the pH from the value of  $x$ , which is equal to  $[\text{H}_3\text{O}^+]$ .

$$\begin{aligned} K_a &= \frac{[\text{H}_3\text{O}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} \\ &= \frac{x(0.110 + x)}{0.090 - x} \quad (x \text{ is small}) \\ 1.8 \times 10^{-5} &= \frac{x(0.110)}{0.090} \end{aligned}$$

$$x = [\text{H}_3\text{O}^+] = 1.47 \times 10^{-5} \text{ M}$$

$$\begin{aligned} \text{pH} &= -\log[\text{H}_3\text{O}^+] \\ &= -\log(1.47 \times 10^{-5}) \\ &= 4.83 \end{aligned}$$

$$\frac{1.47 \times 10^{-5}}{0.090} \times 100\% = 0.016\%$$

Confirm that the  $x$  is small approximation is valid by calculating the ratio of  $x$  to the smallest number it was subtracted from in the approximation. The ratio should be less than 0.05 (5%).

The approximation is valid.

- 2. Equilibrium Alternative (using the Henderson-Hasselbalch equation).** As long as the  $x$  is small approximation is valid, you can substitute the quantities of acid and conjugate base after the addition (from part I) into the Henderson-Hasselbalch equation and calculate the new pH.

$$\begin{aligned} \text{pH} &= \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]} \\ &= -\log(1.8 \times 10^{-5}) + \log \frac{0.110}{0.090} \\ &= 4.74 + 0.087 \\ &= 4.83 \end{aligned}$$

The pH of 1.0 L of water after adding 0.010 mol of NaOH is calculated from the  $[\text{OH}^-]$ . For a strong base,  $[\text{OH}^-]$  is simply the number of moles of  $\text{OH}^-$  divided by the number of liters of solution.

$$\begin{aligned} [\text{OH}^-] &= \frac{0.010 \text{ mol}}{1.0 \text{ L}} = 0.010 \text{ M} \\ \text{pOH} &= -\log[\text{OH}^-] = -\log(0.010) \\ &= 2.00 \\ \text{pOH} + \text{pH} &= 14.00 \\ \text{pH} &= 14.00 - \text{pOH} \\ &= 14.00 - 2.00 \\ &= 12.00 \end{aligned}$$

**CHECK** Notice that the buffer solution changed from pH = 4.74 to pH = 4.83 upon addition of the base (a small fraction of a pH unit). In contrast, the pure water changed from pH = 7.00 to pH = 12.00, five whole pH units (a factor of  $10^5$ ). Notice also that even the buffer solution got slightly more basic upon addition of a base, as we would expect. To check your answer, always make sure the pH goes in the direction you expect: adding base should make the solution more basic (higher pH); adding acid should make the solution more acidic (lower pH).

**FOR PRACTICE 18.3** Calculate the pH of the solution in Example 18.3 upon addition of 0.015 mol of NaOH to the original buffer.

**FOR MORE PRACTICE 18.3** Calculate the pH of the solution in Example 18.3 upon addition of 10.0 mL of 1.00 M HCl to the original buffer.

ANSWER NOW!



## 18.4 Cc Conceptual Connection

**ADDING ACID OR BASE TO A BUFFER** A buffer contains equal amounts of a weak acid and its conjugate base and has a pH of 5.25. Which would be a reasonable value of buffer pH after the addition of a small amount of acid?

- (a) 4.15
- (b) 5.15
- (c) 5.35
- (d) 6.35

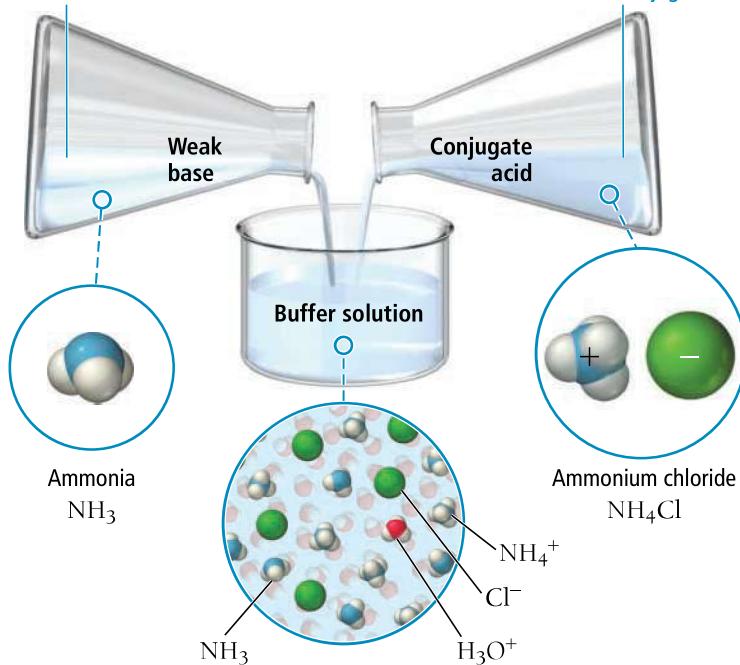
### Buffers Containing a Base and Its Conjugate Acid

So far, we have seen examples of buffers composed of an acid and its conjugate base (where the conjugate base is an ion). A buffer can also be composed of a base and its conjugate acid (where the conjugate acid is an ion). For example, a solution containing significant amounts of both  $\text{NH}_3$  and  $\text{NH}_4\text{Cl}$  acts as a buffer (Figure 18.4▼). The  $\text{NH}_3$  is a weak base that neutralizes small amounts of added acid, and the  $\text{NH}_4^+$  ion is the conjugate acid that neutralizes small amounts of added base.

We calculate the pH of a solution like this in the same way that we calculated the pH of a buffer containing a weak acid and its conjugate base. When using the Henderson–Hasselbalch equation, however, we must first calculate  $pK_a$  for the conjugate acid of the weak base. Recall from Section 17.8 that for a conjugate acid-base pair,  $K_a \times K_b = K_w$  and  $pK_a + pK_b = 14$ . Consequently, we can find  $pK_a$  of the conjugate acid by subtracting  $pK_b$  of the weak base from 14. Example 18.4 illustrates the procedure for calculating the pH of a buffer composed of a weak base and its conjugate acid.

#### Formation of a Buffer

A buffer can also consist of a weak base...  
...and its conjugate acid.



▲ FIGURE 18.4 Buffer Containing a Base

WATCH NOW!

INTERACTIVE WORKED EXAMPLE 18.4

**EXAMPLE 18.4****Using the Henderson–Hasselbalch Equation to Calculate the pH of a Buffer Solution Composed of a Weak Base and Its Conjugate Acid**

Use the Henderson–Hasselbalch equation to calculate the pH of a buffer solution that is 0.50 M in NH<sub>3</sub> and 0.20 M in NH<sub>4</sub>Cl. For ammonia, pK<sub>b</sub> = 4.75.

**SOLUTION**

Since K<sub>b</sub> for NH<sub>3</sub> ( $1.76 \times 10^{-5}$ ) is much smaller than the initial concentrations in this problem, you can use the Henderson–Hasselbalch equation to calculate the pH of the buffer. First calculate pK<sub>a</sub> from pK<sub>b</sub>.

$$\begin{aligned} pK_a + pK_b &= 14 \\ pK_a &= 14 - pK_b \\ &= 14 - 4.75 \\ &= 9.25 \end{aligned}$$

Then substitute the given quantities into the Henderson–Hasselbalch equation and calculate pH.

$$\begin{aligned} \text{pH} &= pK_a + \log \frac{[\text{base}]}{[\text{acid}]} \\ &= 9.25 + \log \frac{0.50}{0.20} \\ &= 9.25 + 0.40 \\ &= 9.65 \end{aligned}$$

**FOR PRACTICE 18.4** Calculate the pH of 1.0 L of the solution in Example 18.4 upon addition of 0.010 mol of solid NaOH to the original buffer solution.

**FOR MORE PRACTICE 18.4** Calculate the pH of 1.0 L of the solution in Example 18.4 upon addition of 30.0 mL of 1.0 M HCl to the original buffer solution.

**18.3****Buffer Effectiveness: Buffer Range and Buffer Capacity**

An effective buffer neutralizes small to moderate amounts of added acid or base. Recall from Section 18.1, however, that a buffer can be destroyed by the addition of too much acid or too much base. What factors influence the effectiveness of a buffer? In this section, we examine two such factors: *the relative amounts of the acid and conjugate base* and *the absolute concentrations of the acid and conjugate base*. We then define the *capacity of a buffer* (how much added acid or base it can effectively neutralize) and the *range of a buffer* (the pH range over which a particular acid and its conjugate base can be effective).

**Relative Amounts of Acid and Base**

A buffer is most effective (most resistant to pH changes) when the concentrations of acid and conjugate base are equal. Let's explore this idea by considering the behavior of a generic buffer composed of HA and A<sup>-</sup> for which pK<sub>a</sub> = 5.00 and calculating the percent change in pH upon addition of 0.010 mol of NaOH for two different 1.0-liter solutions of this buffer system. Both solutions have 0.20 mol of *total* acid and conjugate base. However, solution I has equal amounts of acid and conjugate base (0.10 mol of each), while solution II has much more acid than conjugate base (0.18 mol HA and 0.020 mol A<sup>-</sup>). We can calculate the initial pH values of each solution using the Henderson–Hasselbalch equation. Solution I has an initial pH of 5.00 and solution II has an initial pH of 4.05:

**Solution I: 0.10 mol HA and 0.10 mol A<sup>-</sup>; initial pH = 5.00**

Before addition	≈ 0.00 mol	0.100 mol	0.100 mol
Addition	0.010 mol	—	—
After addition	≈ 0.00 mol	0.090 mol	0.110 mol

$$\begin{aligned}\text{pH} &= \text{p}K_{\text{a}} + \log \frac{[\text{base}]}{[\text{acid}]} \\ &= 5.00 + \log \frac{0.110}{0.090} \\ &= 5.09\end{aligned}$$

$$\begin{aligned}\% \text{ change} &= \frac{5.09 - 5.00}{5.00} \times 100\% \\ &= 1.8\%\end{aligned}$$

**Solution II: 0.18 mol HA and 0.020 mol A<sup>-</sup>; initial pH = 4.05**

Before addition	≈ 0.00 mol	0.18 mol	0.020 mol
Addition	0.010 mol	—	—
After addition	≈ 0.00 mol	0.17 mol	0.030 mol

$$\begin{aligned}\text{pH} &= \text{p}K_{\text{a}} + \log \frac{[\text{base}]}{[\text{acid}]} \\ &= 5.00 + \log \frac{0.030}{0.17} \\ &= 4.25\end{aligned}$$

$$\begin{aligned}\% \text{ change} &= \frac{4.25 - 4.05}{4.05} \times 100\% \\ &= 4.9\%\end{aligned}$$

As you can see, the buffer with equal amounts of acid and conjugate base is more resistant to pH change and is therefore the more effective buffer. A buffer becomes less effective as the difference in the relative amounts of acid and conjugate base increases. As a guideline, we can say that an effective buffer must have a [base]/[acid] ratio in the range of 0.10 to 10. *In order for a buffer to be reasonably effective, the relative concentrations of acid and conjugate base should not differ by more than a factor of 10.*

## Absolute Concentrations of the Acid and Conjugate Base

A buffer is most effective (most resistant to pH changes) when the concentrations of acid and conjugate base are high. Let's explore this idea by again considering a generic buffer composed of HA and A<sup>-</sup> and a pK<sub>a</sub> of 5.00 and calculating the percent change in pH upon addition of 0.010 mol of NaOH for two 1.0-liter solutions of this buffer system. In this case, both the acid and the base in solution I are ten times more concentrated than the acid and base in solution II. Both solutions have equal relative amounts of acid and conjugate base and therefore have the same initial pH of 5.00:

**Solution I: 0.50 mol HA and 0.50 mol A<sup>-</sup>; initial pH = 5.00**

Before addition	≈ 0.00 mol	0.50 mol	0.50 mol
Addition	0.010 mol	—	—
After addition	≈ 0.00 mol	0.49 mol	0.51 mol

$$\begin{aligned}\text{pH} &= \text{p}K_{\text{a}} + \log \frac{[\text{base}]}{[\text{acid}]} \\ &= 5.00 + \log \frac{0.51}{0.49} \\ &= 5.02\end{aligned}$$

$$\begin{aligned}\% \text{ change} &= \frac{5.02 - 5.00}{5.00} \times 100\% \\ &= 0.4\%\end{aligned}$$

**Solution II: 0.050 mol HA and 0.050 mol A<sup>-</sup>; initial pH = 5.00**

Before addition	≈ 0.00 mol	0.050 mol	0.050 mol
Addition	0.010 mol	—	—
After addition	≈ 0.00 mol	0.040 mol	0.060 mol

$$\begin{aligned}\text{pH} &= \text{p}K_{\text{a}} + \log \frac{[\text{base}]}{[\text{acid}]} \\ &= 5.00 + \log \frac{0.060}{0.040} \\ &= 5.18\end{aligned}$$

$$\begin{aligned}\% \text{ change} &= \frac{5.18 - 5.00}{5.00} \times 100\% \\ &= 3.6\%\end{aligned}$$

As you can see, the buffer with greater amounts of acid and conjugate base is more resistant to pH changes and therefore is the more effective buffer. The more dilute the buffer components, the less effective the buffer.

## Buffer Range

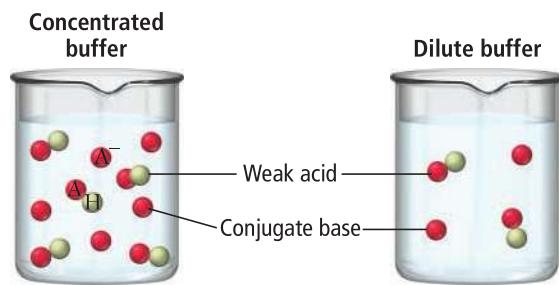
In light of the guideline that the relative concentrations of acid and conjugate base should not differ by more than a factor of 10 in order for a buffer to be reasonably effective, we can calculate the pH range over which a particular acid and its conjugate base make an effective buffer. Because the pH of a buffer is given by the Henderson-Hasselbalch equation, we can calculate the outermost points of the effective range as follows:

*Lowest pH* for effective buffer occurs when the base is one-tenth as concentrated as the acid.

$$\begin{aligned} \text{pH} &= \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]} \\ &= \text{p}K_a + \log 0.10 \\ &= \text{p}K_a - 1 \end{aligned}$$

*Highest pH* for effective buffer occurs when the base is ten times as concentrated as the acid.

$$\begin{aligned} \text{pH} &= \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]} \\ &= \text{p}K_a + \log 10 \\ &= \text{p}K_a + 1 \end{aligned}$$

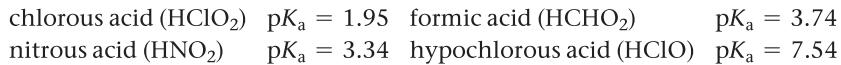


▲ A concentrated buffer contains more of the weak acid and its conjugate base than a weak buffer does. It can therefore neutralize more added acid or added base.

The effective range for a buffering system is one pH unit on either side of  $\text{p}K_a$ . For example, we can use a weak acid with a  $\text{p}K_a$  of 5.0 (and its conjugate base) to prepare a buffer in the range of 4.0–6.0. We can adjust the relative amounts of acid and conjugate base to achieve any pH within this range. As we noted earlier, however, the buffer would be most effective at pH 5.0 because the buffer components would be exactly equal at that pH. Example 18.5 demonstrates how to pick an acid/conjugate base system for a buffer and how to calculate the relative amounts of acid and conjugate base required for a desired pH.

### EXAMPLE 18.5 Preparing a Buffer

Which acid would you choose to combine with its sodium salt to make a solution buffered at pH 4.25? For the best choice, calculate the ratio of the conjugate base to the acid required to attain the desired pH.



#### SOLUTION

The best choice is formic acid because its  $\text{p}K_a$  lies closest to the desired pH. You can calculate the ratio of conjugate base ( $\text{CHO}_2^-$ ) to acid ( $\text{HCHO}_2$ ) required by using the Henderson-Hasselbalch equation as follows:

$$\begin{aligned} \text{pH} &= \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]} \\ 4.25 &= 3.74 + \log \frac{[\text{base}]}{[\text{acid}]} \\ \log \frac{[\text{base}]}{[\text{acid}]} &= 4.25 - 3.74 \\ &= 0.51 \\ \frac{[\text{base}]}{[\text{acid}]} &= 10^{0.51} \\ &= 3.24 \end{aligned}$$

**FOR PRACTICE 18.5** Which acid in Example 18.5 would you choose to create a buffer with pH = 7.35? If you have 500.0 mL of a 0.10 M solution of the acid, what mass of the corresponding sodium salt of the conjugate base do you need to make the buffer?



# CHEMISTRY AND MEDICINE

## Buffer Effectiveness in Human Blood

**A**s we discussed in Section 18.1, blood contains several buffering systems, the most important of which consists of carbonic acid and the bicarbonate ion. The concentrations of these buffer components in normal blood plasma are  $[HCO_3^-] = 0.024\text{ M}$  and  $[H_2CO_3] = 0.0012\text{ M}$ . The  $pK_a$  for carbonic acid at body temperature is 6.1.

If we substitute these quantities into the Henderson–Hasselbalch equation, we can calculate the normal pH of blood:

$$\begin{aligned} \text{pH} &= pK_a + \log \frac{[\text{base}]}{[\text{acid}]} \\ &= 6.1 + \log \frac{[HCO_3^-]}{[H_2CO_3]} \\ &= 6.1 + \log \frac{0.024\text{ M}}{0.0012\text{ M}} \\ &= 7.4 \end{aligned}$$

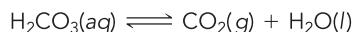
Normal blood has a pH of 7.4. Notice that the concentration of the bicarbonate ion is 20 times higher than the concentration of carbonic acid and the pH of the buffer is more than one pH unit away from  $pK_a$ . Why?

The higher bicarbonate ion concentration in blood makes the buffer capacity of blood greater for acid than for base, which is necessary because the products of metabolism that enter blood are mostly acidic. For example, when we exercise, our bodies produce lactic acid ( $HC_3H_5O_3$ ). The lactic acid enters the bloodstream

and must be neutralized. The bicarbonate ion neutralizes the lactic acid according to the equation:



An enzyme called carbonic anhydrase then catalyzes the conversion of carbonic acid into carbon dioxide and water:



We eliminate the carbon dioxide from our blood when we breathe. When large amounts of lactic acid are produced, we must breathe faster to keep up with the need to eliminate carbon dioxide. This is why we pant when we exert ourselves.

**QUESTION** A 70-kg person has a total blood volume of about 5.0 L. Given the carbonic acid and bicarbonate concentrations stated, what volume (in mL) of 6.0 M HCl can be neutralized by blood without the blood pH dropping below 7.0 (which would result in death)?



► Normal blood has a pH of 7.4.



## Buffer Capacity

**Buffer capacity** is the amount of acid or base that we can add to a buffer without causing a large change in pH. Given what we just learned about the absolute concentrations of acid and conjugate base in an effective buffer, we can conclude that the *buffer capacity increases with increasing absolute concentrations of the buffer components*. The more concentrated the weak acid and conjugate base that compose the buffer, the higher the buffer capacity. In addition, *overall buffer capacity increases as the relative concentrations of the buffer components become more similar to each other*. As the ratio of the buffer components gets closer to 1, the *overall capacity* of the buffer (the ability to neutralize added acid *and* added base) becomes greater. In some cases, however, a buffer that must neutralize primarily added acid (or primarily added base) may be overweighted in one of the buffer components, as shown in the *Chemistry and Medicine* box in this section.

**ANSWER NOW!**



**18.5**  
**Cc**  
Conceptual Connection

**BUFFER CAPACITY** A 1.0-L buffer solution is 0.10 M in HF and 0.050 M in NaF. Which action destroys the buffer?

- (a) adding 0.050 mol of HCl
- (b) adding 0.050 mol of NaOH
- (c) adding 0.050 mol of NaF
- (d) none of the above

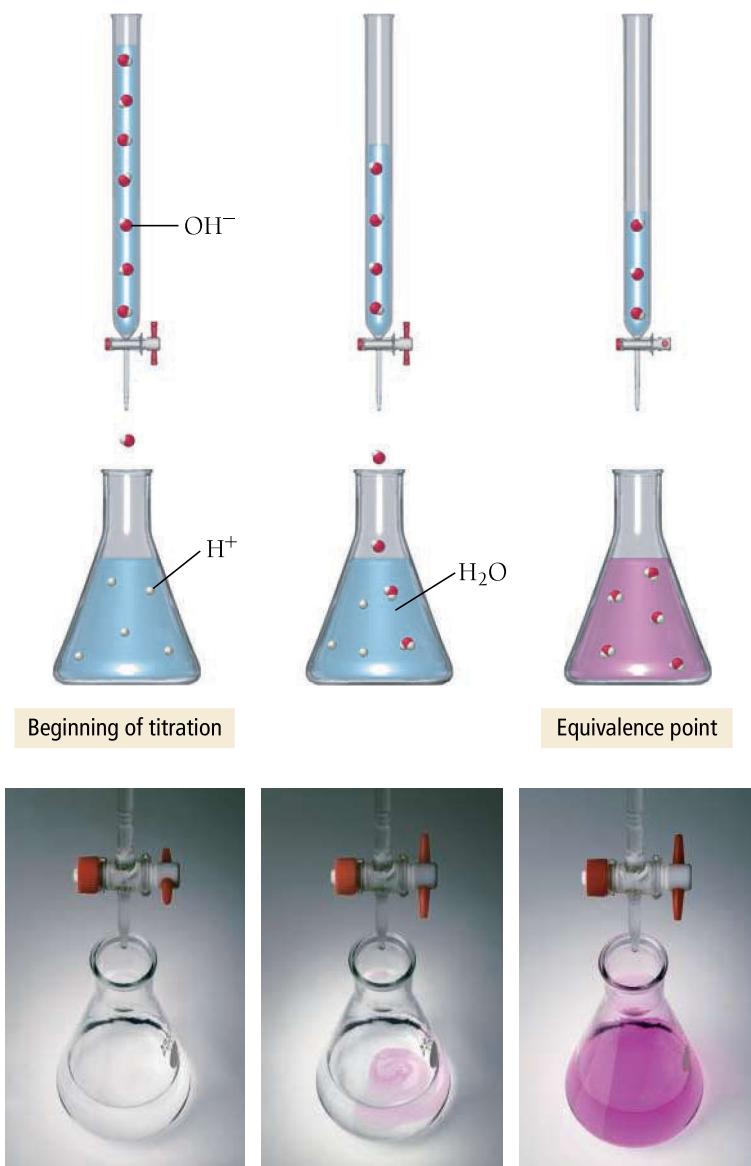
## 18.4

## Titrations and pH Curves

We first examined acid-base titrations in Section 5.7. In an **acid-base titration**, a basic (or acidic) solution of unknown concentration reacts with an acidic (or basic) solution of known concentration. The known solution is slowly added to the unknown one while the pH is monitored with either a pH meter or an **indicator** (a substance whose color depends on the pH). As the acid and base combine, they neutralize each other. At the **equivalence point**—the point in the titration when the number of moles of base is stoichiometrically equal to the number of moles of acid—the titration is complete. When the equivalence point is reached, neither reactant is in excess and the number of moles of the reactants are related by the reaction stoichiometry (Figure 18.5▼).

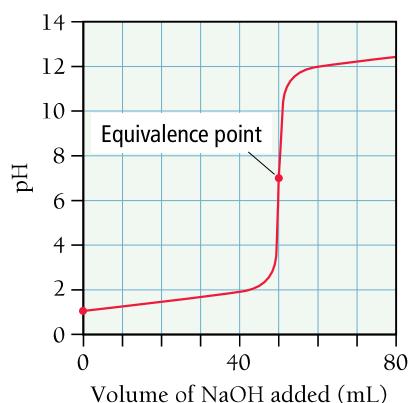
In this section, we examine acid-base titrations more closely, concentrating on the pH changes that occur during the titration. A plot of the pH of the solution during a titration is known as a *titration curve* or *pH curve*. Figure 18.6▼ is a pH curve for the titration of HCl with NaOH. Before any base is added to the solution, the pH is low (as we would expect for a solution of HCl). As the NaOH is added, the solution becomes less

The equivalence point is so named because the number of moles of acid and base are stoichiometrically equivalent at this point.



▲ FIGURE 18.5 Acid-Base Titration As  $\text{OH}^-$  is added in a titration, it neutralizes the  $\text{H}^+$ , forming water. At the equivalence point, the titration is complete.

### Titration of a Strong Acid with a Strong Base



▲ FIGURE 18.6 Titration Curve: Strong Acid + Strong Base This curve represents the titration of 50.0 mL of 0.100 M HCl with 0.100 M NaOH.

acidic because the NaOH begins to neutralize the HCl. The point of inflection in the middle of the curve is the equivalence point. Notice that the pH changes very quickly near the equivalence point (small amounts of added base cause large changes in pH). Beyond the equivalence point, the solution is basic because the HCl has been completely neutralized and excess base is being added to the solution. The exact shape of the pH curve depends on several factors, including the strength of the acid or base being titrated. Let's consider several combinations individually.

## WATCH NOW!

### KEY CONCEPT VIDEO 18.4A

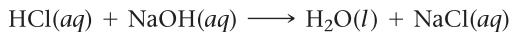
 The Titration of a Strong Acid with a Strong Base

## The Titration of a Strong Acid with a Strong Base

Consider the titration of 25.0 mL of 0.100 M HCl with 0.100 M NaOH. We begin by calculating the volume of base required to reach the equivalence point and then the pH at several points during the titration.

### Volume of NaOH Required to Reach the Equivalence Point

During the titration, the added sodium hydroxide neutralizes the hydrochloric acid:



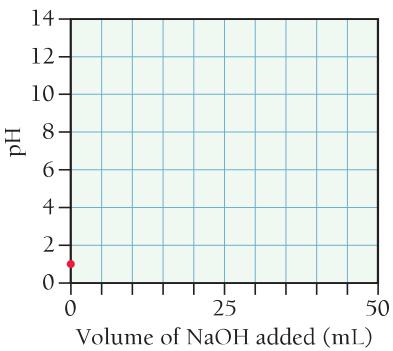
The equivalence point is reached when the number of moles of base added equals the number of moles of acid initially in solution. We calculate the amount of acid initially in solution from its volume and its concentration:

$$\text{Initial mol HCl} = 0.0250 \cancel{L} \times \frac{0.100 \text{ mol}}{1 \cancel{L}} = 0.00250 \text{ mol HCl}$$

The amount of NaOH that must be added is 0.00250 mol NaOH. We calculate the volume of NaOH required from its concentration:

$$\text{Volume NaOH solution} = 0.00250 \cancel{\text{mol}} \times \frac{1 \text{ L}}{0.100 \cancel{\text{mol}}} = 0.0250 \text{ L}$$

The equivalence point is reached when 25.0 mL of NaOH has been added. In this case, the concentrations of both solutions are identical, so the volume of NaOH solution required to reach the equivalence point is equal to the volume of the HCl solution that is being titrated.



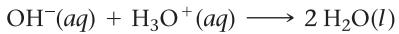
### Initial pH (before Adding Any Base)

The initial pH of the solution is simply the pH of a 0.100 M HCl solution. Since HCl is a strong acid, the concentration of  $\text{H}_3\text{O}^+$  is also 0.100 M and the pH is 1.00:

$$\begin{aligned}\text{pH} &= -\log[\text{H}_3\text{O}^+] \\ &= -\log(0.100) \\ &= 1.00\end{aligned}$$

### pH after Adding 5.00 mL NaOH

As NaOH is added to the solution, it neutralizes  $\text{H}_3\text{O}^+$ :



We calculate the amount of  $\text{H}_3\text{O}^+$  at any given point (before the equivalence point) by using the reaction stoichiometry—1 mol of NaOH neutralizes 1 mol of  $\text{H}_3\text{O}^+$ . The initial number of moles of  $\text{H}_3\text{O}^+$  (as just calculated) is 0.00250 mol. We calculate the number of moles of NaOH added at 5.00 mL by multiplying the added volume (in L) by the concentration of the NaOH solution:

$$\text{mol NaOH added} = 0.00500 \cancel{L} \times \frac{0.100 \text{ mol}}{1 \cancel{L}} = 0.000500 \text{ mol NaOH}$$

The addition of  $\text{OH}^-$  causes the amount of  $\text{H}_3\text{O}^+$  to decrease as shown in the following table:

	$\text{OH}^-(aq)$	+	$\text{H}_3\text{O}^+(aq) \longrightarrow 2 \text{H}_2\text{O}(l)$
Before addition	$\approx 0.00 \text{ mol}$		0.00250 mol
Addition	0.000500 mol		—
After addition	$\approx 0.00 \text{ mol}$		0.00200 mol

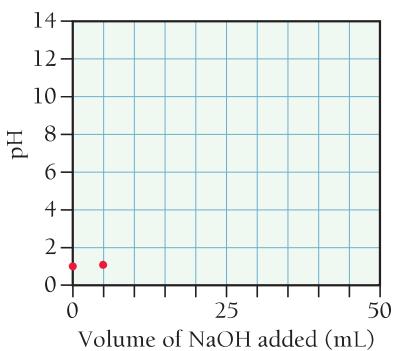
We calculate the  $\text{H}_3\text{O}^+$  concentration by dividing the number of moles of  $\text{H}_3\text{O}^+$  remaining by the *total volume* (initial volume plus added volume):

$$[\text{H}_3\text{O}^+] = \frac{0.00200 \text{ mol H}_3\text{O}^+}{0.0250 \text{ L} + 0.00500 \text{ L}} = 0.0667 \text{ M}$$

Initial volume                          Added volume

The pH is therefore 1.18:

$$\begin{aligned}\text{pH} &= -\log 0.0667 \\ &= 1.18\end{aligned}$$



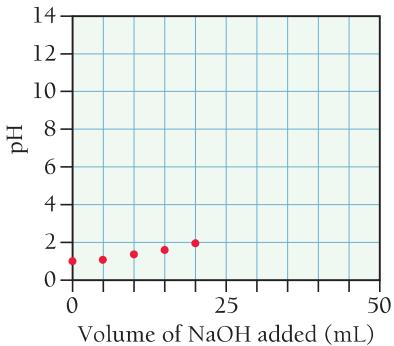
### pH after Adding 10.0, 15.0, and 20.0 mL NaOH

As more NaOH is added, it further neutralizes the  $\text{H}_3\text{O}^+$  in the solution. We calculate the pH at each of these points in the same way that we calculated the pH at the 5.00 mL point. The results are tabulated as follows:

Volume (mL)	pH
10.0	1.37
15.0	1.60
20.0	1.95

### pH after Adding 25.0 mL NaOH (Equivalence Point)

The pH at the equivalence point of a strong acid-strong base titration will always be 7.00 (at 25 °C). At the equivalence point, the strong base has completely neutralized the strong acid. The only source of hydronium ions then is the ionization of water. The  $[\text{H}_3\text{O}^+]$  at 25 °C from the ionization of water is  $1.00 \times 10^{-7} \text{ M}$  and the pH is 7.00.

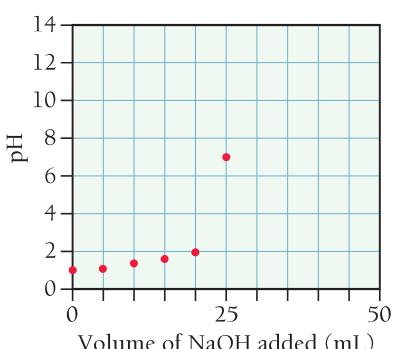


### pH after Adding 30.00 mL NaOH

As NaOH is added beyond the equivalence point, it becomes the excess reagent. We calculate the amount of  $\text{OH}^-$  at any given point (past the equivalence point) by subtracting the initial amount of  $\text{H}_3\text{O}^+$  from the amount of added  $\text{OH}^-$ . The number of moles of  $\text{OH}^-$  added at 30.00 mL is:

$$\text{mol OH}^- \text{ added} = 0.0300 \cancel{\text{L}} \times \frac{0.100 \text{ mol}}{1 \cancel{\text{L}}} = 0.00300 \text{ mol OH}^-$$

The number of moles of  $\text{OH}^-$  remaining after neutralization is shown in the following table:



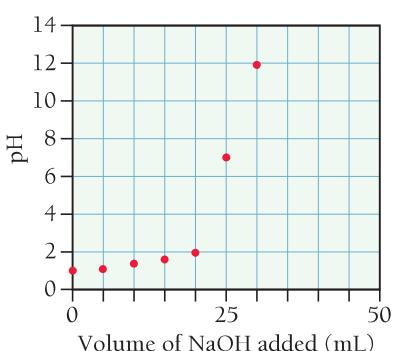
$\text{OH}^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq}) \longrightarrow 2 \text{H}_2\text{O}(\text{l})$		
Before addition	$\approx 0.00 \text{ mol}$	$0.00250 \text{ mol}$
Addition	$0.00300 \text{ mol}$	—
After addition	$0.00050 \text{ mol}$	$\approx 0.00 \text{ mol}$

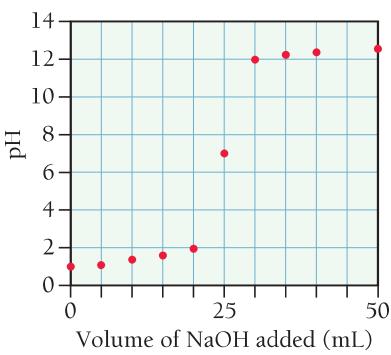
We calculate the  $\text{OH}^-$  concentration by dividing the number of moles of  $\text{OH}^-$  remaining by the *total volume* (initial volume plus added volume):

$$[\text{OH}^-] = \frac{0.000500 \text{ mol OH}^-}{0.0250 \text{ L} + 0.0300 \text{ L}} = 0.00909 \text{ M}$$

We can then calculate the  $[\text{H}_3\text{O}^+]$  and pH:

$$\begin{aligned}[\text{H}_3\text{O}^+][\text{OH}^-] &= 10^{-14} \\ [\text{H}_3\text{O}^+] &= \frac{10^{-14}}{[\text{OH}^-]} = \frac{10^{-14}}{0.00909} \\ &= 1.10 \times 10^{-12} \text{ M} \\ \text{pH} &= -\log(1.10 \times 10^{-12}) \\ &= 11.96\end{aligned}$$





### pH after Adding 35.0, 40.0, and 50.0 mL NaOH

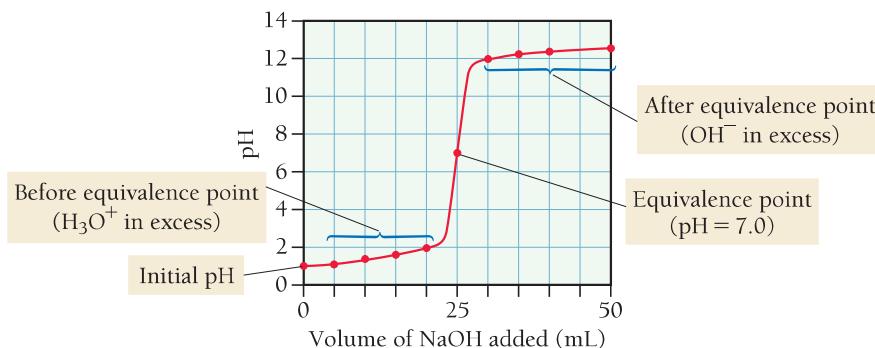
As more NaOH is added, it further increases the basicity of the solution. We calculate the pH at each of these points in the same way that we calculated the pH at the 30.00 mL point. The results are tabulated as follows:

Volume (mL)	pH
35.0	12.22
40.0	12.36
50.0	12.52

### The Overall pH Curve

The overall pH curve for the titration of a strong acid with a strong base has the characteristic S-shape we just plotted. The overall curve is as follows:

#### Titration of a Strong Acid with a Strong Base

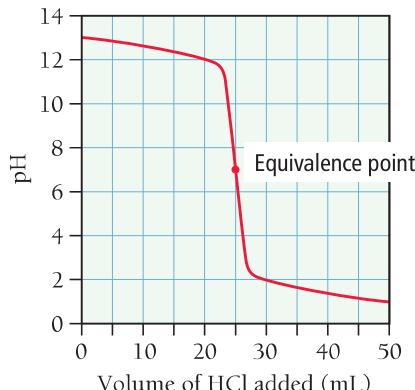


#### Summarizing the Titration of a Strong Acid with a Strong Base:

- The initial pH is simply the pH of the strong acid solution to be titrated.
- Before the equivalence point,  $\text{H}_3\text{O}^+$  is in excess. Calculate the  $[\text{H}_3\text{O}^+]$  by subtracting the number of moles of added  $\text{OH}^-$  from the initial number of moles of  $\text{H}_3\text{O}^+$  and dividing by the *total* volume.
- At the equivalence point, neither reactant is in excess and the pH = 7.00.
- Beyond the equivalence point,  $\text{OH}^-$  is in excess. Calculate the  $[\text{OH}^-]$  by subtracting the initial number of moles of  $\text{H}_3\text{O}^+$  from the number of moles of added  $\text{OH}^-$  and dividing by the *total* volume.

The pH curve for the titration of a strong base with a strong acid is shown in Figure 18.7▼. Calculating the points along this curve is very similar to calculating the points along the pH curve for the titration of a strong acid with a strong base. The main difference is that the curve starts basic and then becomes acidic after the equivalence point (instead of vice versa).

#### Titration of a Strong Base with a Strong Acid



► **FIGURE 18.7** Titration Curve: Strong Base + Strong Acid This curve represents the titration of 25.0 mL of 0.100 M NaOH with 0.100 M HCl.

WATCH NOW!

INTERACTIVE WORKED EXAMPLE 18.6

**EXAMPLE 18.6** Strong Acid–Strong Base Titration pH Curve

A 50.0-mL sample of 0.200 M sodium hydroxide is titrated with 0.200 M nitric acid. Calculate pH:

- (a) after adding 30.00 mL of HNO<sub>3</sub>
- (b) at the equivalence point

**SOLUTION**

(a) Begin by calculating the initial amount of NaOH (in moles) from the volume and molarity of the NaOH solution. Because NaOH is a strong base, it dissociates completely, so the amount of OH<sup>-</sup> is equal to the amount of NaOH.

Calculate the amount of HNO<sub>3</sub> (in moles) added at 30.0 mL from the molarity of the HNO<sub>3</sub> solution.

As HNO<sub>3</sub> is added to the solution, it neutralizes some of the OH<sup>-</sup>. Calculate the number of moles of OH<sup>-</sup> remaining by setting up a table based on the neutralization reaction that shows the amount of OH<sup>-</sup> before the addition, the amount of H<sub>3</sub>O<sup>+</sup> added, and the amounts left after the addition.

Calculate the OH<sup>-</sup> concentration by dividing the amount of OH<sup>-</sup> remaining by the *total volume* (initial volume plus added volume).

Calculate the pOH from [OH<sup>-</sup>].

Calculate the pH from the pOH using the equation pH + pOH = 14.

$$\text{moles NaOH} = 0.0500 \text{ L} \times \frac{0.200 \text{ mol}}{1 \text{ L}} \\ = 0.0100 \text{ mol}$$

$$\text{moles OH}^- = 0.0100 \text{ mol}$$

$$\text{mol HNO}_3 \text{ added} = 0.0300 \text{ L} \times \frac{0.200 \text{ mol}}{1 \text{ L}} \\ = 0.00600 \text{ mol HNO}_3$$

$\text{OH}^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq}) \longrightarrow 2\text{H}_2\text{O}(l)$		
Before addition	0.0100 mol	$\approx 0.00 \text{ mol}$
Addition	—	0.00600 mol
After addition	0.0040 mol	0.00 mol

$$[\text{OH}^-] = \frac{0.0040 \text{ mol}}{0.0500 \text{ L} + 0.0300 \text{ L}} \\ = 0.0500 \text{ M}$$

$$\text{pOH} = -\log(0.0500) \\ = 1.30$$

$$\text{pH} = 14 - \text{pOH} \\ = 14 - 1.30 \\ = 12.70$$

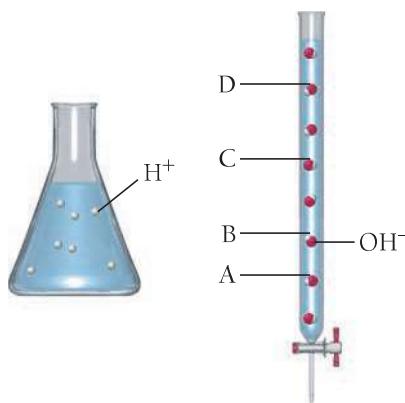
$$\text{pH} = 7.00$$

(b) At the equivalence point, the strong base has completely neutralized the strong acid. The [H<sub>3</sub>O<sup>+</sup>] at 25 °C from the ionization of water is  $1.00 \times 10^{-7} \text{ M}$  and the pH is therefore 7.00.

**FOR PRACTICE 18.6** Calculate the pH in the titration in Example 18.6 after the addition of 60.0 mL of 0.200 M HNO<sub>3</sub>.

**TITRATION EQUIVALENCE POINT** The amount of strong acid in the flask shown here is to be titrated by a strong base. Which mark on the burette next to the flask indicates the amount of base required to reach the equivalence point?

- (a) A
- (b) B
- (c) C
- (d) D



**18.6**  
**Cc**

Conceptual Connection

ANSWER NOW!



**WATCH NOW!****KEY CONCEPT VIDEO 18.4B**

 The Titration of a Weak Acid and a Strong Base
**The Titration of a Weak Acid with a Strong Base**

Consider the titration of 25.0 mL of 0.100 M  $\text{HCHO}_2$  with 0.100 M NaOH:



The concentrations and the volumes here are identical to those in our previous titration, in which we calculated the pH curve for the titration of a *strong* acid with a strong base. The only difference is that  $\text{HCHO}_2$  is a *weak* acid rather than a strong one. We begin by calculating the volume required to reach the equivalence point of the titration.

**Volume of NaOH Required to Reach the Equivalence Point**

From the stoichiometry of the equation, we can see that the equivalence point occurs when the amount (in moles) of added base equals the amount (in moles) of acid initially in solution:

$$\text{Initial mol HCHO}_2 = 0.0250 \cancel{\text{L}} \times \frac{0.100 \text{ mol}}{1 \cancel{\text{L}}} = 0.00250 \text{ mol HCHO}_2$$

The amount of NaOH that must be added is 0.00250 mol NaOH. The volume of NaOH required is therefore:

$$\text{Volume NaOH solution} = 0.00250 \cancel{\text{mol}} \times \frac{1 \text{ L}}{0.100 \cancel{\text{mol}}} = 0.0250 \text{ L NaOH solution}$$

The equivalence point occurs when 25.0 mL of base has been added. Notice that the volume of NaOH required to reach the equivalence point for this weak acid is identical to that required for a strong acid. *The volume at the equivalence point in an acid-base titration does not depend on whether the acid being titrated is a strong acid or a weak acid; it depends only on the amount (in moles) of acid present in solution before the titration begins and on the concentration of the added base.*

**Initial pH (before Adding Any Base)**

The initial pH of the solution is the pH of a 0.100 M  $\text{HCHO}_2$  solution. Since  $\text{HCHO}_2$  is a weak acid, we calculate the concentration of  $\text{H}_3\text{O}^+$  and the pH by doing an equilibrium problem for the ionization of  $\text{HCHO}_2$ . The procedure for solving weak acid ionization problems is given in Examples 17.5 and 17.6. We show a highly condensed calculation here ( $K_a$  for  $\text{HCHO}_2$  is  $1.8 \times 10^{-4}$ ):



	[HCHO <sub>2</sub> ]	[H <sub>3</sub> O <sup>+</sup> ]	[CHO <sub>2</sub> <sup>-</sup> ]
Initial	0.100	≈ 0.00	0.00
Change	-x	+x	+x
Equil	0.100 - x	x	x

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CHO}_2^-]}{[\text{HCHO}_2]}$$

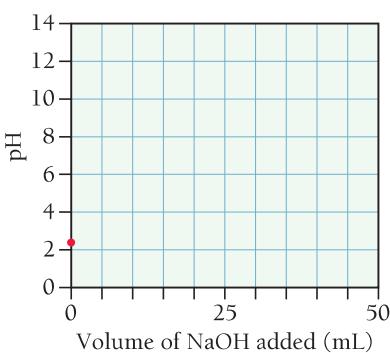
$$= \frac{x^2}{0.100 - \cancel{x}} \quad (\text{x is small})$$

$$1.8 \times 10^{-4} = \frac{x^2}{0.100}$$

$$x = 4.24 \times 10^{-3}$$

Therefore,  $[\text{H}_3\text{O}^+] = 4.24 \times 10^{-3} \text{ M}$ .

$$\begin{aligned} \text{pH} &= -\log(4.24 \times 10^{-3}) \\ &= 2.37 \end{aligned}$$



Notice that the pH is initially at a higher value (less acidic) than it is for a strong acid of the same concentration, as we would expect because the acid is weak.

**pH after Adding 5.00 mL NaOH**

When titrating a *weak acid* with a strong base, the added NaOH *converts a stoichiometric amount of the acid into its conjugate base*. As we calculated previously, 5.00 mL of the 0.100 M NaOH solution contains 0.000500 mol OH<sup>-</sup>. When the 0.000500 mol OH<sup>-</sup> is added to the

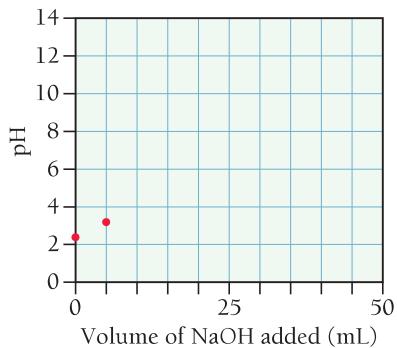
weak acid solution, the  $\text{OH}^-$  reacts stoichiometrically with  $\text{HCHO}_2$  causing the amount of  $\text{HCHO}_2$  to *decrease* by 0.000500 mol and the amount of  $\text{CHO}_2^-$  to *increase* by 0.000500 mol.

This is very similar to what happens when we add strong base to a buffer, and it is summarized in the following table:

$\text{OH}^-(\text{aq}) + \text{HCHO}_2(\text{aq}) \longrightarrow \text{H}_2\text{O}(l) + \text{CHO}_2^-(\text{aq})$				
Before addition	$\approx 0.00 \text{ mol}$	0.00250 mol	—	0.00 mol
Addition	0.000500 mol	—	—	—
After addition	$\approx 0.00 \text{ mol}$	0.00200 mol	—	0.000500 mol

Notice that, after the addition, the solution contains significant amounts of both an acid ( $\text{HCHO}_2$ ) and its conjugate base ( $\text{CHO}_2^-$ )—*the solution is now a buffer*. To calculate the pH of a buffer (when the  $x$  is small approximation applies as it does here), we can use the Henderson–Hasselbalch equation and  $pK_a$  for  $\text{HCHO}_2$  (which is 3.74):

$$\begin{aligned}\text{pH} &= pK_a + \log \frac{[\text{base}]}{[\text{acid}]} \\ &= 3.74 + \log \frac{0.000500}{0.00200} \\ &= 3.74 - 0.60 \\ &= 3.14\end{aligned}$$



### pH after Adding 10.0, 12.5, 15.0, and 20.0 mL NaOH

As more NaOH is added, it converts more  $\text{HCHO}_2$  into  $\text{CHO}_2^-$ . We calculate the relative amounts of  $\text{HCHO}_2$  and  $\text{CHO}_2^-$  at each of these volumes using the reaction stoichiometry and then calculate the pH of the resulting buffer using the Henderson–Hasselbalch equation (as we did for the pH at 5.00 mL). The amounts of  $\text{HCHO}_2$  and  $\text{CHO}_2^-$  (after addition of the  $\text{OH}^-$ ) at each volume and the corresponding values of pH are tabulated as follows:

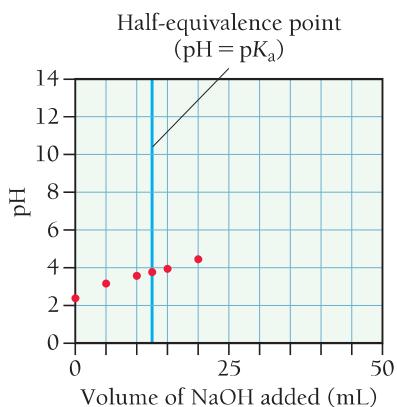
Volume (mL)	mol $\text{HCHO}_2$	mol $\text{CHO}_2^-$	pH
10.0	0.00150	0.00100	3.56
12.5	0.00125	0.00125	3.74
15.0	0.00100	0.00150	3.92
20.0	0.00050	0.00200	4.34

As the titration proceeds, more of the  $\text{HCHO}_2$  is converted to the conjugate base ( $\text{CHO}_2^-$ ). Notice that an added NaOH volume of 12.5 mL corresponds to one-half of the equivalence point. At this volume, one-half of the initial amount of  $\text{HCHO}_2$  has been converted to  $\text{CHO}_2^-$ , resulting in *equal amounts of weak acid and conjugate base*. For any buffer in which the amounts of weak acid and conjugate base are equal, the  $\text{pH} = pK_a$ :

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

If  $[\text{base}] = [\text{acid}]$ , then  $[\text{base}]/[\text{acid}] = 1$ .

$$\begin{aligned}\text{pH} &= pK_a + \log 1 \\ &= pK_a + 0 \\ &= pK_a\end{aligned}$$



### pH after Adding 25.0 mL NaOH (Equivalence Point)

At the equivalence point, 0.00250 mol of  $\text{OH}^-$  has been added and therefore all of the  $\text{HCHO}_2$  has been converted into its conjugate base ( $\text{CHO}_2^-$ ) as summarized in the following table:

$\text{OH}^-(\text{aq}) + \text{HCHO}_2(\text{aq}) \longrightarrow \text{H}_2\text{O}(l) + \text{CHO}_2^-(\text{aq})$				
Before addition	$\approx 0.00 \text{ mol}$	0.00250 mol	—	0.00 mol
Addition	0.00250 mol	—	—	—
After addition	$\approx 0.00 \text{ mol}$	0.00 mol	—	0.00250 mol

Since  $\text{pH} = pK_a$  halfway to the equivalence point, titrations can be used to measure the  $pK_a$  of an acid.

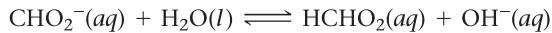
The solution is no longer a buffer (it no longer contains significant amounts of both a weak acid and its conjugate base). Instead, the solution contains an ion ( $\text{CHO}_2^-$ ) acting as a weak base. We discussed how to calculate the pH of solutions such as this in Section 17.8 (see Example 17.14) by solving an equilibrium problem involving the ionization of water by the weak base ( $\text{CHO}_2^-$ ):



We calculate the initial concentration of  $\text{CHO}_2^-$  for the equilibrium problem by dividing the number of moles of  $\text{CHO}_2^-$  (0.00250 mol) by the *total* volume at the equivalence point (initial volume plus added volume):

$$\begin{array}{c} \text{Moles } \text{CHO}_2^- \text{ at equivalence point} \\ \downarrow \\ [\text{CHO}_2^-] = \frac{0.00250 \text{ mol}}{0.0250 \text{ L} + 0.0250 \text{ L}} = 0.0500 \text{ M} \\ \uparrow \quad \uparrow \\ \text{Initial volume} \quad \text{Added volume} \\ \text{at equivalence point} \end{array}$$

We then proceed to solve the equilibrium problem as shown in condensed form as follows:



	$[\text{CHO}_2^-]$	$[\text{HCHO}_2]$	$[\text{OH}^-]$
Initial	0.0500	0.00	$\approx 0.00$
Change	$-x$	$+x$	$+x$
Equil	$0.0500 - x$	$x$	$x$

Before substituting into the expression for  $K_b$ , we find the value of  $K_b$  from  $K_a$  for formic acid ( $K_a = 1.8 \times 10^{-4}$ ) and  $K_w$ :

$$\begin{aligned} K_a \times K_b &= K_w \\ K_b &= \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-4}} = 5.6 \times 10^{-11} \end{aligned}$$

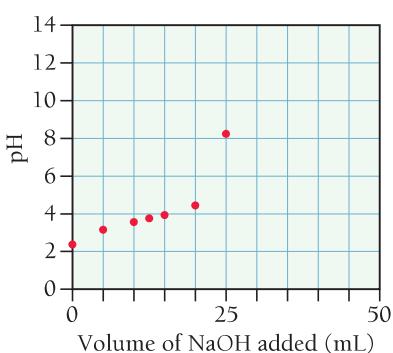
Then we substitute the equilibrium concentrations from the previous table into the expression for  $K_b$ :

$$\begin{aligned} K_b &= \frac{[\text{HCHO}_2][\text{OH}^-]}{[\text{CHO}_2^-]} \\ &= \frac{x^2}{0.0500 - x} \quad (x \text{ is small}) \\ 5.6 \times 10^{-11} &= \frac{x^2}{0.0500} \\ x &= 1.7 \times 10^{-6} \end{aligned}$$

Remember that  $x$  represents the concentration of the hydroxide ion. We calculate  $[\text{H}_3\text{O}^+]$  and pH:

$$\begin{aligned} [\text{OH}^-] &= 1.7 \times 10^{-6} \text{ M} \\ [\text{H}_3\text{O}^+][\text{OH}^-] &= K_w = 1.0 \times 10^{-14} \\ [\text{H}_3\text{O}^+](1.7 \times 10^{-6}) &= 1.0 \times 10^{-14} \\ [\text{H}_3\text{O}^+] &= 5.9 \times 10^{-9} \text{ M} \\ \text{pH} &= -\log[\text{H}_3\text{O}^+] \\ &= -\log(5.9 \times 10^{-9}) \\ &= 8.23 \end{aligned}$$

Notice that the pH at the equivalence point is *not* neutral but basic. *The titration of a weak acid by a strong base always has a basic equivalence point* because, at the equivalence point, all of the acid has been converted into its conjugate base, resulting in a weakly basic solution.



## pH after Adding 30.00 mL NaOH

At this point in the titration, 0.00300 mol of  $\text{OH}^-$  has been added. NaOH has thus become the excess reagent as shown in the following table:

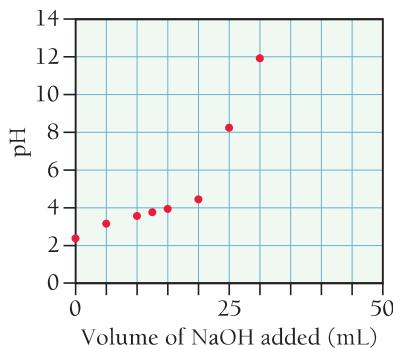
$\text{OH}^-(\text{aq}) + \text{HCHO}_2(\text{aq}) \longrightarrow \text{H}_2\text{O}(l) + \text{CHO}_2^-(\text{aq})$			
Before addition	$\approx 0.00 \text{ mol}$	0.00250 mol	—
Addition	0.00300 mol	—	—
After addition	0.00050 mol	$\approx 0.00 \text{ mol}$	0.00250 mol

The solution is now a mixture of a strong base (NaOH) and a weak base ( $\text{CHO}_2^-$ ). The strong base completely overwhelms the weak base, and we can calculate the pH by considering the strong base alone (as we did for the titration of a strong acid and a strong base). We calculate the  $\text{OH}^-$  concentration by dividing the amount of  $\text{OH}^-$  remaining by the *total volume* (initial volume plus added volume):

$$[\text{OH}^-] = \frac{0.00050 \text{ mol } \text{OH}^-}{0.0250 \text{ L} + 0.0300 \text{ L}} = 0.0091 \text{ M}$$

We can then calculate the  $[\text{H}_3\text{O}^+]$  and pH:

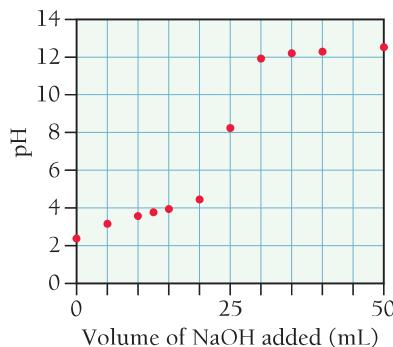
$$\begin{aligned} [\text{H}_3\text{O}^+][\text{OH}^-] &= 10^{-14} \\ [\text{H}_3\text{O}^+] &= \frac{10^{-14}}{[\text{OH}^-]} = \frac{10^{-14}}{0.0091} = 1.1 \times 10^{-12} \text{ M} \\ \text{pH} &= -\log(1.10 \times 10^{-12}) \\ &= 11.96 \end{aligned}$$



## pH after Adding 35.0, 40.0, and 50.0 mL NaOH

As more NaOH is added, the basicity of the solution increases further. We calculate the pH at each of these volumes in the same way we calculated the pH at 30.00 mL of added NaOH. The results are tabulated as follows:

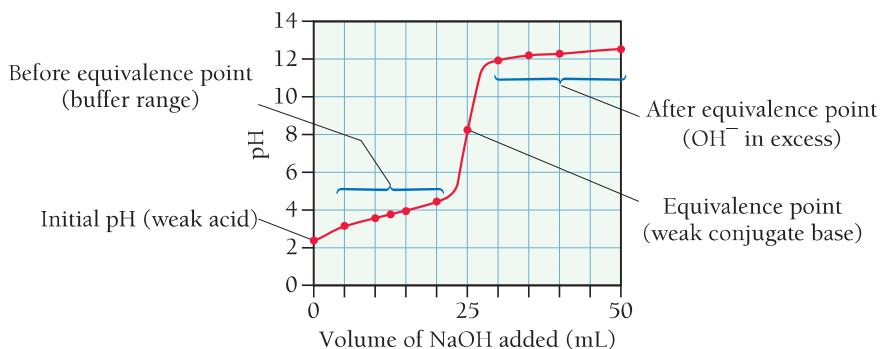
Volume (mL)	pH
35.0	12.22
40.0	12.36
50.0	12.52



## The Overall pH Curve

The overall pH curve for the titration of a weak acid with a strong base has a characteristic S-shape similar to that for the titration of a strong acid with a strong base. The main difference is that the equivalence point pH is basic (not neutral). Notice that calculating the pH in different regions throughout the titration involves working different kinds of acid–base problems, all of which we have encountered before.

### Titration of a Weak Acid with a Strong Base



**Summarizing Titration of a Weak Acid with a Strong Base:**

- The initial pH is that of the weak acid solution to be titrated. Calculate the pH by working an equilibrium problem (similar to Examples 17.5 and 17.6) using the concentration of the weak acid as the initial concentration.
- Between the initial pH and the equivalence point, the solution becomes a buffer. Use the reaction stoichiometry to calculate the amounts of each buffer component and then use the Henderson–Hasselbalch equation to calculate the pH (as in Example 18.3).
- Halfway to the equivalence point, the buffer components are exactly equal and  $\text{pH} = \text{p}K_a$ .
- At the equivalence point, the acid has all been converted into its conjugate base. Calculate the pH by working an equilibrium problem for the ionization of water by the ion acting as a weak base (similar to Example 17.14). (Calculate the concentration of the ion acting as a weak base by dividing the number of moles of the ion by the total volume at the equivalence point.)
- Beyond the equivalence point,  $\text{OH}^-$  is in excess. Ignore the weak base and calculate the  $[\text{OH}^-]$  by subtracting the initial number of moles of the weak acid from the number of moles of added  $\text{OH}^-$  and dividing by the *total* volume.

**WATCH NOW!****INTERACTIVE WORKED EXAMPLE 18.7****EXAMPLE 18.7 Weak Acid–Strong Base Titration pH Curve**

A 40.0-mL sample of 0.100 M  $\text{HNO}_2$  is titrated with 0.200 M KOH. Calculate:

- the volume required to reach the equivalence point
- the pH after adding 5.00 mL of KOH
- the pH at one-half the equivalence point

**SOLUTION**

(a) The equivalence point occurs when the amount (in moles) of added base equals the amount (in moles) of acid initially in the solution. Begin by calculating the amount (in moles) of acid initially in the solution. The amount (in moles) of KOH that must be added is equal to the amount of the weak acid.

Calculate the volume of KOH required from the number of moles of KOH and the molarity.

$$\text{mol HNO}_2 = 0.0400 \text{ L} \times \frac{0.100 \text{ mol}}{\text{L}} \\ = 4.00 \times 10^{-3} \text{ mol}$$

$$\text{mol KOH required} = 4.00 \times 10^{-3} \text{ mol}$$

$$\text{volume KOH solution} = 4.00 \times 10^{-3} \text{ mol} \times \frac{1 \text{ L}}{0.200 \text{ mol}} \\ = 0.0200 \text{ L KOH solution} \\ = 20.0 \text{ mL KOH solution}$$

(b) Use the concentration of the KOH solution to calculate the amount (in moles) of  $\text{OH}^-$  in 5.00 mL of the solution.

Prepare a table showing the amounts of  $\text{HNO}_2$  and  $\text{NO}_2^-$  before and after the addition of 5.00 mL KOH. The addition of the KOH stoichiometrically reduces the concentration of  $\text{HNO}_2$  and increases the concentration of  $\text{NO}_2^-$ .

Since the solution now contains significant amounts of a weak acid and its conjugate base, use the Henderson–Hasselbalch equation and  $\text{p}K_a$  for  $\text{HNO}_2$  (which is 3.34) to calculate the pH of the solution.

$$\text{mol OH}^- = 5.00 \times 10^{-3} \text{ L} \times \frac{0.200 \text{ mol}}{1 \text{ L}} \\ = 1.00 \times 10^{-3} \text{ mol OH}^-$$

$\text{OH}^-(\text{aq}) + \text{HNO}_2(\text{aq}) \longrightarrow \text{H}_2\text{O}(\text{l}) + \text{NO}_2^-(\text{aq})$				
Before addition	$\approx 0.00 \text{ mol}$	$4.00 \times 10^{-3} \text{ mol}$	—	$0.00 \text{ mol}$
Addition	$1.00 \times 10^{-3} \text{ mol}$	—	—	—
After addition	$\approx 0.00 \text{ mol}$	$3.00 \times 10^{-3} \text{ mol}$	—	$1.00 \times 10^{-3} \text{ mol}$

$$\begin{aligned} \text{pH} &= \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]} \\ &= 3.34 + \log \frac{1.00 \times 10^{-3}}{3.00 \times 10^{-3}} \\ &= 3.34 - 0.48 = 2.86 \end{aligned}$$

- (c) At one-half the equivalence point, the amount of added base is exactly one-half the initial amount of acid. The base converts exactly half of the  $\text{HNO}_2$  into  $\text{NO}_2^-$ , resulting in equal amounts of the weak acid and its conjugate base. The pH is therefore equal to  $pK_a$ .

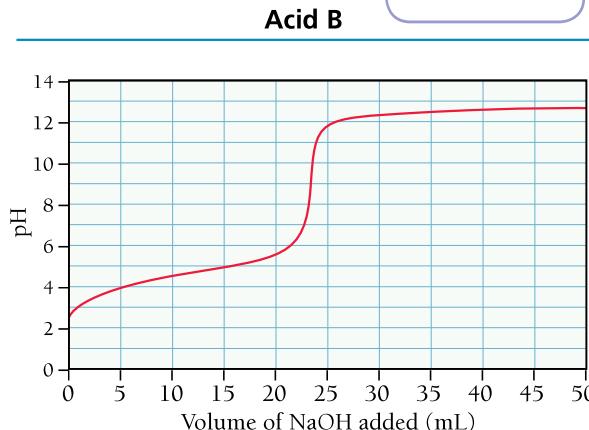
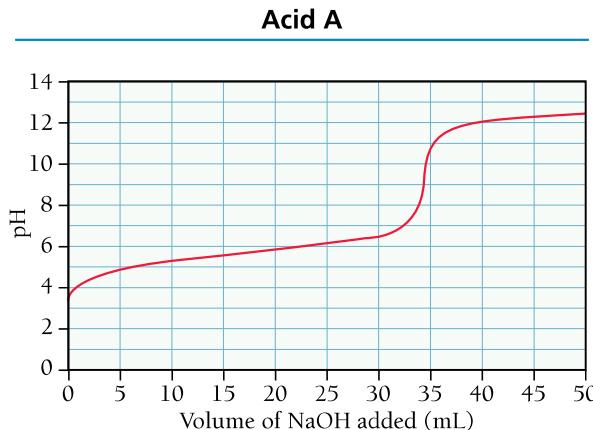
$\text{OH}^-(\text{aq}) + \text{HNO}_2(\text{aq}) \longrightarrow \text{H}_2\text{O}(l) + \text{NO}_2^-(\text{aq})$				
Before addition	$\approx 0.00 \text{ mol}$	$4.00 \times 10^{-3} \text{ mol}$	—	$0.00 \text{ mol}$
Addition	$2.00 \times 10^{-3} \text{ mol}$	—	—	—
After addition	$\approx 0.00 \text{ mol}$	$2.00 \times 10^{-3} \text{ mol}$	—	$2.00 \times 10^{-3} \text{ mol}$

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

$$= 3.34 + \log \frac{2.00 \times 10^{-3}}{2.00 \times 10^{-3}} = 3.34 + 0 = 3.34$$

**FOR PRACTICE 18.7** Determine the pH at the equivalence point for the titration of  $\text{HNO}_2$  and KOH in Example 18.7.

**WEAK ACID–STRONG BASE TITRATION** Two 25.0-mL samples of unknown monoprotic weak acids, A and B, are titrated with 0.100 M NaOH solutions. The titration curve for each acid is shown below. Which of the two weak acid solutions is more concentrated? Which of the two weak acids has the larger  $K_a$ ?

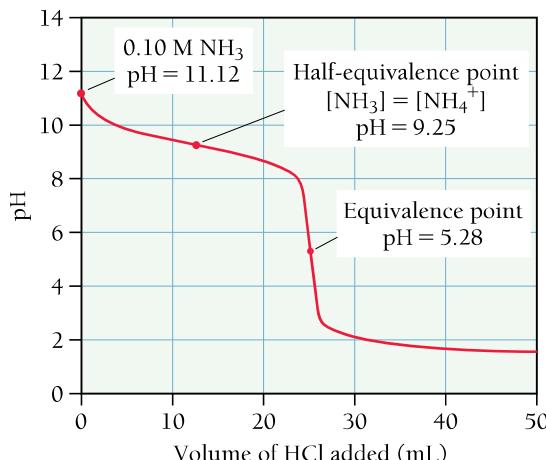


- (a) Acid B is more concentrated and has the larger  $K_a$ .  
 (b) Acid A is more concentrated and has the larger  $K_a$ .  
 (c) Acid A is more concentrated and Acid B has the larger  $K_a$ .  
 (d) Acid B is more concentrated and Acid A has the larger  $K_a$ .

## The Titration of a Weak Base with a Strong Acid

The pH curve for the titration of a weak base with a strong acid is shown in Figure 18.8►. Calculating the points along this curve is very similar to calculating the points along the pH curve for the titration of a weak acid with a strong base (which we just did). The main differences are that the curve starts basic and has an acidic equivalence point. We calculate the pH in the buffer region using  $\text{pH} = pK_a + \log \frac{[\text{base}]}{[\text{acid}]}$  where the  $pK_a$  corresponds to the conjugate acid of the base being titrated.

## Titration of a Weak Base with a Strong Acid



**► FIGURE 18.8** Titration Curve: Weak Base + Strong Acid This curve represents the titration of 0.100 M  $\text{NH}_3$  with 0.100 M  $\text{HCl}$ .

**ANSWER NOW!**

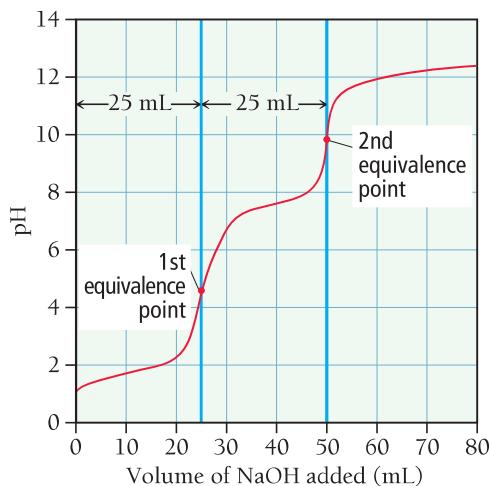


# 18.8

## Cc

### Conceptual Connection

## Titration of a Polyprotic Acid



**▲ FIGURE 18.9 Titration Curve: Diprotic Acid + Strong Base** This curve represents the titration of 25.0 mL of 0.100 M  $\text{H}_2\text{SO}_3$  with 0.100 M NaOH.

ANSWER NOW!



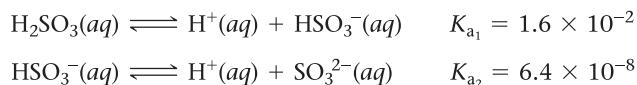
# 18.9

## Cc

### Conceptual Connection

# The Titration of a Polyprotic Acid

When a diprotic acid is titrated with a strong base, if  $K_{a_1}$  and  $K_{a_2}$  are sufficiently different, the pH curve will have two equivalence points. For example, Figure 18.9 shows the pH curve for the titration of sulfurous acid ( $H_2SO_3$ ) with sodium hydroxide. Recall from Section 17.9 that sulfurous acid ionizes in two steps as follows:



The first equivalence point in the titration curve represents the titration of the first proton, whereas the second equivalence point represents the titration of the second proton. Notice that the volume required to reach the first equivalence point is identical to the volume required to reach the second point because the number of moles of  $\text{H}_2\text{SO}_3$  in the first step determines the number of moles of  $\text{HSO}_3^-$  in the second step.

**ACID-BASE TITRATIONS** Consider these three titrations:

- (i) the titration of 25.0 mL of a 0.100 M monoprotic weak acid with 0.100 M NaOH
  - (ii) the titration of 25.0 mL of a 0.100 M diprotic weak acid with 0.100 M NaOH
  - (iii) the titration of 25.0 mL of a 0.100 M strong acid with 0.100 M NaOH

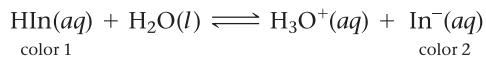
Which statement is most likely to be true?

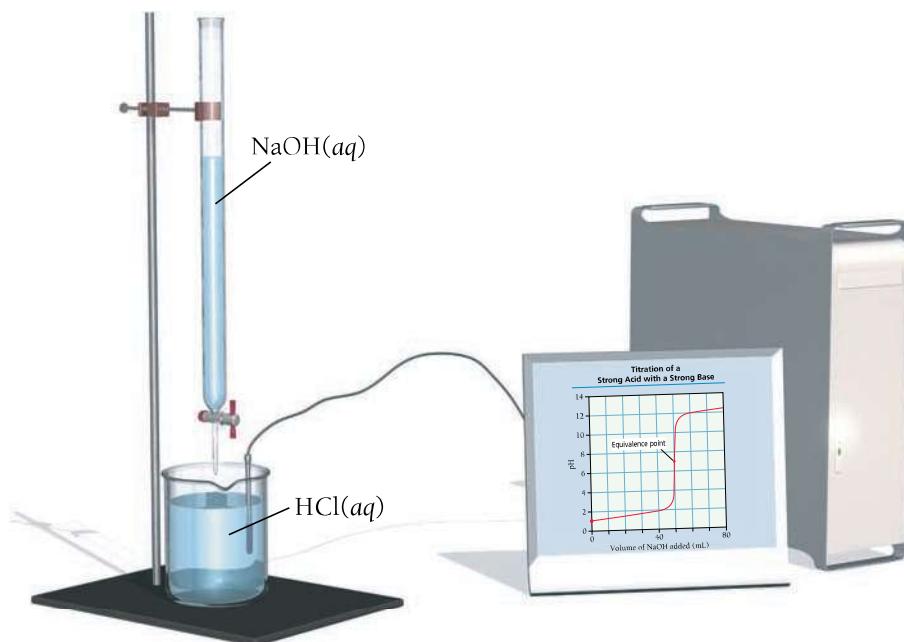
- (a) All three titrations have the same initial pH.
  - (b) All three titrations have the same pH at their first equivalence points.
  - (c) All three titrations require the same volume of NaOH to reach their first equivalence points.

# Indicators: pH-Dependent Colors

We can monitor the pH of a titration with either a pH meter or an indicator. The direct monitoring of pH with a meter yields data like the pH curves we have examined previously, allowing determination of the equivalence point from the pH curve itself, as shown in Figure 18.10▶. With an indicator, we rely on the point where the indicator changes color—called the **endpoint**—to determine the equivalence point, as shown in Figure 18.11▶. With the correct indicator, the endpoint of the titration (indicated by the color change) occurs at the equivalence point (when the amount of acid equals the amount of base).

An indicator is itself a weak organic acid that is a different color than its conjugate base. For example, phenolphthalein (whose structure is shown in Figure 18.12►) is a common indicator whose acid form is colorless and conjugate base form is pink. If we let  $\text{HIn}$  represent the acid form of a generic indicator and  $\text{In}^-$  the conjugate base form, we have the following equilibrium:



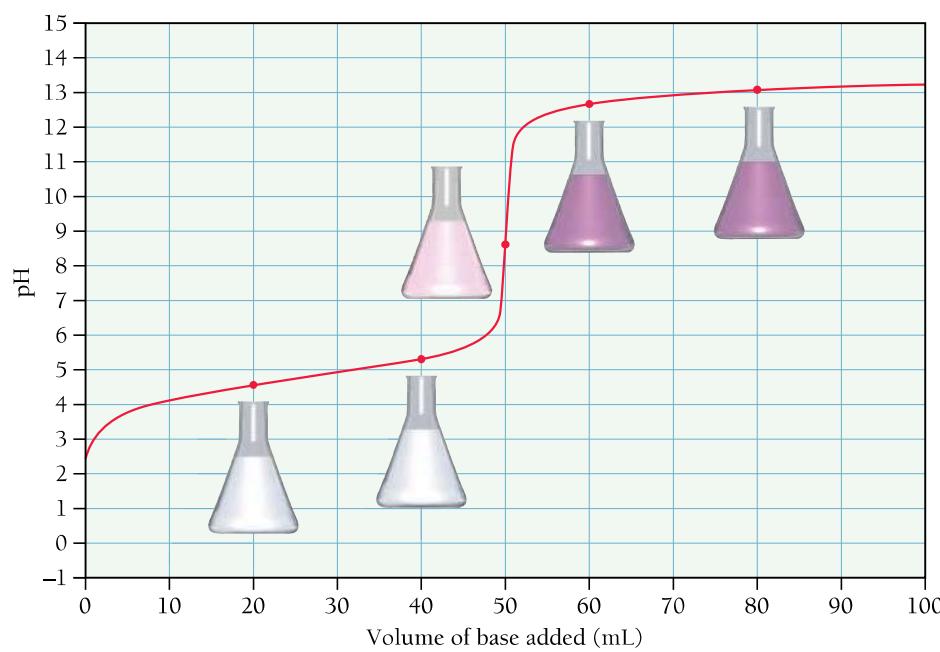


**◀ FIGURE 18.10 Monitoring the pH during a Titration** A pH meter monitors pH during titration. The inflection point in the resulting pH curve signifies the equivalence point.

**► FIGURE 18.11 Monitoring the Color Change during a Titration**

Titration of 0.100 M  $\text{HC}_2\text{H}_3\text{O}_2$  with 0.100 M NaOH. The endpoint of a titration is signaled by a color change in an appropriate indicator (in this case, phenolphthalein).

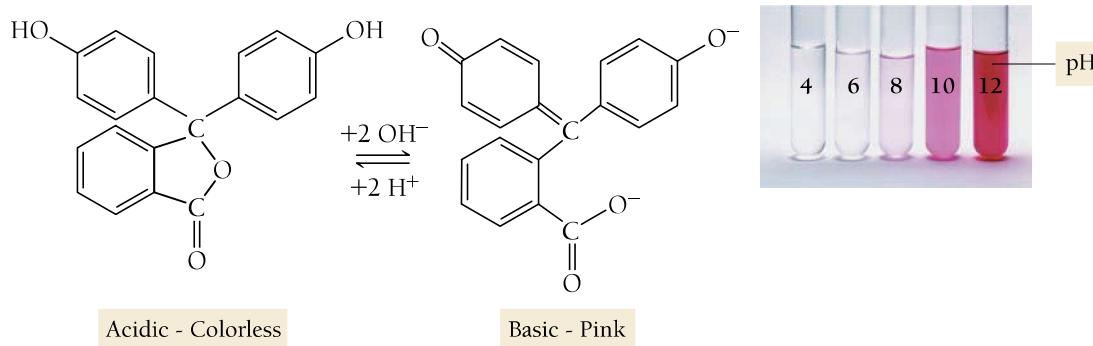
### Using an Indicator



**▼ FIGURE 18.12 Phenolphthalein**

Phenolphthalein, a weakly acidic compound, is colorless. Its conjugate base is pink.

### Phenolphthalein, a Common Indicator



Because its color is intense, only a small amount of indicator is required—an amount that will not affect the pH of the solution or the equivalence point of the neutralization reaction. When the  $[H_3O^+]$  changes during the titration, the equilibrium shifts in response. At low pH, the  $[H_3O^+]$  is high and the equilibrium lies far to the left, resulting in a solution of color 1. As the titration proceeds, the  $[H_3O^+]$  decreases, shifting the equilibrium to the right. Since the pH change is large near the equivalence point of the titration, there is a large change in  $[H_3O^+]$  near the equivalence point. Provided that the correct indicator is chosen, there will also be a correspondingly significant change in color. For the titration of a strong acid with a strong base, one drop of the base near the endpoint is usually enough to change the indicator from color 1 to color 2.

The color of a solution containing an indicator depends on the relative concentrations of  $HIn$  and  $In^-$ . As a useful guideline, we can assume the following:

If  $\frac{[In^-]}{[HIn]} = 1$ , the indicator solution will be intermediate in color.

If  $\frac{[In^-]}{[HIn]} > 10$ , the indicator solution will be the color of  $In^-$ .

If  $\frac{[In^-]}{[HIn]} < 0.1$ , the indicator solution will be the color of  $HIn$ .

From the Henderson-Hasselbalch equation, we can derive an expression for the ratio of  $[In^-]/[HIn]$ :

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

$$= pK_a + \log \frac{[In^-]}{[HIn]}$$

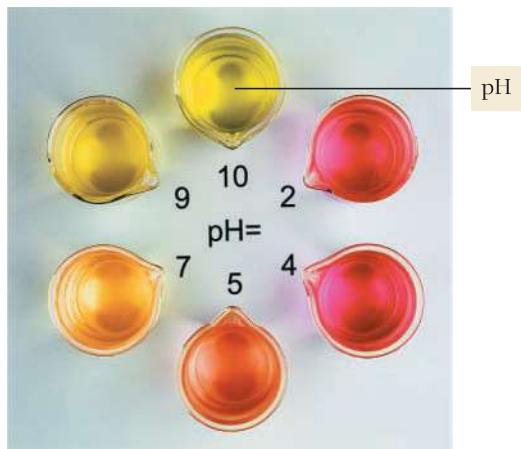
$$\log \frac{[In^-]}{[HIn]} = pH - pK_a$$

$$\frac{[In^-]}{[HIn]} = 10^{(pH - pK_a)}$$

Consider the following three pH values relative to  $pK_a$  and the corresponding colors of the indicator solution:

pH (relative to $pK_a$ )	$[In^-]/[HIn]$ Ratio	Color of Indicator Solution
$pH = pK_a$	$\frac{[In^-]}{[HIn]} = 10^0 = 1$	Intermediate color
$pH = pK_a + 1$	$\frac{[In^-]}{[HIn]} = 10^1 = 10$	Color of $In^-$
$pH = pK_a - 1$	$\frac{[In^-]}{[HIn]} = 10^{-1} = 0.10$	Color of $HIn$

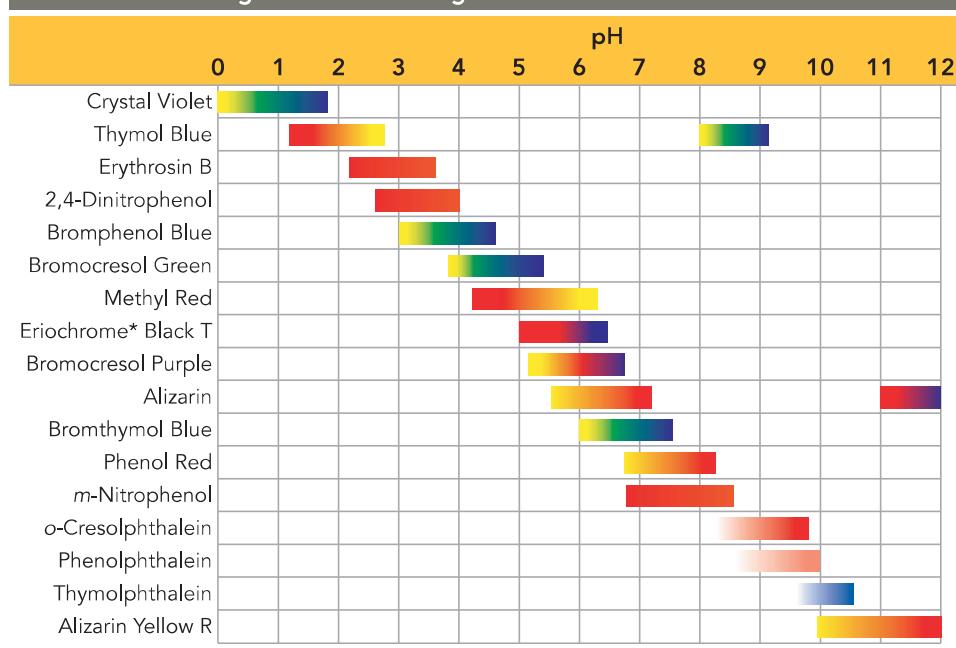
### Indicator Color Change: Methyl Red



When the pH of the solution equals the  $pK_a$  of the indicator, the solution has an intermediate color. When the pH is 1 unit (or more) above  $pK_a$ , the indicator is the color of  $In^-$ , and when the pH is 1 unit (or more) below  $pK_a$ , the indicator is the color of  $HIn$ . As you can see, the indicator changes color within a range of two pH units centered at  $pK_a$  (Figure 18.13). Table 18.1 shows various indicators and their colors as a function of pH.

◀ FIGURE 18.13 Indicator Color Change

An indicator (in this case, methyl red) generally changes color within a range of two pH units.

**TABLE 18.1** ■ Ranges of Color Changes for Several Acid–Base Indicators

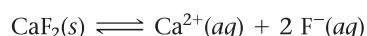
\*Trademark of CIBA GEIGY CORP.

## 18.5

### Solubility Equilibria and the Solubility Product Constant

Recall from Chapter 5 that a compound is considered *soluble* if it dissolves in water and *insoluble* if it does not. Recall also that, with the solubility rules in Table 5.1, we were able to classify ionic compounds simply as soluble or insoluble. Now we have the tools to examine *degrees* of solubility.

We can better understand the solubility of an ionic compound by applying the concept of equilibrium to the process of dissolution. For example, we can represent the dissolution of calcium fluoride in water as an equilibrium:



The equilibrium constant for a chemical equation representing the dissolution of an ionic compound is the **solubility product constant ( $K_{\text{sp}}$ )**. For  $\text{CaF}_2$ , the expression of the solubility product constant is:

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

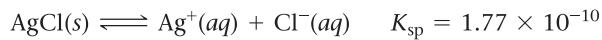
Notice that, as we discussed in Section 16.5, solids are omitted from the equilibrium expression because the concentration of a solid is constant (it is determined by its density and does not change when more solid is added).

The value of  $K_{\text{sp}}$  is a measure of the solubility of a compound. Table 18.2 lists the values of  $K_{\text{sp}}$  for a number of ionic compounds. A more complete list can be found in Appendix IIC.

### $K_{\text{sp}}$ and Molar Solubility

Recall from Section 14.2 that the *solubility* of a compound is the quantity of the compound that dissolves in a certain amount of liquid. The **molar solubility** is the solubility in units of moles per liter (mol/L). We can calculate the molar solubility of a compound directly from  $K_{\text{sp}}$ .

Consider silver chloride:



**TABLE 18.2 ■ Selected Solubility Product Constants ( $K_{sp}$ ) at 25 °C**

Compound	Formula	$K_{sp}$	Compound	Formula	$K_{sp}$
Barium fluoride	$\text{BaF}_2$	$2.45 \times 10^{-5}$	Lead(II) chloride	$\text{PbCl}_2$	$1.17 \times 10^{-5}$
Barium sulfate	$\text{BaSO}_4$	$1.07 \times 10^{-10}$	Lead(II) bromide	$\text{PbBr}_2$	$4.67 \times 10^{-6}$
Calcium carbonate	$\text{CaCO}_3$	$4.96 \times 10^{-9}$	Lead(II) sulfate	$\text{PbSO}_4$	$1.82 \times 10^{-8}$
Calcium fluoride	$\text{CaF}_2$	$1.46 \times 10^{-10}$	Lead(II) sulfide*	$\text{PbS}$	$9.04 \times 10^{-29}$
Calcium hydroxide	$\text{Ca}(\text{OH})_2$	$4.68 \times 10^{-6}$	Magnesium carbonate	$\text{MgCO}_3$	$6.82 \times 10^{-6}$
Calcium sulfate	$\text{CaSO}_4$	$7.10 \times 10^{-5}$	Magnesium hydroxide	$\text{Mg}(\text{OH})_2$	$2.06 \times 10^{-13}$
Copper(II) sulfide*	$\text{CuS}$	$1.27 \times 10^{-36}$	Silver chloride	$\text{AgCl}$	$1.77 \times 10^{-10}$
Iron(II) carbonate	$\text{FeCO}_3$	$3.07 \times 10^{-11}$	Silver chromate	$\text{Ag}_2\text{CrO}_4$	$1.12 \times 10^{-12}$
Iron(II) hydroxide	$\text{Fe}(\text{OH})_2$	$4.87 \times 10^{-17}$	Silver bromide	$\text{AgBr}$	$5.35 \times 10^{-13}$
Iron(II) sulfide*	$\text{FeS}$	$3.72 \times 10^{-19}$	Silver iodide	$\text{Agl}$	$8.51 \times 10^{-17}$

\*Sulfide equilibrium is of the type:  $\text{MS}(s) + \text{H}_2\text{O}(l) \rightleftharpoons \text{M}^{2+}(aq) + \text{HS}^-(aq) + \text{OH}^-(aq)$

Notice that  $K_{sp}$  is *not* the molar solubility, but the solubility product constant. The solubility product constant has only one value at a given temperature. The solubility, however, can have different values in different kinds of solutions. For example, due to the common ion effect, the solubility of AgCl in pure water is different from its solubility in an NaCl solution, even though the solubility product constant is the same for both solutions. Notice also that the solubility of AgCl is directly related (by the reaction stoichiometry) to the amount of  $\text{Ag}^+$  or  $\text{Cl}^-$  present in solution when equilibrium is reached. Consequently, finding molar solubility from  $K_{sp}$  involves solving an equilibrium problem.

For AgCl, we set up an ICE table for the dissolution of AgCl into its ions in pure water:



	$[\text{Ag}^+]$	$[\text{Cl}^-]$
Initial	0.00	0.00
Change	$+S$	$+S$
Equil	$S$	$S$

Alternatively, the variable  $x$  can be used in place of  $S$ , as it was for other equilibrium calculations.

We let  $S$  represent the concentration of AgCl that dissolves (which is the molar solubility) and then represent the concentrations of the ions formed in terms of  $S$ . In this case, for every 1 mol of AgCl that dissolves, 1 mol of  $\text{Ag}^+$  and 1 mol of  $\text{Cl}^-$  are produced. Therefore, the concentrations of  $\text{Ag}^+$  or  $\text{Cl}^-$  present in solution are equal to  $S$ . Substituting the equilibrium concentrations of  $\text{Ag}^+$  and  $\text{Cl}^-$  into the expression for the solubility product constant, we get:

$$\begin{aligned} K_{sp} &= [\text{Ag}^+][\text{Cl}^-] \\ &= S \times S \\ &= S^2 \end{aligned}$$

Therefore,

$$\begin{aligned} S &= \sqrt{K_{sp}} \\ &= \sqrt{1.77 \times 10^{-10}} \\ &= 1.33 \times 10^{-5} \text{ M} \end{aligned}$$

The molar solubility of AgCl is  $1.33 \times 10^{-5}$  mol per liter.

WATCH NOW!

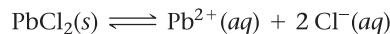
## INTERACTIVE WORKED EXAMPLE 18.8

**EXAMPLE 18.8****Calculating Molar Solubility from  $K_{sp}$** 

Calculate the molar solubility of  $\text{PbCl}_2$  in pure water.

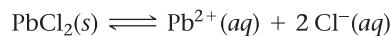
**SOLUTION**

Begin by writing the reaction by which solid  $\text{PbCl}_2$  dissolves into its constituent aqueous ions and write the corresponding expression for  $K_{sp}$ .



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

Refer to the stoichiometry of the reaction and prepare an ICE table, showing the equilibrium concentrations of  $\text{Pb}^{2+}$  and  $\text{Cl}^-$  relative to  $S$ , the amount of  $\text{PbCl}_2$  that dissolves.



	$[\text{Pb}^{2+}]$	$[\text{Cl}^-]$
Initial	0.00	0.00
Change	$+S$	$+2S$
Equil	$S$	$2S$

Substitute the equilibrium expressions for  $[\text{Pb}^{2+}]$  and  $[\text{Cl}^-]$  from the previous step into the expression for  $K_{sp}$ .

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

$$= S(2S)^2 = 4S^3$$

Solve for  $S$  and substitute the numerical value of  $K_{sp}$  (from Table 18.2) to calculate  $S$ .

$$S = \sqrt[3]{\frac{K_{sp}}{4}}$$

$$S = \sqrt[3]{\frac{1.17 \times 10^{-5}}{4}} = 1.43 \times 10^{-2} \text{ M}$$

**FOR PRACTICE 18.8** Calculate the molar solubility of  $\text{Fe(OH)}_2$  in pure water.

**CHEMISTRY IN YOUR DAY****Hard Water**

In many parts of the United States, significant concentrations of  $\text{CaCO}_3$  and  $\text{MgCO}_3$  dissolve into rainwater runoff as it flows through soils rich in these compounds. Water containing dissolved calcium and magnesium ions is known as hard water. Hard water is not a health hazard because both calcium and magnesium are part of a healthy diet. However, their presence in water can be a nuisance. Because of their relatively low solubility, hard water becomes saturated with  $\text{CaCO}_3$  and  $\text{MgCO}_3$  as it evaporates. If evaporation continues, some dissolved ions precipitate out as salts. These precipitates show up as scaly deposits on faucets, sinks, or cookware. Washing cars or dishes with hard water leaves spots of  $\text{CaCO}_3$  and  $\text{MgCO}_3$ .

Water can be softened with water softeners. These devices replace the  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions present in hard water with ions such as  $\text{K}^+$  or  $\text{Na}^+$ . Since potassium and sodium salts are

soluble, they do not form scaly deposits in the way that

$\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions do. However, when sodium is used to soften drinking water, the resulting water is high in sodium content, a disadvantage to those who must control their sodium intake due to high blood pressure.



▲ The water in reservoirs where the soil is rich in limestone (calcium carbonate) contains  $\text{Ca}^{2+}$  ions. This so-called hard water contains dissolved  $\text{CaCO}_3$  and  $\text{MgCO}_3$ . When hard water evaporates, it can leave deposits of these salts on the shores of lakes and reservoirs (at left) and on plumbing fixtures (such as the pipe shown here).

**QUESTION** Use the  $K_{sp}$  values from Table 18.2 to calculate the molar solubility of  $\text{CaCO}_3$  and  $\text{MgCO}_3$ . What mass of  $\text{CaCO}_3$  (in grams) is in 5 L of water that is saturated with  $\text{CaCO}_3$ ?



## EXAMPLE 18.9 Calculating $K_{\text{sp}}$ from Molar Solubility

The molar solubility of  $\text{Ag}_2\text{SO}_4$  in pure water is  $1.4 \times 10^{-2}$  M. Calculate  $K_{\text{sp}}$ .

### SOLUTION

Begin by writing the reaction by which solid  $\text{Ag}_2\text{SO}_4$  dissolves into its constituent aqueous ions; then write the corresponding expression for  $K_{\text{sp}}$ .



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

Use an ICE table to define  $[\text{Ag}^+]$  and  $[\text{SO}_4^{2-}]$  in terms of  $S$ , the amount of  $\text{Ag}_2\text{SO}_4$  that dissolves.



	$[\text{Ag}^+]$	$[\text{SO}_4^{2-}]$
Initial	0.00	0.00
Change	$+2S$	$+S$
Equil	$2S$	$S$

Substitute the expressions for  $[\text{Ag}^+]$  and  $[\text{SO}_4^{2-}]$  from the previous step into the expression for  $K_{\text{sp}}$ . Substitute the given value of the molar solubility for  $S$  and calculate  $K_{\text{sp}}$ .

$$\begin{aligned} K_{\text{sp}} &= [\text{Ag}^+]^2[\text{SO}_4^{2-}] \\ &= (2S)^2S \\ &= 4S^3 \\ &= 4(1.4 \times 10^{-2})^3 \\ &= 1.1 \times 10^{-5} \end{aligned}$$

**FOR PRACTICE 18.9** The molar solubility of  $\text{AgBr}$  in pure water is  $7.3 \times 10^{-7}$  M. Calculate  $K_{\text{sp}}$ .

## $K_{\text{sp}}$ and Relative Solubility

As we have just seen, molar solubility and  $K_{\text{sp}}$  are related, and each can be calculated from the other; however, we cannot generally use the  $K_{\text{sp}}$  values of two different compounds to directly compare their relative solubilities.

For example, consider the following compounds, their  $K_{\text{sp}}$  values, and their molar solubilities:

Compound	$K_{\text{sp}}$	Solubility
$\text{Mg}(\text{OH})_2$	$2.06 \times 10^{-13}$	$3.72 \times 10^{-5}$ M
$\text{FeCO}_3$	$3.07 \times 10^{-11}$	$5.54 \times 10^{-6}$ M

Magnesium hydroxide has a smaller  $K_{\text{sp}}$  than iron(II) carbonate, but a higher molar solubility. Why? The relationship between  $K_{\text{sp}}$  and molar solubility depends on the stoichiometry of the dissociation reaction. Consequently, any direct comparison of  $K_{\text{sp}}$  values for different compounds can only be made if the compounds have the same dissociation stoichiometry.

Consider the following compounds with the same dissociation stoichiometry, their  $K_{\text{sp}}$  values, and their molar solubilities:

Compound	$K_{\text{sp}}$	Solubility
$\text{Mg}(\text{OH})_2$	$2.06 \times 10^{-13}$	$3.72 \times 10^{-5}$ M
$\text{CaF}_2$	$1.46 \times 10^{-10}$	$3.32 \times 10^{-4}$ M

In this case, magnesium hydroxide and calcium fluoride have the same dissociation stoichiometry (1 mol of each compound produces 3 mol of dissolved ions); therefore, the  $K_{\text{sp}}$  values can be directly compared as a measure of relative solubility.

## The Effect of a Common Ion on Solubility

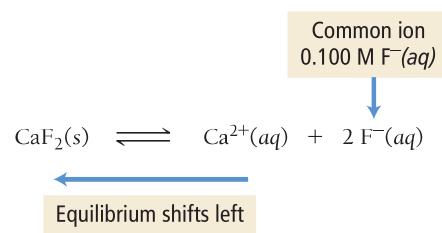
How is the solubility of an ionic compound affected when the compound is dissolved in a solution that already contains one of its ions? For example, what is the solubility of  $\text{CaF}_2$  in a solution that is 0.100 M in  $\text{NaF}$ ? We can determine the change in solubility by considering

the common ion effect, which we first encountered in Section 18.2. We represent the dissociation of  $\text{CaF}_2$  in a 0.100 M NaF solution as shown in the margin.

In accordance with Le Châtelier's principle, the presence of the  $\text{F}^-$  ion in solution causes the equilibrium to shift to the left (compared to its position in pure water), which means that less  $\text{CaF}_2$  dissolves—that is, its solubility is decreased.

**In general, the solubility of an ionic compound is lower in a solution containing a common ion than in pure water.**

We can calculate the exact value of the solubility by working an equilibrium problem in which the concentration of the common ion is accounted for in the initial conditions, as shown in Example 18.10.

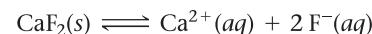


### EXAMPLE 18.10 Calculating Molar Solubility in the Presence of a Common Ion

What is the molar solubility of  $\text{CaF}_2$  in a solution containing 0.100 M NaF?

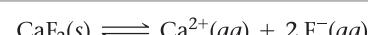
#### SOLUTION

Begin by writing the reaction by which solid  $\text{CaF}_2$  dissolves into its constituent aqueous ions. Write the corresponding expression for  $K_{\text{sp}}$ .



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

Use the stoichiometry of the reaction to prepare an ICE table showing the initial concentration of the common ion. Fill in the equilibrium concentrations of  $\text{Ca}^{2+}$  and  $\text{F}^-$  relative to  $S$ , the amount of  $\text{CaF}_2$  that dissolves.



	$[\text{Ca}^{2+}]$	$[\text{F}^-]$
Initial	0.00	0.100
Change	$+S$	$+2S$
Equil	$S$	$0.100 + 2S$

Substitute the equilibrium expressions for  $[\text{Ca}^{2+}]$  and  $[\text{F}^-]$  from the previous step into the expression for  $K_{\text{sp}}$ . Because  $K_{\text{sp}}$  is small, you can make the approximation that  $2S$  is much less than 0.100 and will therefore be insignificant when added to 0.100 (this is similar to the *x is small* approximation in equilibrium problems).

$$\begin{aligned} K_{\text{sp}} &= [\text{Ca}^{2+}][\text{F}^-]^2 \\ &= S(0.100 + 2S)^2 \quad (\text{S is small}) \\ &= S(0.100)^2 \end{aligned}$$

Solve for  $S$  and substitute the numerical value of  $K_{\text{sp}}$  (from Table 18.2) to calculate  $S$ . Note that the calculated value of  $S$  is indeed small compared to 0.100; our approximation is valid.

$$\begin{aligned} K_{\text{sp}} &= S(0.100)^2 \\ S &= \frac{K_{\text{sp}}}{0.0100} = \frac{1.46 \times 10^{-10}}{0.0100} = 1.46 \times 10^{-8} \text{ M} \end{aligned}$$

For comparison, the molar solubility of  $\text{CaF}_2$  in pure water is  $3.32 \times 10^{-4}$  M, which means  $\text{CaF}_2$  is over 20,000 times more soluble in water than in the NaF solution. (Confirm this for yourself by calculating its solubility in pure water from the value of  $K_{\text{sp}}$ .)

**FOR PRACTICE 18.10** Calculate the molar solubility of  $\text{CaF}_2$  in a solution containing 0.250 M  $\text{Ca}(\text{NO}_3)_2$ .

### COMMON ION EFFECT

In which solution is  $\text{BaSO}_4$  most soluble?

- (a) a solution that is 0.10 M in  $\text{BaNO}_3$
- (b) a solution that is 0.10 M in  $\text{Na}_2\text{SO}_4$
- (c) a solution that is 0.10 M in  $\text{NaNO}_3$

**18.10**

**C**

Conceptual Connection

**ANSWER NOW!**

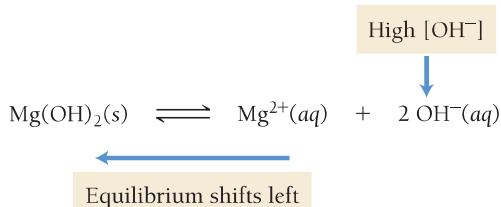


## The Effect of pH on Solubility

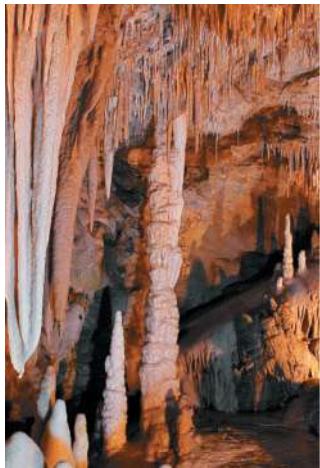
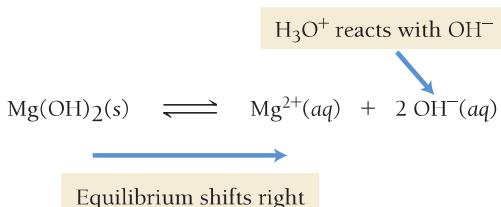
The pH of a solution can affect the solubility of a compound in that solution. For example, consider the dissociation of  $\text{Mg}(\text{OH})_2$ , the active ingredient in milk of magnesia:



The solubility of this compound is highly dependent on the pH of the solution into which it dissolves. If the pH is high, then the concentration of  $\text{OH}^-$  in the solution is high. In accordance with the common ion effect, this shifts the equilibrium to the left, lowering the solubility:



If the pH is low, then the concentration of  $\text{H}_3\text{O}^+(aq)$  in the solution is high. As the  $\text{Mg}(\text{OH})_2$  dissolves, these  $\text{H}_3\text{O}^+$  ions neutralize the newly dissolved  $\text{OH}^-$  ions, driving the reaction to the right:



▲ Stalactites (which hang from the ceiling) and stalagmites (which grow up from the ground) form as calcium carbonate precipitates out of the water evaporating in underground caves.

Consequently, the solubility of  $\text{Mg}(\text{OH})_2$  in an acidic solution is higher than that in a pH-neutral or basic solution.

**In general, the solubility of an ionic compound with a strongly basic or weakly basic anion increases with increasing acidity (decreasing pH).**

Common basic anions include  $\text{OH}^-$ ,  $\text{S}^{2-}$ , and  $\text{CO}_3^{2-}$ . Therefore, hydroxides, sulfides, and carbonates are more soluble in acidic water than in pure water. Since rainwater is naturally acidic due to dissolved carbon dioxide, it can dissolve rocks high in limestone ( $\text{CaCO}_3$ ) as it flows through the ground. This process sometimes results in huge underground caverns such as those at Carlsbad Caverns National Park in New Mexico. Dripping water saturated in  $\text{CaCO}_3$  within the cave creates the dramatic mineral formations known as stalagmites and stalactites.

### EXAMPLE 18.11 The Effect of pH on Solubility

Determine whether each compound is more soluble in an acidic solution than it is in a neutral solution.

- (a)  $\text{BaF}_2$       (b)  $\text{AgI}$       (c)  $\text{Ca}(\text{OH})_2$

#### SOLUTION

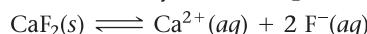
- (a) The solubility of  $\text{BaF}_2$  is greater in an acidic solution than it is in a neutral solution because the  $\text{F}^-$  ion is a weak base. ( $\text{F}^-$  is the conjugate base of the weak acid HF and is therefore a weak base.)
- (b) The solubility of  $\text{AgI}$  is not greater in an acidic solution than it is in a neutral solution because the  $\text{I}^-$  is *not* a base. ( $\text{I}^-$  is the conjugate base of the *strong* acid HI and is therefore pH-neutral.)
- (c) The solubility of  $\text{Ca}(\text{OH})_2$  is greater in an acidic solution than it is in a neutral solution because the  $\text{OH}^-$  ion is a strong base.

**FOR PRACTICE 18.11** Which compound,  $\text{FeCO}_3$  or  $\text{PbBr}_2$ , is more soluble in acid than in base? Why?

## 18.6 Precipitation

In Chapter 5, we learned that a precipitation reaction can occur when we mix two solutions containing ionic compounds when one of the possible cross products—the combination of a cation from one solution and the anion from the other—is insoluble. In this chapter, however, we have seen that the terms *soluble* and *insoluble* are extremes in a continuous range of solubility—many compounds are slightly soluble, and even those that we categorize as insoluble in Chapter 5 actually have some limited degree of solubility (they have very small solubility product constants).

We can better understand precipitation reactions by revisiting a concept from Chapter 16—the reaction quotient ( $Q$ ). The reaction quotient for the reaction by which an ionic compound dissolves is the product of the concentrations of the ionic components raised to their stoichiometric coefficients. For example, consider the reaction by which  $\text{CaF}_2$  dissolves:



The reaction quotient for this reaction is:

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

The difference between  $Q$  and  $K_{\text{sp}}$  is that  $K_{\text{sp}}$  is the value of this product *at equilibrium only*, whereas  $Q$  is the value of the product under any conditions. We can therefore use the value of  $Q$  to compare a solution containing any concentrations of the component ions to a solution that is at equilibrium.

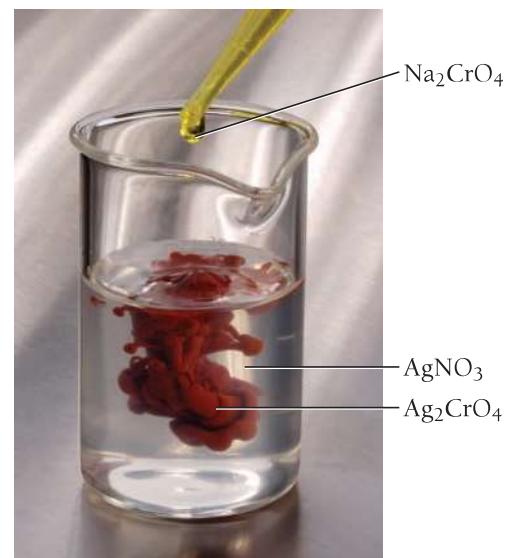
Consider a solution of calcium fluoride in which  $Q$  is less than  $K_{\text{sp}}$ . Recall from Chapter 16 that if  $Q$  is less than  $K_{\text{sp}}$ , the reaction will proceed to the right (toward products). Consequently, as long as solid  $\text{CaF}_2$  is present, the  $\text{CaF}_2$  will continue to dissolve. If all of the solid has already dissolved, the solution will simply remain as it is, containing less than the equilibrium amount of the dissolved ions. Such a solution is an *unsaturated solution*. If more solid is added to an unsaturated solution, it will dissolve, as long as  $Q$  remains less than  $K_{\text{sp}}$ .

Now consider a solution in which  $Q$  is exactly equal to  $K_{\text{sp}}$ . In this case, the reaction is at equilibrium and does not make progress in either direction. Such a solution most likely contains at least a small amount of the solid in equilibrium with its component ions. However, the amount of solid may be too small to be visible. Such a solution is a *saturated solution*.

Finally, consider a solution in which  $Q$  is greater than  $K_{\text{sp}}$ . In this case, the reaction proceeds to the left (toward the reactants) and solid calcium fluoride forms from the dissolved calcium and fluoride ions. In other words, the solid normally precipitates out of a solution in which  $Q$  is greater than  $K_{\text{sp}}$ . Under certain circumstances, however,  $Q$  can remain greater than  $K_{\text{sp}}$  for an unlimited period of time. Such a solution, called a *supersaturated solution*, is unstable and forms a precipitate when sufficiently disturbed. Figure 18.14▶ shows a supersaturated solution of sodium acetate. When a small seed crystal of solid sodium acetate is dropped into the solution, it triggers the precipitation reaction.

### Summarizing the Relationship of $Q$ and $K_{\text{sp}}$ in Solutions Containing an Ionic Compound:

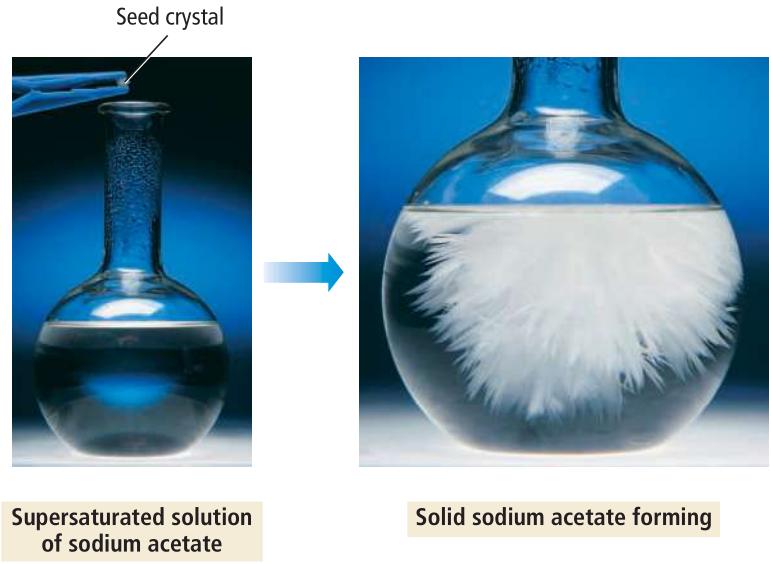
- If  $Q < K_{\text{sp}}$ , the solution is unsaturated and more of the solid ionic compound can dissolve in the solution.
- If  $Q = K_{\text{sp}}$ , the solution is saturated. The solution is holding the equilibrium amount of the dissolved ions, and additional solid does not dissolve in the solution.
- If  $Q > K_{\text{sp}}$ , the solution is supersaturated. Under most circumstances, the excess solid precipitates out of a supersaturated solution.



▲ Precipitation reaction

### ▼ FIGURE 18.14 Precipitation from a Supersaturated Solution

The excess solute in a supersaturated solution of sodium acetate precipitates out if a small sodium acetate crystal is added.



We can use  $Q$  to predict whether a precipitation reaction will occur upon the mixing of two solutions containing dissolved ionic compounds. For example, consider mixing a silver nitrate solution with a potassium iodide solution to form a mixture that is 0.010 M in  $\text{AgNO}_3$  and 0.015 M in  $\text{KI}$ . Will a precipitate form in the newly mixed solution? From Chapter 5 we know that one of the cross products,  $\text{KNO}_3$ , is soluble and will therefore not precipitate. The other cross product,  $\text{AgI}$ , *may* precipitate if the concentrations of  $\text{Ag}^+$  and  $\text{I}^-$  are high enough in the newly mixed solution: we can compare  $Q$  to  $K_{\text{sp}}$  to determine if a precipitate will form. For  $\text{AgI}$ ,  $K_{\text{sp}} = 8.51 \times 10^{-17}$ . For the newly mixed solution,  $[\text{Ag}^+] = 0.010 \text{ M}$  and  $[\text{I}^-] = 0.015 \text{ M}$ . We calculate  $Q$  as follows:

$$Q = [\text{Ag}^+][\text{I}^-] = (0.010)(0.015) = 1.5 \times 10^{-4}$$

The value of  $Q$  is much greater than  $K_{\text{sp}}$ ; therefore,  $\text{AgI}$  should precipitate out of the newly mixed solution.

### WATCH NOW!

### INTERACTIVE WORKED EXAMPLE 18.12

#### EXAMPLE 18.12 Predicting Precipitation Reactions by Comparing $Q$ and $K_{\text{sp}}$

A solution containing lead(II) nitrate is mixed with one containing sodium bromide to form a solution that is 0.0150 M in  $\text{Pb}(\text{NO}_3)_2$  and 0.00350 M in  $\text{NaBr}$ . Does a precipitate form in the newly mixed solution?

##### SOLUTION

First, determine the possible cross products and their  $K_{\text{sp}}$  values (Table 18.2). Any cross products that are soluble do *not* precipitate (see Table 4.1).

Possible cross products:

$\text{NaNO}_3$  soluble

$\text{PbBr}_2 \quad K_{\text{sp}} = 4.67 \times 10^{-6}$

Calculate  $Q$  and compare it to  $K_{\text{sp}}$ . A precipitate will only form if  $Q > K_{\text{sp}}$ .

$$\begin{aligned} Q &= [\text{Pb}^{2+}][\text{Br}^-]^2 \\ &= (0.0150)(0.00350)^2 \\ &= 1.84 \times 10^{-7} \end{aligned}$$

$Q < K_{\text{sp}}$ ; therefore no precipitate forms.

**FOR PRACTICE 18.12** If the original solutions in Example 18.12 are concentrated through evaporation and mixed again to form a solution that is 0.0600 M in  $\text{Pb}(\text{NO}_3)_2$  and 0.0158 M in  $\text{NaBr}$ , will a precipitate form in this newly mixed solution?



### Selective Precipitation

A solution may contain several different dissolved metal cations that can often be separated by **selective precipitation**, a process involving the addition of a reagent that forms a precipitate with one of the dissolved cations but not the others. For example, seawater contains dissolved magnesium and calcium cations with the concentrations  $[\text{Mg}^{2+}] = 0.059 \text{ M}$  and  $[\text{Ca}^{2+}] = 0.011 \text{ M}$ . We can separate these ions by adding a reagent that will precipitate one of the ions but not the other. From Table 18.2, we find that  $\text{Mg}(\text{OH})_2$  has a  $K_{\text{sp}}$  of  $2.06 \times 10^{-13}$  and that  $\text{Ca}(\text{OH})_2$  has a  $K_{\text{sp}}$  of  $4.68 \times 10^{-6}$ , indicating that the hydroxide ion forms a precipitate with magnesium at a much lower concentration than it does with calcium. Consequently, a soluble hydroxide—such as KOH or NaOH—is a good choice for the precipitating reagent. When we add an appropriate amount of KOH or NaOH to seawater, the hydroxide ion causes the precipitation of  $\text{Mg}(\text{OH})_2$  (the compound with the lowest  $K_{\text{sp}}$ ) but not  $\text{Ca}(\text{OH})_2$ . Calculations for this selective precipitation are shown in Examples 18.13 and 18.14. In these calculations, you compare  $Q$  to  $K_{\text{sp}}$  to determine the concentration that triggers precipitation.

The difference in  $K_{\text{sp}}$  values required for selective precipitation is a factor of at least  $10^3$ .

**SELECTIVE PRECIPITATION** A solution contains equal concentrations of  $\text{Ba}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Ca}^{2+}$  ions. When potassium sulfate is added to this solution, which cation precipitates first? (*Hint:* See Table 18.2.)

- (a)  $\text{Ba}^{2+}$       (b)  $\text{Pb}^{2+}$       (c)  $\text{Ca}^{2+}$



ANSWER NOW!

**EXAMPLE 18.13****Finding the Minimum Required Reagent Concentration for Selective Precipitation**

The magnesium and calcium ions present in seawater ( $[\text{Mg}^{2+}] = 0.059 \text{ M}$  and  $[\text{Ca}^{2+}] = 0.011 \text{ M}$ ) can be separated by selective precipitation with KOH. What minimum  $[\text{OH}^-]$  triggers the precipitation of the  $\text{Mg}^{2+}$  ion?

**SOLUTION**

The precipitation commences when the value of  $Q$  for the precipitating compound just equals the value of  $K_{\text{sp}}$ . Set the expression for  $Q$  for magnesium hydroxide equal to the value of  $K_{\text{sp}}$ , and solve for  $[\text{OH}^-]$ . This is the concentration above which  $\text{Mg}(\text{OH})_2$  precipitates.

$$\begin{aligned} Q &= [\text{Mg}^{2+}][\text{OH}^-]^2 \\ &= (0.059)[\text{OH}^-]^2 \end{aligned}$$

When  $Q = K_{\text{sp}}$ ,

$$\begin{aligned} (0.059)[\text{OH}^-]^2 &= K_{\text{sp}} = 2.06 \times 10^{-13} \\ [\text{OH}^-]^2 &= \frac{2.06 \times 10^{-13}}{0.059} \\ [\text{OH}^-] &= 1.9 \times 10^{-6} \text{ M} \end{aligned}$$

**FOR PRACTICE 18.13** If the concentration of  $\text{Mg}^{2+}$  in the previous solution was  $0.025 \text{ M}$ , what minimum  $[\text{OH}^-]$  triggers precipitation of the  $\text{Mg}^{2+}$  ion?

**EXAMPLE 18.14****Finding the Concentrations of Ions Left in Solution after Selective Precipitation**

You add potassium hydroxide to the solution in Example 18.13. When the  $[\text{OH}^-]$  reaches  $1.9 \times 10^{-6} \text{ M}$  (as you just calculated), magnesium hydroxide begins to precipitate out of solution. As you continue to add KOH, the magnesium hydroxide continues to precipitate. However, at some point, the  $[\text{OH}^-]$  becomes high enough to begin to precipitate the calcium ions as well. What is the concentration of  $\text{Mg}^{2+}$  when  $\text{Ca}^{2+}$  begins to precipitate?

**SOLUTION**

First, find the  $\text{OH}^-$  concentration at which  $\text{Ca}^{2+}$  begins to precipitate by writing the expression for  $Q$  for calcium hydroxide and substituting the concentration of  $\text{Ca}^{2+}$  from Example 18.13.

$$\begin{aligned} Q &= [\text{Ca}^{2+}][\text{OH}^-]^2 \\ &= (0.011)[\text{OH}^-]^2 \end{aligned}$$

Set the expression for  $Q$  equal to the value of  $K_{\text{sp}}$  for calcium hydroxide and solve for  $[\text{OH}^-]$ . This is the concentration above which  $\text{Ca}(\text{OH})_2$  precipitates.

$$\begin{aligned} \text{When } Q &= K_{\text{sp}}, \\ (0.011)[\text{OH}^-]^2 &= K_{\text{sp}} = 4.68 \times 10^{-6} \\ [\text{OH}^-]^2 &= \frac{4.68 \times 10^{-6}}{0.011} \\ [\text{OH}^-] &= 2.06 \times 10^{-2} \text{ M} \end{aligned}$$

Find the concentration of  $\text{Mg}^{2+}$  when  $\text{OH}^-$  reaches the concentration you just calculated by writing the expression for  $Q$  for magnesium hydroxide and substituting the concentration of  $\text{OH}^-$  that you just calculated. Then set the expression for  $Q$  equal to the value of  $K_{\text{sp}}$  for magnesium hydroxide and solve for  $[\text{Mg}^{2+}]$ . This is the concentration of  $\text{Mg}^{2+}$  that remains when  $\text{Ca}(\text{OH})_2$  begins to precipitate.

$$\begin{aligned} Q &= [\text{Mg}^{2+}][\text{OH}^-]^2 \\ &= [\text{Mg}^{2+}](2.06 \times 10^{-2})^2 \end{aligned}$$

When  $Q = K_{\text{sp}}$ ,

$$\begin{aligned} [\text{Mg}^{2+}](2.06 \times 10^{-2})^2 &= K_{\text{sp}} = 2.06 \times 10^{-13} \\ [\text{Mg}^{2+}] &= \frac{2.06 \times 10^{-13}}{(2.06 \times 10^{-2})^2} \\ [\text{Mg}^{2+}] &= 4.9 \times 10^{-10} \text{ M} \end{aligned}$$

—Continued on the next page

*Continued—*

As you can see from the results, the selective precipitation worked very well. The concentration of  $Mg^{2+}$  dropped from 0.059 M to  $4.9 \times 10^{-10}$  M before any calcium began to precipitate, which means that the process separated 99.99% of the magnesium out of the solution.

**FOR PRACTICE 18.14** A solution is 0.085 M in  $Pb^{2+}$  and 0.025 M in  $Ag^+$ . (a) If selective precipitation is to be achieved using NaCl, what minimum concentration of NaCl do you need to begin to precipitate the ion that precipitates first? (b) What is the concentration of each ion left in solution at the point where the second ion begins to precipitate?

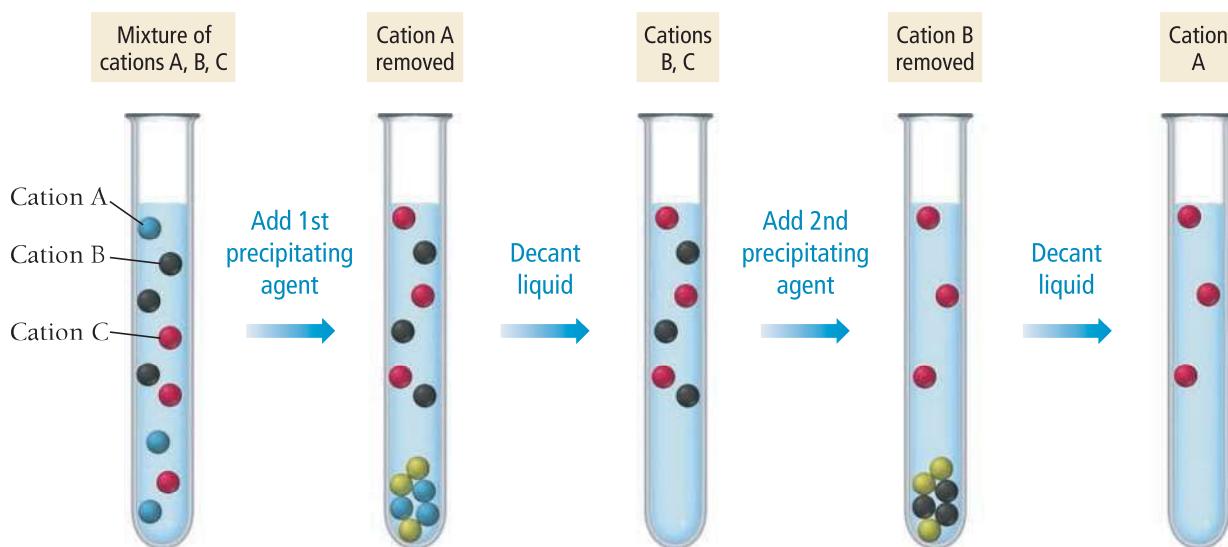
## 18.7

### Qualitative Chemical Analysis

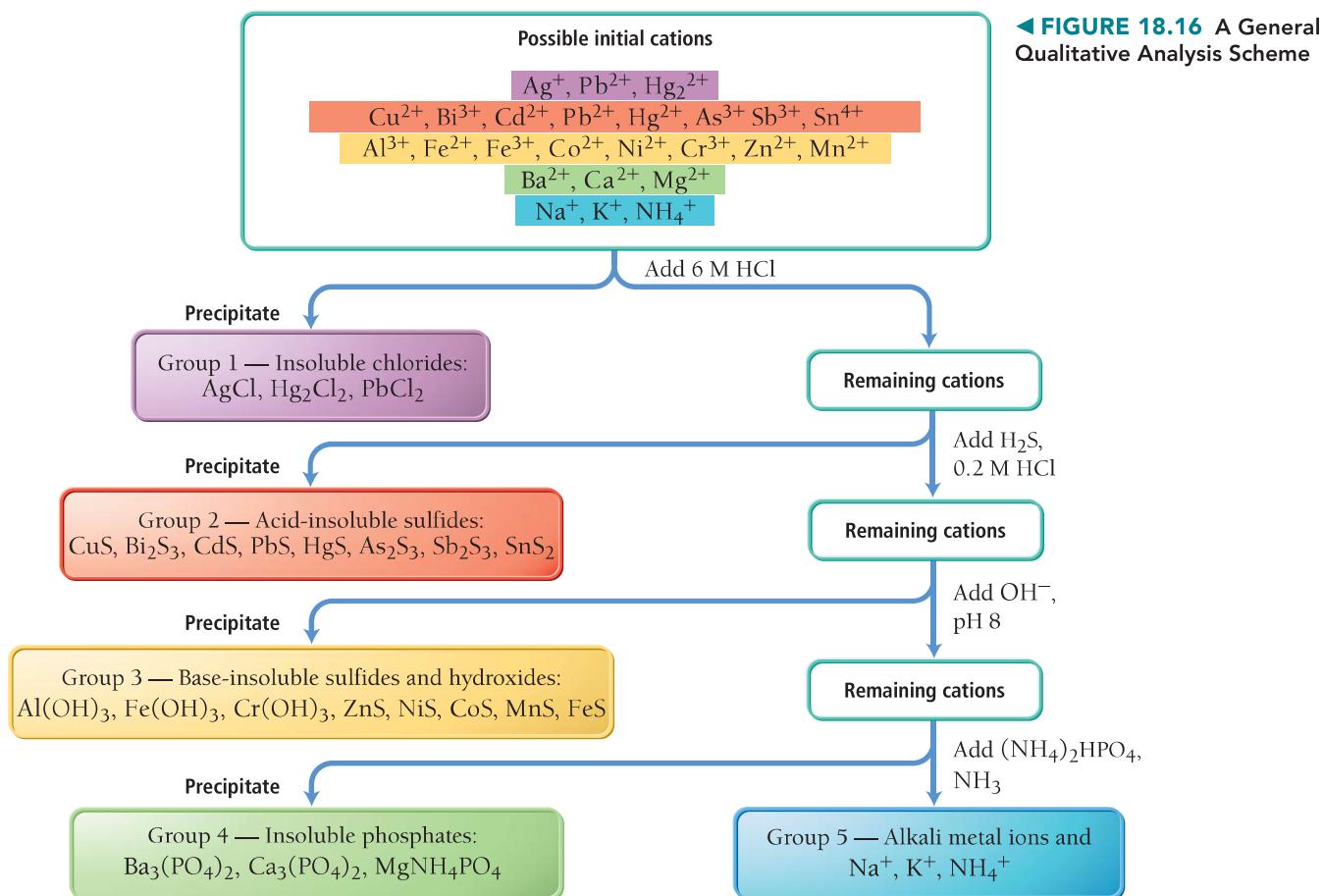
Selective precipitation as discussed in Section 18.6 can be used in a systematic way to determine which metal ions are present in an unknown solution. This method is known as **qualitative analysis**. The word *qualitative* means *involving quality or kind*. Qualitative analysis involves finding the *kind* of ions present in the solution. This stands in contrast to **quantitative analysis**, which is concerned with quantity, or the amounts of substances in a solution or mixture.

In the past, qualitative analysis by selective precipitation was used extensively to determine the metals present in a sample. This process—dubbed *wet chemistry* because it involves the mixing of many aqueous solutions in the lab—has been replaced by more precise and less time-intensive instrumental techniques. Nonetheless, both for the sake of history and also because of the importance of the principles involved, we now examine a traditional qualitative analysis scheme. You may use such a scheme in your general chemistry laboratory as an exercise in qualitative analysis.

The basic idea behind qualitative analysis is straightforward. A sample containing a mixture of metal cations is subjected to the addition of several precipitating agents. At each step, some of the metal cations—those that form insoluble compounds with the precipitating agent—precipitate from the mixture and are separated out as solids. The remaining aqueous mixture is then subjected to the next precipitating agent, and so on (Figure 18.15▼).



▲ **FIGURE 18.15** Qualitative Analysis In qualitative analysis, specific ions are precipitated successively by the addition of appropriate reagents.



◀ FIGURE 18.16 A General Qualitative Analysis Scheme

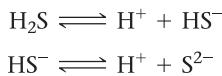
Figure 18.16▲ is a diagram of a general qualitative analysis scheme. The scheme involves separating a mixture of the common ions into five groups by sequentially adding five different precipitating agents. After each precipitating agent is added, the mixture is put into a centrifuge to separate the solid from the liquid. The liquid is decanted for the next step, and the solid is set aside for subsequent analysis. We examine each group separately.

## Group 1: Insoluble Chlorides

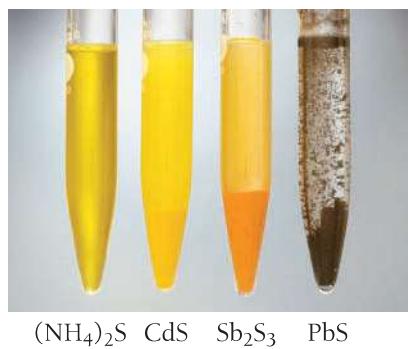
In the first step, the aqueous mixture containing the metal cations is treated with 6 M HCl. Since most chlorides are soluble, the chloride ions *do not form* a precipitate with the majority of the cations in the mixture. However, Ag<sup>+</sup>, Pb<sup>2+</sup>, and Hg<sub>2</sub><sup>2+</sup> *do form* insoluble chlorides. So, if any of those metal cations are present, they precipitate out. The absence of a precipitate constitutes a negative test for Ag<sup>+</sup>, Pb<sup>2+</sup>, and Hg<sub>2</sub><sup>2+</sup>. If a precipitate forms, one or more of these ions is present. After the solid is separated from the liquid, the solution is ready for the next step.

## Group 2: Acid-Insoluble Sulfides

In the second step, the acidic aqueous mixture containing the remaining metal cations is treated with H<sub>2</sub>S, a weak diprotic acid that dissociates in two steps:



The concentration of S<sup>2-</sup> ions in an H<sub>2</sub>S solution is pH-dependent. At low pH (high H<sup>+</sup> concentration) the equilibria shift left, minimizing the amount of available S<sup>2-</sup>. At high pH (low H<sup>+</sup> concentration) the equilibria shift right, maximizing the amount of available S<sup>2-</sup>. At this stage, the solution is acidic (from the addition of HCl in the previous step),



and the concentration of  $S^{2-}$  in solution is relatively low. Only the most insoluble metal sulfides (those with the smallest  $K_{sp}$  values) precipitate under these conditions. These include  $Hg^{2+}$ ,  $Cd^{2+}$ ,  $Bi^{3+}$ ,  $Cu^{2+}$ ,  $Sn^{4+}$ ,  $As^{3+}$ ,  $Pb^{2+}$ , and  $Sb^{3+}$ . If any of these metal cations are present, they precipitate out as sulfides. After the solid is separated from the liquid, the solution is ready for the next step.

## Group 3: Base-Insoluble Sulfides and Hydroxides

In the third step, additional base and  $\text{H}_2\text{S}$  are added to the acidic aqueous mixture containing the remaining metal cations. The added base reacts with acid, shifting the  $\text{H}_2\text{S}$  ionization equilibria to the right and creating a higher  $\text{S}^{2-}$  concentration. This causes the precipitation of those sulfides that were too soluble to precipitate out in the previous step but not soluble enough to prevent precipitation with the higher sulfide ion concentration. The ions that precipitate as sulfides at this point (if they are present) are  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mn}^{2+}$ , and  $\text{Ni}^{2+}$ . In addition, the additional base causes  $\text{Cr}^{3+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Al}^{3+}$  to precipitate as hydroxides. After the solid is separated from the liquid, the solution is ready for the next step.

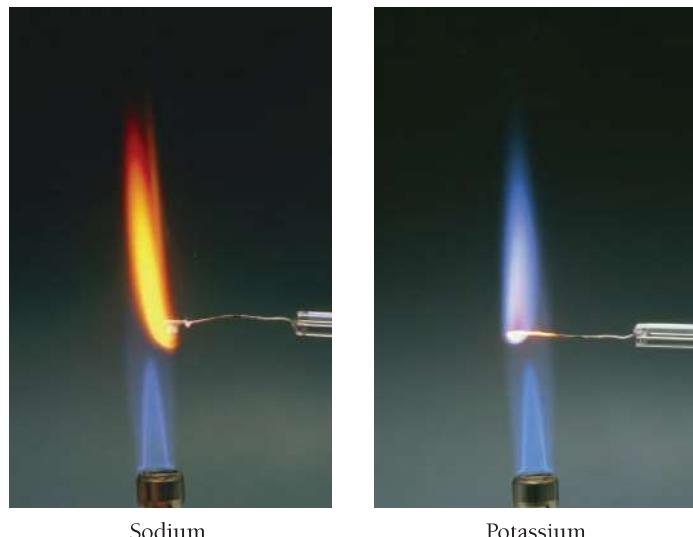
## Group 4: Insoluble Phosphates

At this stage, all of the cations have precipitated except those belonging to the alkali metal family (group 1A in the periodic table) and the alkaline earth metal family (group 2A in the periodic table). The alkaline earth metal cations can be precipitated by adding  $(\text{NH}_4)_2 \text{HPO}_4$  to the solution, causing  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ , and  $\text{Ba}^{2+}$  to precipitate as metal phosphates, which are separated from the liquid.

## Group 5: Alkali Metals and $\text{NH}_4^+$

The only dissolved ions that the liquid decanted from the previous step can now contain are  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{NH}_4^+$ . These cations do not form insoluble compounds with any anions and cannot be precipitated from the solution. Their presence can be determined, however, by other means. Sodium and potassium ions, for example, are usually identified through flame tests. The sodium ion produces a yellow-orange flame, and the potassium ion produces a violet flame, as shown in Figure 18.17▼.

By applying this procedure, nearly two dozen metal cations can be separated from a solution initially containing all of them. Each of the groups can be further analyzed to determine which specific ions are present. The procedures for these steps are found in many general chemistry laboratory manuals.



► **FIGURE 18.17** Flame Tests

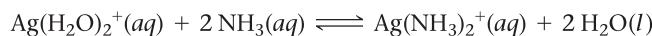
The sodium ion produces a yellow-orange flame. The potassium ion produces a violet flame.

## 18.8

## Complex Ion Equilibria

We have discussed several different types of equilibria so far, including acid–base equilibria and solubility equilibria. We now turn to equilibria of another type, which primarily involve transition metal ions in solution. Transition metal ions tend to be good electron acceptors (good Lewis acids). In aqueous solutions, water molecules can act as electron donors (Lewis bases) to hydrate transition metal ions. For example, silver ions are hydrated by water in solution to form  $\text{Ag}(\text{H}_2\text{O})_2^+(aq)$ . Chemists often write  $\text{Ag}^+(aq)$  as a shorthand notation for the hydrated silver ion, but the bare ion does not really exist by itself in solution.

Species such as  $\text{Ag}(\text{H}_2\text{O})_2^+$  are known as *complex ions*. A **complex ion** contains a central metal ion bound to one or more *ligands*. A **ligand** is a neutral molecule or ion that acts as a Lewis base with the central metal ion. In  $\text{Ag}(\text{H}_2\text{O})_2^+$ , water is the ligand. If a stronger Lewis base is put into a solution containing  $\text{Ag}(\text{H}_2\text{O})_2^+$ , the stronger Lewis base displaces the water in the complex ion. For example, ammonia reacts with  $\text{Ag}(\text{H}_2\text{O})_2^+$  according to the following reaction:



For simplicity, we often leave water out of the equation:



The equilibrium constant associated with the reaction for the formation of a complex ion, such as the one just shown, is called the **formation constant ( $K_f$ )**. The expression for  $K_f$  is determined by the law of mass action, like any equilibrium constant. For  $\text{Ag}(\text{NH}_3)_2^+$ , the expression for  $K_f$  is:

$$K_f = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}^+][\text{NH}_3]^2}$$

Notice that the value of  $K_f$  for  $\text{Ag}(\text{NH}_3)_2^+$  is large, indicating that the formation of the complex ion is highly favored. Table 18.3 lists the formation constants for a number of common complex ions. You can see that, in general, values of  $K_f$  are very large, indicating that the formation of complex ions is highly favored in each case. Example 18.15 illustrates how to use  $K_f$  in calculations.

We cover complex ions in more detail in Chapter 26. Here, we focus on the equilibria associated with their formation.

**TABLE 18.3 ■ Formation Constants of Selected Complex Ions in Water at 25 °C**

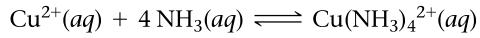
Complex Ion	$K_f$	Complex Ion	$K_f$
$\text{Ag}(\text{CN})_2^-$	$1 \times 10^{21}$	$\text{Cu}(\text{NH}_3)_4^{2+}$	$1.7 \times 10^{13}$
$\text{Ag}(\text{NH}_3)_2^+$	$1.7 \times 10^7$	$\text{Fe}(\text{CN})_6^{4-}$	$1.5 \times 10^{35}$
$\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$	$2.8 \times 10^{13}$	$\text{Fe}(\text{CN})_6^{3-}$	$2 \times 10^{43}$
$\text{AlF}_6^{3-}$	$7 \times 10^{19}$	$\text{Hg}(\text{CN})_4^{2-}$	$1.8 \times 10^{41}$
$\text{Al}(\text{OH})_4^-$	$3 \times 10^{33}$	$\text{HgCl}_4^{2-}$	$1.1 \times 10^{16}$
$\text{CdBr}_4^{2-}$	$5.5 \times 10^3$	$\text{HgI}_4^{2-}$	$2 \times 10^{30}$
$\text{CdI}_4^{2-}$	$2 \times 10^6$	$\text{Ni}(\text{NH}_3)_6^{2+}$	$2.0 \times 10^8$
$\text{Cd}(\text{CN})_4^{2-}$	$3 \times 10^{18}$	$\text{Pb}(\text{OH})_3^-$	$8 \times 10^{13}$
$\text{Co}(\text{NH}_3)_6^{3+}$	$2.3 \times 10^{33}$	$\text{Sn}(\text{OH})_3^-$	$3 \times 10^{25}$
$\text{Co}(\text{OH})_4^{2-}$	$5 \times 10^9$	$\text{Zn}(\text{CN})_4^{2-}$	$2.1 \times 10^{19}$
$\text{Co}(\text{SCN})_4^{2-}$	$1 \times 10^3$	$\text{Zn}(\text{NH}_3)_4^{2+}$	$2.8 \times 10^9$
$\text{Cr}(\text{OH})_4^-$	$8.0 \times 10^{29}$	$\text{Zn}(\text{OH})_4^{2-}$	$2 \times 10^{15}$
$\text{Cu}(\text{CN})_4^{2-}$	$1.0 \times 10^{25}$		

**EXAMPLE 18.15** Complex Ion Equilibria

You mix a 200.0-mL sample of a solution that is  $1.5 \times 10^{-3}$  M in  $\text{Cu}(\text{NO}_3)_2$  with a 250.0-mL sample of a solution that is 0.20 M in  $\text{NH}_3$ . After the solution reaches equilibrium, what concentration of  $\text{Cu}^{2+}(aq)$  remains?

**SOLUTION**

Write the balanced equation for the complex ion equilibrium that occurs and look up the value of  $K_f$  in Table 18.3. Since this is an equilibrium problem, you have to create an ICE table, which requires the initial concentrations of  $\text{Cu}^{2+}$  and  $\text{NH}_3$ . Calculate those concentrations from the given values.

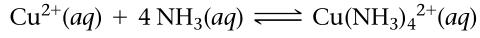


$$K_f = 1.7 \times 10^{13}$$

$$[\text{Cu}^{2+}]_{\text{initial}} = \frac{0.200 \text{ L} \times \frac{1.5 \times 10^{-3} \text{ mol}}{\text{L}}}{0.200 \text{ L} + 0.250 \text{ L}} = 6.7 \times 10^{-4} \text{ M}$$

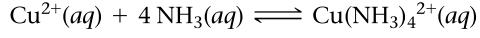
$$[\text{NH}_3]_{\text{initial}} = \frac{0.250 \text{ L} \times \frac{0.20 \text{ mol}}{1 \text{ L}}}{0.200 \text{ L} + 0.250 \text{ L}} = 0.11 \text{ M}$$

Construct an ICE table for the reaction and write down the initial concentrations of each species.



	$[\text{Cu}^{2+}]$	$[\text{NH}_3]$	$[\text{Cu}(\text{NH}_3)_4^{2+}]$
I <sub>Initial</sub>	$6.7 \times 10^{-4}$	0.11	0.0
C <sub>Change</sub>			
E <sub>Equil</sub>			

Since the equilibrium constant is large and the concentration of ammonia is much larger than the concentration of  $\text{Cu}^{2+}$ , you can assume that the reaction will be driven to the right so that most of the  $\text{Cu}^{2+}$  is consumed. Unlike previous ICE tables, where you used  $x$  to represent the change in concentration in going to equilibrium, here you let  $x$  represent the small amount of  $\text{Cu}^{2+}$  that remains when equilibrium is reached.



	$[\text{Cu}^{2+}]$	$[\text{NH}_3]$	$[\text{Cu}(\text{NH}_3)_4^{2+}]$
I <sub>Initial</sub>	$6.7 \times 10^{-4}$	0.11	0.0
C <sub>Change</sub>	$\approx (-6.7 \times 10^{-4})$	$\approx 4(-6.7 \times 10^{-4})$	$\approx (+6.7 \times 10^{-4})$
E <sub>Equil</sub>	x	0.11	$6.7 \times 10^{-4}$

Substitute the expressions for the equilibrium concentrations into the expression for  $K_f$  and solve for  $x$ .

$$K_f = \frac{[\text{Cu}(\text{NH}_3)_4^{2+}]}{[\text{Cu}^{2+}][\text{NH}_3]^4}$$

$$= \frac{6.7 \times 10^{-4}}{x(0.11)^4}$$

$$x = \frac{6.7 \times 10^{-4}}{K_f(0.11)^4}$$

$$= \frac{6.7 \times 10^{-4}}{1.7 \times 10^{13}(0.11)^4}$$

$$= 2.7 \times 10^{-13}$$

Confirm that  $x$  is indeed small compared to the initial concentration of the metal cation.

The remaining  $\text{Cu}^{2+}$  is very small because the formation constant is very large.

Since  $x = 2.7 \times 10^{-13} \ll 6.7 \times 10^{-4}$ , the approximation is valid.

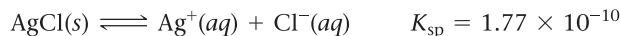
The remaining  $[\text{Cu}^{2+}] = 2.7 \times 10^{-13} \text{ M}$ .

**FOR PRACTICE 18.15** You mix a 125.0-mL sample of a solution that is 0.0117 M in  $\text{NiCl}_2$  with a 175.0-mL sample of a solution that is 0.250 M in  $\text{NH}_3$ . After the solution reaches equilibrium, what concentration of  $\text{Ni}^{2+}(aq)$  remains?

## The Effect of Complex Ion Equilibria on Solubility

Recall from Section 18.5 that the solubility of an ionic compound with a basic anion increases with increasing acidity because the acid reacts with the anion and drives the reaction to the right. Similarly, *the solubility of an ionic compound containing a metal cation that forms complex ions increases in the presence of Lewis bases that complex with the cation*. The most common Lewis bases that increase the solubility of metal cations are  $\text{NH}_3$ ,  $\text{CN}^-$ , and  $\text{OH}^-$ .

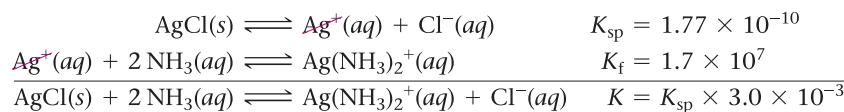
For example, silver chloride is only slightly soluble in pure water:



However, adding ammonia increases its solubility dramatically because, as we saw previously in this section, the ammonia forms a complex ion with the silver cations:

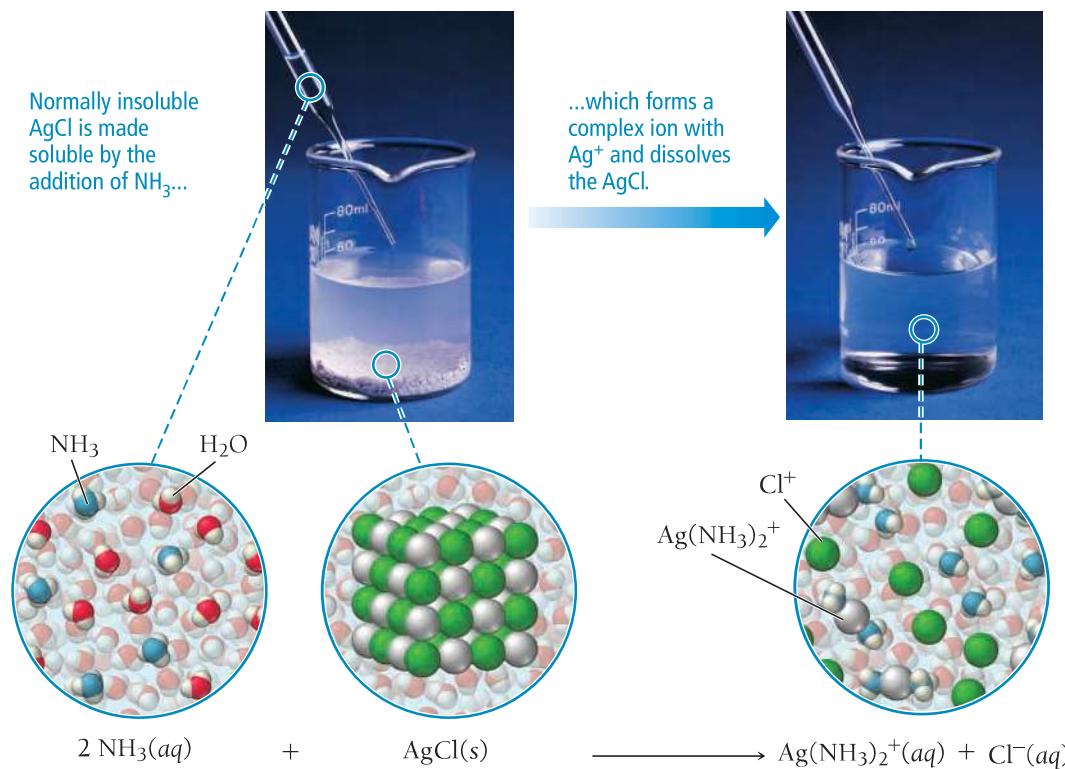
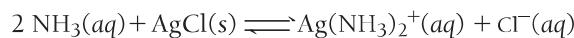


The large value of  $K_f$  significantly lowers the concentration of  $\text{Ag}^+(aq)$  in solution and therefore drives the dissolution of  $\text{AgCl}(s)$ . The two previous reactions can be added together:



As we learned in Section 16.3, the equilibrium constant for a reaction that is the sum of two other reactions is the product of the equilibrium constants for the two other reactions. Adding ammonia changes the equilibrium constant for the dissolution of  $\text{AgCl}(s)$  by a factor of  $3.0 \times 10^{-3}/1.77 \times 10^{-10} = 1.7 \times 10^7$  (17 million), which makes the otherwise relatively insoluble  $\text{AgCl}(s)$  quite soluble, as shown in Figure 18.18▼.

### Complex Ion Formation



◀ FIGURE 18.18  
Complex Ion Formation

ANSWER NOW!



## 18.12 Cc Conceptual Connection

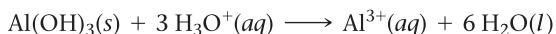
### SOLUBILITY AND COMPLEX ION EQUILIBRIA

Which compound, when added to water, is most likely to increase the solubility of CuS?

- (a) NaCl      (b) KNO<sub>3</sub>      (c) NaCN      (d) MgBr<sub>2</sub>

### The Solubility of Amphoteric Metal Hydroxides

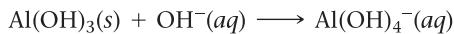
Many metal hydroxides are insoluble or only very slightly soluble in pH-neutral water. For example, Al(OH)<sub>3</sub> has  $K_{sp} = 1.3 \times 10^{-33}$ , which means that if we put Al(OH)<sub>3</sub> in water, the vast majority of it will settle to the bottom as an undissolved solid. All metal hydroxides, however, have a basic anion (OH<sup>-</sup>) and therefore become more soluble in acidic solutions (see the previous subsection and Section 18.5). The metal hydroxides become more soluble because they can act as bases and react with H<sub>3</sub>O<sup>+(aq)</sup>. For example, Al(OH)<sub>3</sub> dissolves in acid according to the reaction:



Al(OH)<sub>3</sub> acts as a base in this reaction.

Recall from Section 17.3 that a substance that can act as either an acid or a base is said to be amphoteric.

Interestingly, some metal hydroxides can also act as acids—they are *amphoteric*. The ability of an amphoteric metal hydroxide to act as an acid increases its solubility in basic solution. For example, Al(OH)<sub>3</sub>(s) dissolves in basic solution according to the reaction:



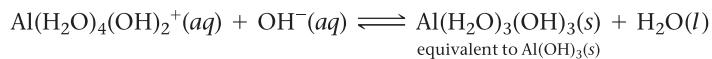
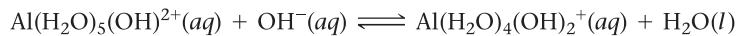
Al(OH)<sub>3</sub> acts as an acid in this reaction.

Al(OH)<sub>3</sub> is soluble at high pH and soluble at low pH but *insoluble* in a pH-neutral solution.

We can observe the whole range of the pH-dependent solubility behavior of Al<sup>3+</sup> by considering a hydrated aluminum ion in solution, beginning at an acidic pH. We know from Section 17.8 that Al<sup>3+</sup> in solution is inherently acidic because it complexes with water to form Al(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup>(aq). The complex ion then acts as an acid by losing a proton from one of the complexed water molecules according to the reaction:



Addition of base to the solution drives the reaction to the right and continues to remove protons from complexed water molecules:



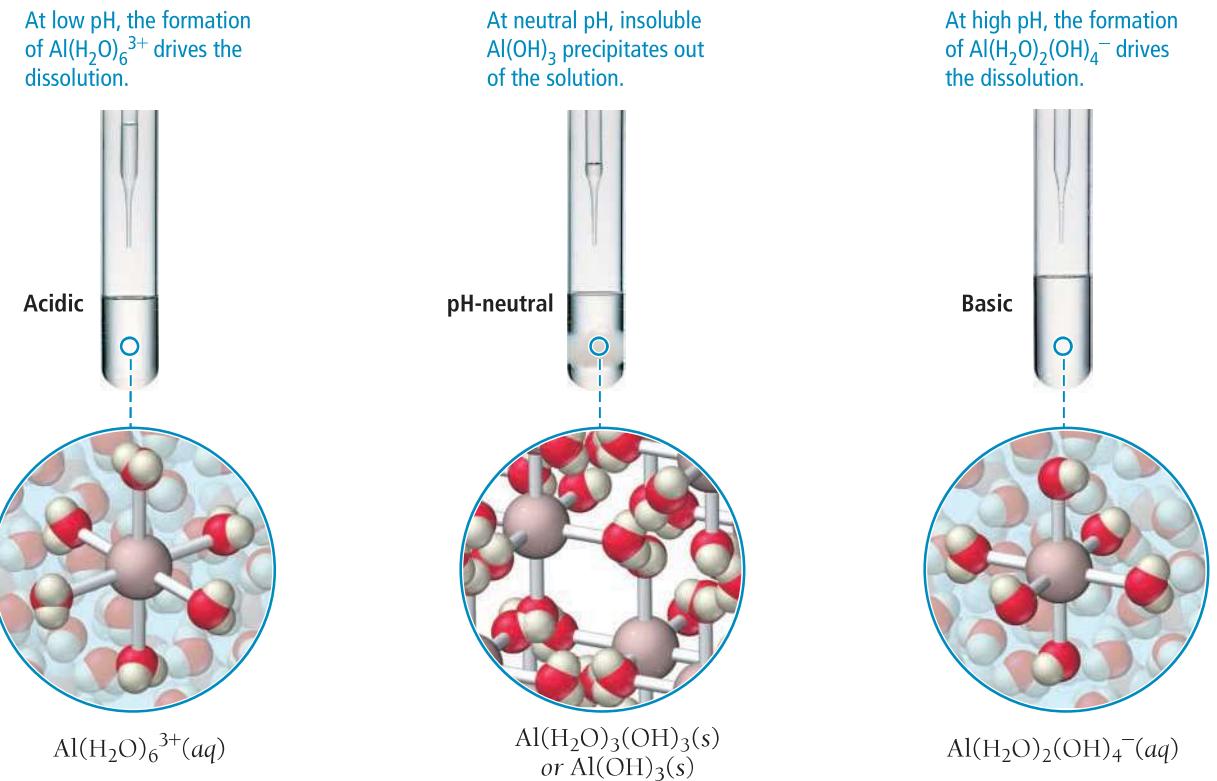
The result of removing three protons from Al(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup>(aq) is the solid white precipitate Al(H<sub>2</sub>O)<sub>3</sub>(OH)<sub>3</sub>(s), which is more commonly written as Al(OH)<sub>3</sub>(s). The solution is now pH-neutral and the hydroxide is insoluble. Addition of more OH<sup>-</sup> makes the solution basic and dissolves the solid precipitate:



As the solution goes from acidic to neutral to basic, the solubility of Al<sup>3+</sup> changes accordingly, as illustrated in Figure 18.19►.

The extent to which a metal hydroxide dissolves in both acid and base depends on the degree to which it is amphoteric. Cations that form amphoteric hydroxides include Al<sup>3+</sup>, Cr<sup>3+</sup>, Zn<sup>2+</sup>, Pb<sup>2+</sup>, and Sn<sup>2+</sup>. Other metal hydroxides, such as those of Ca<sup>2+</sup>, Fe<sup>2+</sup>, and Fe<sup>3+</sup>, are not amphoteric—they become soluble in acidic solutions, but not in basic ones.

## pH-Dependent Solubility of an Amphoteric Hydroxide



**▲ FIGURE 18.19 Solubility of an Amphoteric Hydroxide** Because aluminum hydroxide is amphoteric, its solubility is pH-dependent.

### QUIZ YOURSELF NOW!

## Self-Assessment Quiz

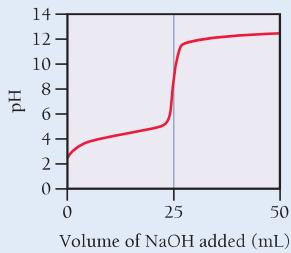


- Q1.** A buffer is 0.100 M in  $\text{NH}_4\text{Cl}$  and 0.100 M in  $\text{NH}_3$ . When a small amount of hydrobromic acid is added to this buffer, which buffer component neutralizes the added acid?
- MISSED THIS? Read Section 18.2; Watch KCV 18.2A**
- a)  $\text{NH}_4^+$     b)  $\text{Cl}^-$     c)  $\text{NH}_3$   
d) None of the above (hydrobromic acid will not be neutralized by this buffer).
- Q2.** What is the pH of a buffer that is 0.120 M in formic acid ( $\text{HCHO}_2$ ) and 0.080 M in potassium formate ( $\text{KCHO}_2$ )? For formic acid,  $K_a = 1.8 \times 10^{-4}$ .
- MISSED THIS? Read Section 18.2; Watch KCV 18.2B, IWE 18.2**
- a) 2.33    b) 3.57    c) 3.74    d) 3.91
- Q3.** A buffer with a pH of 9.85 contains  $\text{CH}_3\text{NH}_2$  and  $\text{CH}_3\text{NH}_3\text{Cl}$  in water. What can you conclude about the relative concentrations of  $\text{CH}_3\text{NH}_2$  and  $\text{CH}_3\text{NH}_3\text{Cl}$  in this buffer? For  $\text{CH}_3\text{NH}_2$ ,  $pK_b = 3.36$ .
- MISSED THIS? Read Section 18.2; Watch KCV 18.2B, IWE 18.2**
- a)  $\text{CH}_3\text{NH}_2 > \text{CH}_3\text{NH}_3\text{Cl}$     b)  $\text{CH}_3\text{NH}_2 < \text{CH}_3\text{NH}_3\text{Cl}$   
c)  $\text{CH}_3\text{NH}_2 = \text{CH}_3\text{NH}_3\text{Cl}$   
d) Nothing can be concluded about the relative concentrations of  $\text{CH}_3\text{NH}_2$  and  $\text{CH}_3\text{NH}_3\text{Cl}$ .
- Q4.** A 500.0-mL buffer solution is 0.10 M in benzoic acid and 0.10 M in sodium benzoate and has an initial pH of 4.19. What is the pH of the buffer upon addition of 0.010 mol of NaOH?
- MISSED THIS? Read Section 18.2; Watch KCV 18.2B, IWE 18.3**
- a) 1.70    b) 4.01    c) 4.29    d) 4.37
- Q5.** Consider a buffer composed of the weak acid HA and its conjugate base  $\text{A}^-$ . Which pair of concentrations results in the most effective buffer?
- MISSED THIS? Read Section 18.3**
- a) 0.10 M HA; 0.10 M  $\text{A}^-$     b) 0.50 M HA; 0.50 M  $\text{A}^-$   
c) 0.90 M HA; 0.10 M  $\text{A}^-$     d) 0.10 M HA; 0.90 M  $\text{A}^-$
- Q6.** Which combination is the best choice to prepare a buffer with a pH of 9.0?
- MISSED THIS? Read Section 18.3**
- a)  $\text{NH}_3$ ;  $\text{NH}_4\text{Cl}$  ( $pK_b$  for  $\text{NH}_3$  is 4.75)  
b)  $\text{C}_5\text{H}_5\text{N}$ ;  $\text{C}_5\text{H}_5\text{NHCl}$  ( $pK_b$  for  $\text{C}_5\text{H}_5\text{N}$  is 8.76)  
c)  $\text{HNO}_2$ ;  $\text{NaNO}_2$  ( $pK_a$  for  $\text{HNO}_2$  is 3.33)  
d)  $\text{HCHO}_2$ ;  $\text{NaCHO}_2$  ( $pK_a$  for  $\text{HCHO}_2$  is 3.74)
- Q7.** A 25.0-mL sample of an unknown HBr solution is titrated with 0.100 M NaOH. The equivalence point is reached upon the addition of 18.88 mL of the base. What is the concentration of the HBr solution?
- MISSED THIS? Read Section 18.4; Watch KCV 18.4A, IWE 18.6**
- a) 0.0755 M    b) 0.0376 M  
c) 0.100 M    d) 0.00188 M
- Q8.** A 10.0-mL sample of 0.200 M hydrocyanic acid (HCN) is titrated with 0.0998 M NaOH. What is the pH at the equivalence point? For hydrocyanic acid,  $pK_a = 9.31$ .
- MISSED THIS? Read Section 18.4; Watch KCV 18.4B, IWE 18.7**
- a) 7.00    b) 8.76    c) 9.31    d) 11.07

—Continued on the next page

*Continued—*

- Q9.** A 20.0-mL sample of 0.150 M ethylamine is titrated with 0.0981 M HCl. What is the pH after the addition of 5.0 mL of HCl? For ethylamine,  $pK_b = 3.25$ .
- MISSED THIS?** Read Section 18.4; Watch KCV 18.4B, IWE 18.7
- 10.75
  - 11.04
  - 2.96
  - 11.46
- Q10.** Three 15.0-mL acid samples—0.10 M HA, 0.10 M HB, and 0.10 M H<sub>2</sub>C—are all titrated with 0.100 M NaOH. If HA is a weak acid, HB is a strong acid, and H<sub>2</sub>C is a diprotic acid, which statement is true of all three titrations?
- MISSED THIS?** Read Section 18.4; Watch KCV 18.4A, KCV 18.4B
- All three titrations have the same pH at the first equivalence point.
  - All three titrations have the same initial pH.
  - All three titrations have the same final pH.
  - All three titrations require the same volume of NaOH to reach the first equivalence point.
- Q11.** A weak unknown monoprotic acid is titrated with a strong base. The titration curve is shown. Find  $K_a$  for the unknown acid.
- MISSED THIS?** Read Section 18.4; Watch KCV 18.4B, IWE 18.7



- $2.5 \times 10^{-3}$
- $3.2 \times 10^{-5}$
- $3.2 \times 10^{-7}$
- $2.5 \times 10^{-9}$

**Answers:** 1. (c) 2. (b) 3. (b) 4. (d) 5. (b) 6. (a) 7. (a) 8. (d) 9. (d) 10. (d) 11. (b) 12. (b) 13. (d) 14. (c) 15. (d)

- Q12.** Calculate the molar solubility of lead(II) bromide ( $PbBr_2$ ).

For lead(II) bromide,  $K_{sp} = 4.67 \times 10^{-6}$ .

**MISSED THIS?** Read Section 18.5; Watch IWE 18.8

- 0.00153 M
- 0.0105 M
- 0.0167 M
- 0.0211 M

- Q13.** Calculate the molar solubility of magnesium fluoride ( $MgF_2$ ) in a solution that is 0.250 M in NaF. For magnesium fluoride,  $K_{sp} = 5.16 \times 10^{-11}$ .

**MISSED THIS?** Read Section 18.5

- $2.35 \times 10^{-4}$  M
- $2.06 \times 10^{-10}$  M
- $2.87 \times 10^{-5}$  M
- $8.26 \times 10^{-10}$  M

- Q14.** A solution is 0.0250 M in Pb<sup>2+</sup>. What minimum concentration of Cl<sup>-</sup> is required to begin to precipitate PbCl<sub>2</sub>? For PbCl<sub>2</sub>,  $K_{sp} = 1.17 \times 10^{-5}$ .

**MISSED THIS?** Read Section 18.6; Watch IWE 18.12

- $1.17 \times 10^{-5}$  M
- 0.0108 M
- 0.0216 M
- $5.41 \times 10^{-4}$  M

- Q15.** Which compound is more soluble in an acidic solution than in a neutral solution?

**MISSED THIS?** Read Section 18.5

- PbBr<sub>2</sub>
- CuCl
- AgI
- BaF<sub>2</sub>

## CHAPTER 18 IN REVIEW

### TERMS

#### Section 18.2

- buffer (788)
- common ion effect (790)
- Henderson–Hasselbalch equation (792)

#### Section 18.3

- buffer capacity (802)

#### Section 18.4

- acid–base titration (803)
- indicator (803)
- equivalence point (803)
- endpoint (814)

#### Section 18.5

- solubility product constant ( $K_{sp}$ ) (817)

- molar solubility (817)

#### Section 18.6

- selective precipitation (824)

#### Section 18.7

- qualitative analysis (826)
- quantitative analysis (826)

#### Section 18.8

- complex ion (829)
- ligand (829)
- formation constant ( $K_f$ ) (829)

## CONCEPTS

### The Danger of Antifreeze (18.1)

- Although buffers closely regulate the pH of mammalian blood, the capacity of these buffers to neutralize can be overwhelmed.
- Ethylene glycol, the main component of antifreeze, is metabolized by the liver into glycolic acid. The resulting acidity can exceed the buffering capacity of blood and cause acidosis, a serious condition that results in oxygen deprivation.

### Buffers: Solutions That Resist pH Change (18.2)

- Buffers contain significant amounts of both a weak acid and its conjugate base (or a weak base and its conjugate acid), enabling the buffer to neutralize added acid or added base.
- Adding a small amount of acid to a buffer converts a stoichiometric amount of base to the conjugate acid. Adding a small amount of base to a buffer converts a stoichiometric amount of the acid to the conjugate base.

- We can determine the pH of a buffer solution by solving an equilibrium problem, focusing on the common ion effect, or by using the Henderson–Hasselbalch equation.

### Buffer Range and Buffer Capacity (18.3)

- A buffer works best when the amounts of acid and conjugate base it contains are large and approximately equal.
- If the relative amounts of acid and base in a buffer differ by more than a factor of 10, the ability of the buffer to neutralize added acid and added base diminishes. The maximum pH range at which a buffer is effective is one pH unit on either side of the acid's  $pK_a$ .

### Titrations and pH Curves (18.4)

- A titration curve is a graph of the change in pH versus added volume of acid or base during a titration.
- This chapter examines three types of titration curves, representing three types of acid–base reactions: a strong acid with a strong base, a weak acid with a strong base (or vice versa), and a polyprotic acid with a strong base.
- The equivalence point of a titration can be made visible by an indicator, a compound that changes color over a specific pH range.

### Solubility Equilibria and the Solubility Product Constant (18.5)

- The solubility product constant ( $K_{sp}$ ) is an equilibrium constant for the dissolution of an ionic compound in water.
- We can determine the molar solubility of an ionic compound from  $K_{sp}$  and vice versa. Although the value of  $K_{sp}$  is constant at a given temperature, the solubility of an ionic substance can depend on other factors such as the presence of common ions and the pH of the solution.

## EQUATIONS AND RELATIONSHIPS

### The Henderson–Hasselbalch Equation (18.2)

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

### Effective Buffer Range (18.3)

$$\text{pH range} = \text{p}K_a \pm 1$$

### Precipitation (18.6)

- We can compare the magnitude of  $K_{sp}$  to the reaction quotient, Q, in order to determine the relative saturation of a solution.
- Substances with cations that have sufficiently different values of  $K_{sp}$  can be separated by selective precipitation, in which an added reagent forms a precipitate with one of the dissolved cations but not others.

### Qualitative Chemical Analysis (18.7)

- Qualitative analysis operates on the principle that a mixture of cations can be separated and analyzed based on the differences in the solubilities of their salts.
- In a classic qualitative analysis scheme, an unknown mixture of cations is sequentially treated with different reagents, each of which precipitates a known subgroup of cations.

### Complex Ion Equilibria (18.8)

- A complex ion contains a central metal ion coordinated to two or more ligands.
- The equilibrium constant for the formation of a complex ion is called a formation constant and is usually quite large.
- The solubility of an ionic compound containing a metal cation that forms complex ions increases in the presence of Lewis bases that complex with the cation because the formation of the complex ion drives the dissolution reaction to the right.
- All metal hydroxides become more soluble in the presence of acids, but amphoteric metal hydroxides also become more soluble in the presence of bases.

### The Relation between Q and $K_{sp}$ (18.6)

If  $Q < K_{sp}$ , the solution is unsaturated. More of the solid ionic compound can dissolve in the solution.

If  $Q = K_{sp}$ , the solution is saturated. The solution is holding the equilibrium amount of the dissolved ions, and additional solid will not dissolve in the solution.

If  $Q > K_{sp}$ , the solution is supersaturated. Under most circumstances, the solid will precipitate out of a supersaturated solution.

## LEARNING OUTCOMES

Chapter Objectives	Assessment
Perform pH calculations for buffer solutions containing a common ion (18.2)	Example 18.1 For Practice 18.1 For More Practice 18.1 Exercises 27–34
Perform pH calculations for buffer solutions using the Henderson–Hasselbalch equation (18.2)	Example 18.2 For Practice 18.2 Exercises 35–46
Perform pH calculations for buffer solutions after the addition of a small amount of strong acid or strong base (18.2)	Example 18.3 For Practice 18.3 For More Practice 18.3 Exercises 47–50
Perform pH calculations for buffer solutions containing a weak base and its conjugate acid before and after the addition of an acid or base (18.2)	Example 18.4 For Practice 18.4 For More Practice 18.4 Exercises 51–52
Describe the preparation of an effective buffer solution (18.3)	Example 18.5 For Practice 18.5 Exercises 53–60
Perform pH calculations for the titration of a strong acid with a strong base (18.4)	Example 18.6 For Practice 18.6 Exercise 61

Perform calculations for the titration of a weak acid with a strong base (18.4)	Example 18.7 For Practice 18.7 Exercises 62–77
Identify specific points along the titration curve for a diprotic acid with a strong base (18.4)	Exercises 78–80
Predict properties of indicators in solutions (18.4)	Exercises 81–84
Perform $K_{sp}$ calculations for ionic compounds in pure water (18.5)	Examples 18.8, 18.9 For Practice 18.8, 18.9 Exercises 85–94
Perform $K_{sp}$ calculations involving the common ion effect (18.5)	Example 18.10 For Practice 18.10 Exercises 95–96
Determine the effect of pH on solubility (18.5)	Example 18.11 For Practice 18.11 Exercises 97–100
Predict precipitation reactions by comparing $Q$ to $K_{sp}$ (18.6)	Example 18.12 For Practice 18.12 Exercises 101–106
Perform calculations involving selective precipitation (18.6)	Examples 18.13, 18.14 For Practice 18.13, 18.14 Exercises 107–108
Perform calculations involving complex ion equilibria (18.8)	Example 18.15 For Practice 18.15 Exercises 109–111

## EXERCISES

**Mastering Chemistry** provides end-of-chapter exercises, feedback-enriched tutorial problems, animations, and interactive activities to encourage problem-solving practice and deeper understanding of key concepts and topics.

## REVIEW QUESTIONS

- What is the pH range of human blood? How is human blood maintained in this pH range?
- What is a buffer? How does a buffer work? How does it neutralize added acid? Added base?
- What is the common ion effect?
- What is the Henderson–Hasselbalch equation, and why is it useful?
- What is the pH of a buffer solution when the concentrations of both buffer components (the weak acid and its conjugate base) are equal? What happens to the pH when the buffer contains more of the weak acid than the conjugate base? More of the conjugate base than the weak acid?
- Suppose that a buffer contains equal amounts of a weak acid and its conjugate base. What happens to the relative amounts of the weak acid and conjugate base when a small amount of strong acid is added to the buffer? What happens when a small amount of strong base is added?
- How do you use the Henderson–Hasselbalch equation to calculate the pH of a buffer containing a base and its conjugate acid? Specifically, how do you determine the correct value for  $pK_a$ ?
- What factors influence the effectiveness of a buffer? What are the characteristics of an effective buffer?
- What is the effective pH range of a buffer (relative to the  $pK_a$  of the weak acid component)?
- Describe acid–base titration. What is the equivalence point?
- The pH at the equivalence point of the titration of a strong acid with a strong base is 7.0. However, the pH at the equivalence point of the titration of a weak acid with a strong base is above 7.0. Explain.
- The volume required to reach the equivalence point of an acid–base titration depends on the volume and concentration of the acid or base to be titrated and on the concentration of the acid or base used to do the titration. It does not, however, depend on whether or not the acid or base being titrated is strong or weak. Explain.
- In the titration of a strong acid with a strong base, how do you calculate these quantities?
  - initial pH
  - pH before the equivalence point
  - pH at the equivalence point
  - pH beyond the equivalence point
- In the titration of a weak acid with a strong base, how do you calculate these quantities?
  - initial pH
  - pH before the equivalence point
  - pH at one-half the equivalence point
  - pH at the equivalence point
  - pH beyond the equivalence point
- The titration of a polyprotic acid with sufficiently different  $pK_a$ s displays two equivalence points. Why?
- In the titration of a polyprotic acid, the volume required to reach the first equivalence point is identical to the volume required to reach the second one. Why?
- What is the difference between the endpoint and the equivalence point in a titration?
- What is an indicator? How can an indicator signal the equivalence point of a titration?
- What is the solubility product constant? Write a general expression for the solubility constant of a compound with the general formula  $A_mX_n$ .
- What is molar solubility? How can you obtain the molar solubility of a compound from  $K_{sp}$ ?
- How does a common ion affect the solubility of a compound? More specifically, how is the solubility of a compound with the general formula  $AX$  different in a solution containing one of the common ions ( $A^+$  or  $X^-$ ) than it is in pure water? Explain.
- How is the solubility of an ionic compound with a basic anion affected by pH? Explain.

23. For a given solution containing an ionic compound, what is the relationship between  $Q$ ,  $K_{sp}$ , and the relative saturation of the solution?
24. What is selective precipitation? Under which conditions does selective precipitation occur?

## PROBLEMS BY TOPIC

### The Common Ion Effect and Buffers

27. In which of these solutions will  $\text{HNO}_2$  ionize less than it does in pure water? **MISSED THIS? Read Section 18.2.**
- 0.10 M NaCl
  - 0.10 M  $\text{KNO}_3$
  - 0.10 M NaOH
  - 0.10 M  $\text{NaNO}_2$
28. A formic acid solution has a pH of 3.25. Which of these substances will raise the pH of the solution upon addition? Explain your answer.
- HCl
  - NaBr
  - $\text{NaCHO}_2$
  - KCl
29. Solve an equilibrium problem (using an ICE table) to calculate the pH of each solution.  
**MISSED THIS? Read Section 18.2; Watch KCV 18.2A, 18.2B, IWE 18.2.**
- a solution that is 0.20 M in  $\text{HCHO}_2$  and 0.15 M in  $\text{NaCHO}_2$
  - a solution that is 0.16 M in  $\text{NH}_3$  and 0.22 M in  $\text{NH}_4\text{Cl}$
30. Solve an equilibrium problem (using an ICE table) to calculate the pH of each solution.
- a solution that is 0.195 M in  $\text{HC}_2\text{H}_3\text{O}_2$  and 0.125 M in  $\text{KC}_2\text{H}_3\text{O}_2$
  - a solution that is 0.255 M in  $\text{CH}_3\text{NH}_2$  and 0.135 M in  $\text{CH}_3\text{NH}_3\text{Br}$
31. Calculate the percent ionization of a 0.15 M benzoic acid solution in pure water and in a solution containing 0.10 M sodium benzoate. Why does the percent ionization differ significantly in the two solutions?  
**MISSED THIS? Read Section 18.2; Watch KCV 18.2A**
32. Calculate the percent ionization of a 0.13 M formic acid solution in pure water and also in a solution containing 0.11 M potassium formate. Explain the difference in percent ionization in the two solutions.
33. Solve an equilibrium problem (using an ICE table) to calculate the pH of each solution.  
**MISSED THIS? Read Section 18.2; Watch KCV 18.2B, IWE 18.2.**
- 0.15 M HF
  - 0.15 M NaF
  - a mixture that is 0.15 M in HF and 0.15 M in NaF
34. Solve an equilibrium problem (using an ICE table) to calculate the pH of each solution.
- 0.18 M  $\text{CH}_3\text{NH}_2$
  - 0.18 M  $\text{CH}_3\text{NH}_3\text{Cl}$
  - a mixture that is 0.18 M in  $\text{CH}_3\text{NH}_2$  and 0.18 M in  $\text{CH}_3\text{NH}_3\text{Cl}$
35. A buffer contains significant amounts of acetic acid and sodium acetate. Write equations showing how this buffer neutralizes added acid and added base.  
**MISSED THIS? Read Section 18.2; Watch KCV 18.2A**
25. What is qualitative analysis? How does *qualitative* analysis differ from *quantitative* analysis?
26. What are the main groups in the general qualitative analysis scheme described in this chapter? Describe the steps and reagents necessary to identify each group.
36. A buffer contains significant amounts of ammonia and ammonium chloride. Write equations showing how this buffer neutralizes added acid and added base.
37. Use the Henderson–Hasselbalch equation to calculate the pH of each solution in Problem 29.  
**MISSED THIS? Read Section 18.2; Watch KCV 18.2B, IWE 18.2**
38. Use the Henderson–Hasselbalch equation to calculate the pH of each solution in Problem 30.
39. Use the Henderson–Hasselbalch equation to calculate the pH of each solution.  
**MISSED THIS? Read Section 18.2; Watch KCV 18.2B, IWE 18.2**
- a solution that is 0.135 M in  $\text{HClO}$  and 0.155 M in  $\text{KClO}$
  - a solution that contains 1.05%  $\text{C}_2\text{H}_5\text{NH}_2$  by mass and 1.10%  $\text{C}_2\text{H}_5\text{NH}_3\text{Br}$  by mass
  - a solution that contains 10.0 g of  $\text{HC}_2\text{H}_3\text{O}_2$  and 10.0 g of  $\text{NaC}_2\text{H}_3\text{O}_2$  in 150.0 mL of solution
40. Use the Henderson–Hasselbalch equation to calculate the pH of each solution.
- a solution that is 0.145 M in propanoic acid and 0.115 M in potassium propanoate
  - a solution that contains 0.785%  $\text{C}_5\text{H}_5\text{N}$  by mass and 0.985%  $\text{C}_5\text{H}_5\text{NHCl}$  by mass
  - a solution that contains 15.0 g of HF and 25.0 g of NaF in 125 mL of solution
41. Calculate the pH of the solution that results from each mixture.  
**MISSED THIS? Read Section 18.2; Watch KCV 18.2B, IWE 18.2**
- 50.0 mL of 0.15 M  $\text{HCHO}_2$  with 75.0 mL of 0.13 M  $\text{NaCHO}_2$
  - 125.0 mL of 0.10 M  $\text{NH}_3$  with 250.0 mL of 0.10 M  $\text{NH}_4\text{Cl}$
42. Calculate the pH of the solution that results from each mixture.
- 150.0 mL of 0.25 M HF with 225.0 mL of 0.30 M NaF
  - 175.0 mL of 0.10 M  $\text{C}_2\text{H}_5\text{NH}_2$  with 275.0 mL of 0.20 M  $\text{C}_2\text{H}_5\text{NH}_3\text{Cl}$
43. Calculate the ratio of NaF to HF required to create a buffer with  $\text{pH} = 4.00$ .  
**MISSED THIS? Read Section 18.2; Watch KCV 18.2B, IWE 18.2**
44. Calculate the ratio of  $\text{CH}_3\text{NH}_2$  to  $\text{CH}_3\text{NH}_3\text{Cl}$  concentration required to create a buffer with  $\text{pH} = 10.24$ .
45. What mass of sodium benzoate should you add to 150.0 mL of a 0.15 M benzoic acid solution to obtain a buffer with a pH of 4.25? (Assume no volume change.)  
**MISSED THIS? Read Section 18.2; Watch KCV 18.2B, IWE 18.2**
46. What mass of ammonium chloride should you add to 2.55 L of a 0.155 M  $\text{NH}_3$  to obtain a buffer with a pH of 9.55? (Assume no volume change.)
47. A 250.0-mL buffer solution is 0.250 M in acetic acid and 0.250 M in sodium acetate.  
**MISSED THIS? Read Section 18.2; Watch KCV 18.2B, IWE 18.2, 18.3**
- What is the initial pH of this solution?
  - What is the pH after addition of 0.0050 mol of HCl?
  - What is the pH after addition of 0.0050 mol of NaOH?

48. A 100.0-mL buffer solution is 0.175 M in HClO and 0.150 M in NaClO.
- What is the initial pH of this solution?
  - What is the pH after addition of 150.0 mg of HBr?
  - What is the pH after addition of 85.0 mg of NaOH?
49. For each solution, calculate the initial and final pH after adding 0.010 mol of HCl.
- MISSED THIS? Read Section 18.2; Watch KCV 18.2B, IWE 18.2, 18.3**
- 500.0 mL of pure water
  - 500.0 mL of a buffer solution that is 0.125 M in  $\text{HC}_2\text{H}_3\text{O}_2$  and 0.115 M in  $\text{NaC}_2\text{H}_3\text{O}_2$
  - 500.0 mL of a buffer solution that is 0.155 M in  $\text{C}_2\text{H}_5\text{NH}_2$  and 0.145 M in  $\text{C}_2\text{H}_5\text{NH}_3\text{Cl}$
50. For each solution, calculate the initial and final pH after adding 0.010 mol of NaOH.
- 250.0 mL of pure water
  - 250.0 mL of a buffer solution that is 0.195 M in  $\text{HCHO}_2$  and 0.275 M in  $\text{KCHO}_2$
  - 250.0 mL of a buffer solution that is 0.255 M in  $\text{CH}_3\text{CH}_2\text{NH}_2$  and 0.235 M in  $\text{CH}_3\text{CH}_2\text{NH}_3\text{Cl}$
51. A 350.0-mL buffer solution is 0.150 M in HF and 0.150 M in NaF. What mass of NaOH can this buffer neutralize before the pH rises above 4.00? If the same volume of the buffer were 0.350 M in HF and 0.350 M in NaF, what mass of NaOH could be handled before the pH rises above 4.00? **MISSED THIS? Read Section 18.3**
52. A 100.0-mL buffer solution is 0.100 M in  $\text{NH}_3$  and 0.125 M in  $\text{NH}_4\text{Br}$ . What mass of HCl can this buffer neutralize before the pH falls below 9.00? If the same volume of the buffer were 0.250 M in  $\text{NH}_3$  and 0.400 M in  $\text{NH}_4\text{Br}$ , what mass of HCl could be handled before the pH fell below 9.00?
53. Determine whether or not the mixing of each pair of solutions results in a buffer. **MISSED THIS? Read Section 18.3**
- 100.0 mL of 0.10 M  $\text{NH}_3$ ; 100.0 mL of 0.15 M  $\text{NH}_4\text{Cl}$
  - 50.0 mL of 0.10 M HCl; 35.0 mL of 0.150 M NaOH
  - 50.0 mL of 0.15 M HF; 20.0 mL of 0.15 M NaOH
  - 175.0 mL of 0.10 M  $\text{NH}_3$ ; 150.0 mL of 0.12 M NaOH
  - 125.0 mL of 0.15 M  $\text{NH}_3$ ; 150.0 mL of 0.20 M NaOH
54. Determine whether or not the mixing of each pair of solutions results in a buffer.
- 75.0 mL of 0.10 M HF; 55.0 mL of 0.15 M NaF
  - 150.0 mL of 0.10 M HF; 135.0 mL of 0.175 M HCl
  - 165.0 mL of 0.10 M HF; 135.0 mL of 0.050 M KOH
  - 125.0 mL of 0.15 M  $\text{CH}_3\text{NH}_2$ ; 120.0 mL of 0.25 M  $\text{CH}_3\text{NH}_3\text{Cl}$
  - 105.0 mL of 0.15 M  $\text{CH}_3\text{NH}_2$ ; 95.0 mL of 0.10 M HCl
55. Blood is buffered by carbonic acid and the bicarbonate ion. Normal blood plasma is 0.024 M in  $\text{HCO}_3^-$  and 0.0012 M  $\text{H}_2\text{CO}_3$  ( $pK_{\text{a}_1}$  for  $\text{H}_2\text{CO}_3$  at body temperature is 6.1). **MISSED THIS? Read Sections 18.2, 18.3; Watch KCV 18.2B, IWE 18.2, 18.3**
- What is the pH of blood plasma?
  - If the volume of blood in a normal adult is 5.0 L, what mass of HCl can be neutralized by the buffering system in blood before the pH falls below 7.0 (which would result in death)?
  - Given the volume from part (b), what mass of NaOH can be neutralized before the pH rises above 7.8?
56. The fluids within cells are buffered by  $\text{H}_2\text{PO}_4^-$  and  $\text{HPO}_4^{2-}$ .
- Calculate the ratio of  $\text{HPO}_4^{2-}$  to  $\text{H}_2\text{PO}_4^-$  required to maintain a pH of 7.1 within a cell.
  - Could a buffer system employing  $\text{H}_3\text{PO}_4$  as the weak acid and  $\text{H}_2\text{PO}_4^-$  as the weak base be used as a buffer system within cells? Explain.

57. Which buffer system is the best choice to create a buffer with pH = 7.20? For the best system, calculate the ratio of the masses of the buffer components required to make the buffer.

**MISSED THIS? Read Section 18.3**

58. Which buffer system is the best choice to create a buffer with pH = 9.00? For the best system, calculate the ratio of the masses of the buffer components required to make the buffer.



59. A 500.0-mL buffer solution is 0.100 M in  $\text{HNO}_2$  and 0.150 M in  $\text{KNO}_2$ . Determine if each addition would exceed the capacity of the buffer to neutralize it. **MISSED THIS? Read Section 18.3**

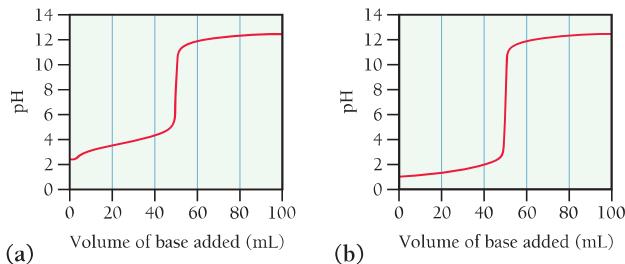
- 250 mg NaOH
- 350 mg KOH
- 1.25 g HBr
- 1.35 g HI

60. A 1.0-L buffer solution is 0.125 M in  $\text{HNO}_2$  and 0.145 M in  $\text{NaNO}_2$ . Determine the concentrations of  $\text{HNO}_2$  and  $\text{NaNO}_2$  after the addition of each substance:

- 1.5 g HCl
- 1.5 g NaOH
- 1.5 g HI

### Titrations, pH Curves, and Indicators

61. The graphs labeled (a) and (b) show the titration curves for two equal-volume samples of monoprotic acids, one weak and one strong. Both titrations were carried out with the same concentration of strong base. **MISSED THIS? Read Section 18.4**



- What is the approximate pH at the equivalence point of each curve?
- Which graph corresponds to the titration of the strong acid and which one to the titration of the weak acid?

62. Two 25.0-mL samples, one 0.100 M HCl and the other 0.100 M HF, are titrated with 0.200 M KOH.

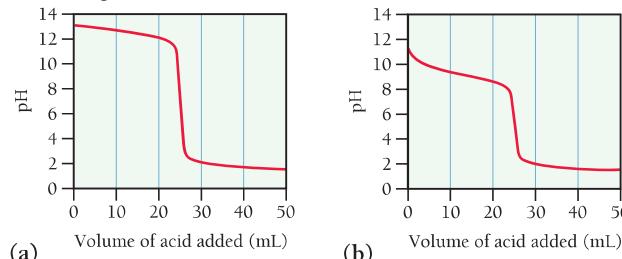
- What is the volume of added base at the equivalence point for each titration?
- Is the pH at the equivalence point for each titration acidic, basic, or neutral?
- Which titration curve has the lower initial pH?
- Sketch each titration curve.

63. Two 20.0-mL samples, one 0.200 M KOH and the other 0.200 M  $\text{CH}_3\text{NH}_2$ , are titrated with 0.100 M HI.

**MISSED THIS? Read Section 18.4; Watch KCV 18.4A, 18.4B**

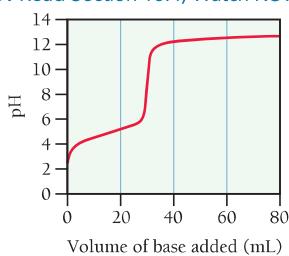
- What is the volume of added acid at the equivalence point for each titration?
- Is the pH at the equivalence point for each titration acidic, basic, or neutral?
- Which titration curve has the lower initial pH?
- Sketch each titration curve.

- 64.** The graphs labeled (a) and (b) show the titration curves for two equal-volume samples of bases, one weak and one strong. Both titrations were carried out with the same concentration of strong acid.

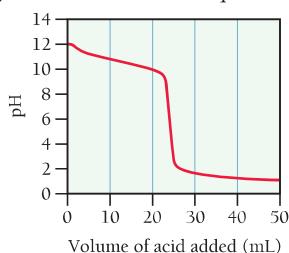


- What is the approximate pH at the equivalence point of each curve?
  - Which graph corresponds to the titration of the strong base and which one to the weak base?
- 65.** Consider the curve shown here for the titration of a weak monoprotic acid with a strong base and answer each question.

**MISSED THIS? Read Section 18.4; Watch KCV 18.4A, IWE 18.6**



- What is the pH and what is the volume of added base at the equivalence point?
  - At what volume of added base is the pH calculated by working an equilibrium problem based on the initial concentration and  $K_a$  of the weak acid?
  - At what volume of added base does  $\text{pH} = \text{p}K_a$ ?
  - At what volume of added base is the pH calculated by working an equilibrium problem based on the concentration and  $K_b$  of the conjugate base?
  - Beyond what volume of added base is the pH calculated by focusing on the amount of excess strong base added?
- 66.** Consider the curve shown here for the titration of a weak base with a strong acid and answer each question.



- What is the pH and what is the volume of added acid at the equivalence point?
- At what volume of added acid is the pH calculated by working an equilibrium problem based on the initial concentration and  $K_b$  of the weak base?
- At what volume of added acid does  $\text{pH} = 14 - \text{p}K_b$ ?
- At what volume of added acid is the pH calculated by working an equilibrium problem based on the concentration and  $K_a$  of the conjugate acid?
- Beyond what volume of added acid is the pH calculated by focusing on the amount of excess strong acid added?

- 67.** Consider the titration of a 35.0-mL sample of 0.175 M HBr with 0.200 M KOH. Determine each quantity.

**MISSED THIS? Read Section 18.4; Watch KCV 18.4A, IWE 18.6**

- the initial pH
- the volume of added base required to reach the equivalence point
- the pH at 10.0 mL of added base
- the pH at the equivalence point
- the pH after adding 5.0 mL of base beyond the equivalence point

- 68.** A 20.0-mL sample of 0.125 M HNO<sub>3</sub> is titrated with 0.150 M NaOH. Calculate the pH for at least five different points throughout the titration curve and sketch the curve. Indicate the volume at the equivalence point on your graph.

- 69.** Consider the titration of a 25.0-mL sample of 0.115 M RbOH with 0.100 M HCl. Determine each quantity.

**MISSED THIS? Read Section 18.4; Watch KCV 18.4A, IWE 18.6**

- the initial pH
- the volume of added acid required to reach the equivalence point
- the pH at 5.0 mL of added acid
- the pH at the equivalence point
- the pH after adding 5.0 mL of acid beyond the equivalence point

- 70.** A 15.0-mL sample of 0.100 M Ba(OH)<sub>2</sub> is titrated with 0.125 M HCl. Calculate the pH for at least five different points throughout the titration curve and sketch the curve. Indicate the volume at the equivalence point on your graph.

- 71.** Consider the titration of a 20.0-mL sample of 0.105 M HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> with 0.125 M NaOH. Determine each quantity.

**MISSED THIS? Read Section 18.4; Watch KCV 18.4B, IWE 18.7**

- the initial pH
- the volume of added base required to reach the equivalence point
- the pH at 5.0 mL of added base
- the pH at one-half of the equivalence point
- the pH at the equivalence point
- the pH after adding 5.0 mL of base beyond the equivalence point

- 72.** A 30.0-mL sample of 0.165 M propanoic acid is titrated with 0.300 M KOH. Calculate the pH at each volume of added base: 0 mL, 5 mL, 10 mL, equivalence point, one-half equivalence point, 20 mL, 25 mL. Sketch the titration curve.

- 73.** Consider the titration of a 25.0-mL sample of 0.175 M CH<sub>3</sub>NH<sub>2</sub> with 0.150 M HBr. Determine each quantity.

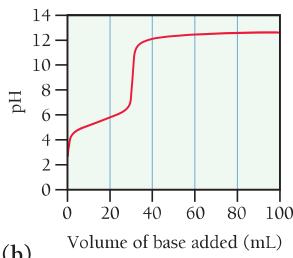
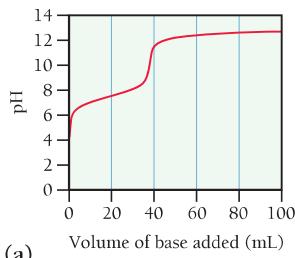
**MISSED THIS? Read Section 18.4; Watch KCV 18.4B, IWE 18.7**

- the initial pH
- the volume of added acid required to reach the equivalence point
- the pH at 5.0 mL of added acid
- the pH at one-half of the equivalence point
- the pH at the equivalence point
- the pH after adding 5.0 mL of acid beyond the equivalence point

- 74.** A 25.0-mL sample of 0.125 M pyridine is titrated with 0.100 M HCl. Calculate the pH at each volume of added acid: 0 mL, 10 mL, 20 mL, equivalence point, one-half equivalence point, 40 mL, 50 mL. Sketch the titration curve.

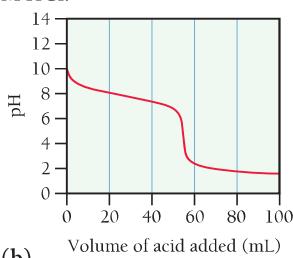
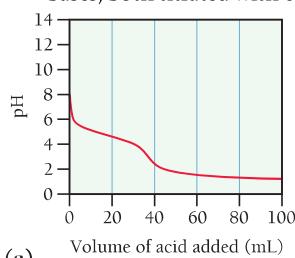
75. Consider the titration curves (labeled a and b) for two weak acids, both titrated with 0.100 M NaOH.

**MISSED THIS? Read Section 18.4; Watch KCV 18.4B, IWE 18.7**



- Which acid solution is more concentrated?
- Which acid has the larger  $K_a$ ?

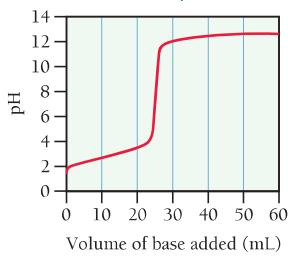
76. Consider the titration curves (labeled a and b) for two weak bases, both titrated with 0.100 M HCl.



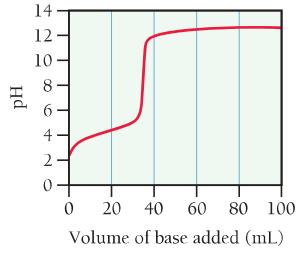
- Which base solution is more concentrated?
- Which base has the larger  $K_b$ ?

77. A 0.229-g sample of an unknown monoprotic acid is titrated with 0.112 M NaOH. The resulting titration curve is shown here. Determine the molar mass and  $pK_a$  of the acid.

**MISSED THIS? Read Section 18.4; Watch KCV 18.4B, IWE 18.7**



78. A 0.446-g sample of an unknown monoprotic acid is titrated with 0.105 M KOH. The resulting titration curve is shown here. Determine the molar mass and  $pK_a$  of the acid.



79. A 20.0-mL sample of 0.115 M sulfurous acid ( $H_2SO_3$ ) solution is titrated with 0.1014 M KOH. At what added volume of base solution does each equivalence point occur?

**MISSED THIS? Read Section 18.4**

80. A 20.0-mL sample of a 0.125 M diprotic acid ( $H_2A$ ) solution is titrated with 0.1019 M KOH. The acid ionization constants for the acid are  $K_{a_1} = 5.2 \times 10^{-5}$  and  $K_{a_2} = 3.4 \times 10^{-10}$ . At what added volume of base does each equivalence point occur?

81. Methyl red has a  $pK_a$  of 5.0 and is red in its acid form and yellow in its basic form. If several drops of this indicator are placed in a 25.0-mL sample of 0.100 M HCl, what color will the solution appear? If 0.100 M NaOH is slowly added to the HCl sample, in what pH range will the indicator change color?

**MISSED THIS? Read Section 18.4**

82. Phenolphthalein has a  $pK_a$  of 9.7. It is colorless in its acid form and pink in its basic form. For each of the values of pH, calculate  $[In^-]/[HIn]$  and predict the color of a phenolphthalein solution.

- pH = 2.0
- pH = 5.0
- pH = 8.0
- pH = 11.0

83. Referring to Table 18.1, pick an indicator for use in the titration of each acid with a strong base. **MISSED THIS? Read Section 18.4**

- HF
- HCl
- HCN

84. Referring to Table 18.1, pick an indicator for use in the titration of each base with a strong acid.

- $CH_3NH_2$
- NaOH
- $C_6H_5NH_2$

## Solubility Equilibria

85. Write balanced equations and expressions for  $K_{sp}$  for the dissolution of each ionic compound. **MISSED THIS? Read Section 18.5**

- $BaSO_4$
- $PbBr_2$
- $Ag_2CrO_4$

86. Write balanced equations and expressions for  $K_{sp}$  for the dissolution of each ionic compound.

- $CaCO_3$
- $PbCl_2$
- $AgI$

87. Refer to the  $K_{sp}$  values in Table 18.2 to calculate the molar solubility of each compound in pure water.

**MISSED THIS? Read Section 18.5; Watch IWE 18.8**

- $AgBr$
- $Mg(OH)_2$
- $CaF_2$

88. Refer to the  $K_{sp}$  values in Table 18.2 to calculate the molar solubility of each compound in pure water.

- $MX$  ( $K_{sp} = 1.27 \times 10^{-36}$ )
- $Ag_2CrO_4$
- $Ca(OH)_2$

89. Use the given molar solubilities in pure water to calculate  $K_{sp}$  for each compound. **MISSED THIS? Read Section 18.5**

- $MX$ ; molar solubility =  $3.27 \times 10^{-11}$  M
- $PbF_2$ ; molar solubility =  $5.63 \times 10^{-3}$  M
- $MgF_2$ ; molar solubility =  $2.65 \times 10^{-4}$  M

90. Use the given molar solubilities in pure water to calculate  $K_{sp}$  for each compound.

- $BaCrO_4$ ; molar solubility =  $1.08 \times 10^{-5}$  M
- $Ag_2SO_3$ ; molar solubility =  $1.55 \times 10^{-5}$  M
- $Pd(SCN)_2$ ; molar solubility =  $2.22 \times 10^{-8}$  M

91. Two compounds with general formulas  $AX$  and  $AX_2$  have  $K_{sp} = 1.5 \times 10^{-5}$ . Which of the two compounds has the higher molar solubility?

**MISSED THIS? Read Section 18.5; Watch IWE 18.8**

- 92.** Consider the compounds with the generic formulas listed and their corresponding molar solubilities in pure water. Which compound has the smallest value of  $K_{sp}$ ?
- $AX$ ; molar solubility =  $1.35 \times 10^{-4} M$
  - $AX_2$ ; molar solubility =  $2.25 \times 10^{-4} M$
  - $A_2X$ ; molar solubility =  $1.75 \times 10^{-4} M$
- 93.** Refer to the  $K_{sp}$  value from Table 18.2 to calculate the solubility of iron(II) hydroxide in pure water in grams per 100.0 mL of solution. **MISSED THIS? Read Section 18.5; Watch IWE 18.8**
- 94.** The solubility of copper(I) chloride is 3.91 mg per 100.0 mL of solution. Calculate  $K_{sp}$  for  $CuCl$ .
- 95.** Calculate the molar solubility of barium fluoride in each liquid or solution. **MISSED THIS? Read Section 18.5**
- pure water
  - 0.10 M  $Ba(NO_3)_2$
  - 0.15 M  $NaF$
- 96.** Calculate the molar solubility of  $MX$  ( $K_{sp} = 1.27 \times 10^{-36}$ ) in each liquid or solution.
- pure water
  - 0.25 M  $MCl_2$
  - 0.20 M  $Na_2X$
- 97.** Calculate the molar solubility of calcium hydroxide in a solution buffered at each pH. **MISSED THIS? Read Section 18.5**
- pH = 4
  - pH = 7
  - pH = 9
- 98.** Calculate the solubility (in grams per  $1.00 \times 10^2$  mL of solution) of magnesium hydroxide in a solution buffered at pH = 10. How does this compare to the solubility of  $Mg(OH)_2$  in pure water?
- 99.** Determine if each compound is more soluble in acidic solution than it is in pure water. Explain. **MISSED THIS? Read Section 18.5**
- $BaCO_3$
  - $CuS$
  - $AgCl$
  - $PbI_2$
- 100.** Determine if each compound is more soluble in acidic solution than it is in pure water. Explain.
- $Hg_2Br_2$
  - $Mg(OH)_2$
  - $CaCO_3$
  - $AgI$

### Precipitation and Qualitative Analysis

- 101.** A solution containing sodium fluoride is mixed with one containing calcium nitrate to form a solution that is 0.015 M in  $NaF$  and 0.010 M in  $Ca(NO_3)_2$ . Does a precipitate form in the mixed solution? If so, identify the precipitate.  
**MISSED THIS? Read Section 18.6; Watch IWE 18.12**
- 102.** A solution containing potassium bromide is mixed with one containing lead acetate to form a solution that is 0.013 M in  $KBr$  and 0.0035 M in  $Pb(C_2H_3O_2)_2$ . Does a precipitate form in the mixed solution? If so, identify the precipitate.

- 103.** Predict whether a precipitate will form if you mix 75.0 mL of a  $NaOH$  solution with  $pOH = 2.58$  with 125.0 mL of a 0.018 M  $MgCl_2$  solution. Identify the precipitate, if any.  
**MISSED THIS? Read Section 18.6; Watch IWE 18.12**

- 104.** Predict whether a precipitate will form if you mix 175.0 mL of a 0.0055 M  $KCl$  solution with 145.0 mL of a 0.0015 M  $AgNO_3$  solution. Identify the precipitate, if any.

- 105.** Potassium hydroxide is used to precipitate each of the cations from their respective solution. Determine the minimum concentration of  $KOH$  required for precipitation to begin in each case. **MISSED THIS? Read Section 18.6; Watch IWE 18.12**

- 0.015 M  $CaCl_2$
- 0.0025 M  $Fe(NO_3)_2$
- 0.0018 M  $MgBr_2$

- 106.** Determine the minimum concentration of the precipitating agent on the right to cause precipitation of the cation from the solution on the left.

- 0.035 M  $Ba(NO_3)_2$ ;  $NaF$
- 0.085 M  $CaI_2$ ;  $K_2SO_4$
- 0.0018 M  $AgNO_3$ ;  $RbCl$

- 107.** A solution is 0.010 M in  $Ba^{2+}$  and 0.020 M in  $Ca^{2+}$ .

- MISSED THIS? Read Section 18.6; Watch IWE 18.12**

- a. If sodium sulfate is used to selectively precipitate one of the cations while leaving the other cation in solution, which cation will precipitate first? What minimum concentration of  $Na_2SO_4$  will trigger the precipitation of the cation that precipitates first?

- b. What is the remaining concentration of the cation that precipitates first, when the other cation begins to precipitate?

- 108.** A solution is 0.022 M in  $Fe^{2+}$  and 0.014 M in  $Mg^{2+}$ .

- a. If potassium carbonate is used to selectively precipitate one of the cations while leaving the other cation in solution, which cation will precipitate first? What minimum concentration of  $K_2CO_3$  will trigger the precipitation of the cation that precipitates first?

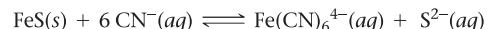
- b. What is the remaining concentration of the cation that precipitates first, when the other cation begins to precipitate?

### Complex Ion Equilibria

- 109.** A solution is  $1.1 \times 10^{-3}$  M in  $Zn(NO_3)_2$  and 0.150 M in  $NH_3$ . After the solution reaches equilibrium, what concentration of  $Zn^{2+}(aq)$  remains? **MISSED THIS? Read Section 18.8**

- 110.** A 120.0-mL sample of a solution that is  $2.8 \times 10^{-3}$  M in  $AgNO_3$  is mixed with a 225.0-mL sample of a solution that is 0.10 M in  $NaCN$ . After the solution reaches equilibrium, what concentration of  $Ag^+(aq)$  remains?

- 111.** Use the appropriate values of  $K_{sp}$  and  $K_f$  to find the equilibrium constant for the reaction. **MISSED THIS? Read Section 18.8**



- 112.** Use the appropriate values of  $K_{sp}$  and  $K_f$  to find the equilibrium constant for the reaction.



## CUMULATIVE PROBLEMS

- 113.** A 150.0-mL solution contains 2.05 g of sodium benzoate and 2.47 g of benzoic acid. Calculate the pH of the solution.
- 114.** A solution is made by combining 10.0 mL of 17.5 M acetic acid with 5.54 g of sodium acetate and diluting to a total volume of 1.50 L. Calculate the pH of the solution.
- 115.** A buffer is created by combining 150.0 mL of 0.25 M  $\text{HCHO}_2$  with 75.0 mL of 0.20 M NaOH. Determine the pH of the buffer.
- 116.** A buffer is created by combining 3.55 g of  $\text{NH}_3$  with 4.78 g of HCl and diluting to a total volume of 750.0 mL. Determine the pH of the buffer.
- 117.** A 1.0-L buffer solution initially contains 0.25 mol of  $\text{NH}_3$  and 0.25 mol of  $\text{NH}_4\text{Cl}$ . In order to adjust the buffer pH to 8.75, should you add NaOH or HCl to the buffer mixture? What mass of the correct reagent should you add?
- 118.** A 250.0-mL buffer solution initially contains 0.025 mol of  $\text{HCHO}_2$  and 0.025 mol of  $\text{NaCHO}_2$ . In order to adjust the buffer pH to 4.10, should you add NaOH or HCl to the buffer mixture? What mass of the correct reagent should you add?
- 119.** In analytical chemistry, bases used for titrations must often be standardized; that is, their concentration must be precisely determined. Standardization of sodium hydroxide solutions can be accomplished by titrating potassium hydrogen phthalate ( $\text{KHC}_8\text{H}_4\text{O}_4$ ), also known as KHP, with the NaOH solution to be standardized.
  - Write an equation for the reaction between NaOH and KHP.
  - The titration of 0.5527 g of KHP required 25.87 mL of an NaOH solution to reach the equivalence point. What is the concentration of the NaOH solution?
- 120.** A 0.5224-g sample of an unknown monoprotic acid was titrated with 0.0998 M NaOH. The equivalence point of the titration occurred at 23.82 mL. Determine the molar mass of the unknown acid.
- 121.** A 0.25-mol sample of a weak acid with an unknown  $\text{p}K_a$  was combined with 10.0 mL of 3.00 M KOH, and the resulting solution was diluted to 1.500 L. The measured pH of the solution was 3.85. What is the  $\text{p}K_a$  of the weak acid?
- 122.** A 5.55-g sample of a weak acid with  $K_a = 1.3 \times 10^{-4}$  was combined with 5.00 mL of 6.00 M NaOH, and the resulting solution was diluted to 750.0 mL. The measured pH of the solution was 4.25. What is the molar mass of the weak acid?
- 123.** A 0.552-g sample of ascorbic acid (vitamin C) was dissolved in water to a total volume of 20.0 mL and titrated with 0.1103 M KOH. The equivalence point occurred at 28.42 mL. The pH of the solution at 10.0 mL of added base was 3.72. From this data, determine the molar mass and  $K_a$  for vitamin C.
- 124.** Sketch the titration curve from Problem 123 by calculating the pH at the beginning of the titration, at one-half of the equivalence point, at the equivalence point, and at 5.0 mL beyond the equivalence point. Pick a suitable indicator for this titration from Table 18.1.
- 125.** One of the main components of hard water is  $\text{CaCO}_3$ . When hard water evaporates, some of the  $\text{CaCO}_3$  is left behind as a white mineral deposit. If a hard water solution is saturated with calcium carbonate, what volume of the solution has to evaporate to deposit  $1.00 \times 10^2$  mg of  $\text{CaCO}_3$ ?
- 126.** Gout—a condition that results in joint swelling and pain—is caused by the formation of sodium urate ( $\text{NaC}_5\text{H}_3\text{N}_4\text{O}_3$ ) crystals within tendons, cartilage, and ligaments. Sodium urate precipitates out of blood plasma when uric acid levels become abnormally high. This sometimes happens as a result of eating too many rich foods and consuming too much alcohol, which is why gout is sometimes referred to as the “disease of kings.” If the sodium concentration in blood plasma is 0.140 M, and  $K_{\text{sp}}$  for sodium urate is  $5.76 \times 10^{-8}$ , what minimum concentration of urate would result in precipitation?
- 127.** Pseudogout, a condition with symptoms similar to those of gout (see Problem 126), is caused by the formation of calcium diphosphate ( $\text{Ca}_2\text{P}_2\text{O}_7$ ) crystals within tendons, cartilage, and ligaments. Calcium diphosphate will precipitate out of blood plasma when diphosphate levels become abnormally high. If the calcium concentration in blood plasma is 9.2 mg/dL, and  $K_{\text{sp}}$  for calcium diphosphate is  $8.64 \times 10^{-13}$ , what minimum concentration of diphosphate results in precipitation?
- 128.** Calculate the solubility of silver chloride in a solution that is 0.100 M in  $\text{NH}_3$ .
- 129.** Calculate the solubility of  $\text{CuX}$  in a solution that is 0.150 M in NaCN.  $K_{\text{sp}}$  for  $\text{CuX}$  is  $1.27 \times 10^{-36}$ .
- 130.** Aniline, abbreviated  $\phi\text{NH}_2$ , where  $\phi$  is  $\text{C}_6\text{H}_5$ , is an important organic base used in the manufacture of dyes. It has  $K_b = 4.3 \times 10^{-10}$ . In a certain manufacturing process, it is necessary to keep the concentration of  $\phi\text{NH}_3^+$  (aniline's conjugate acid, the anilinium ion) below  $1.0 \times 10^{-9}$  M in a solution that is 0.10 M in aniline. Find the concentration of NaOH required for this process.
- 131.** The  $K_b$  of hydroxylamine,  $\text{NH}_2\text{OH}$ , is  $1.10 \times 10^{-8}$ . A buffer solution is prepared by mixing 100.0 mL of a 0.36 M hydroxylamine solution with 50.0 mL of a 0.26 M HCl solution. Determine the pH of the resulting solution.
- 132.** A 0.867-g sample of an unknown acid requires 32.2 mL of a 0.182 M barium hydroxide solution for neutralization. Assuming the acid is diprotic, calculate the molar mass of the acid.
- 133.** A 25.0-mL volume of a sodium hydroxide solution requires 19.6 mL of a 0.189 M hydrochloric acid for neutralization. A 10.0-mL volume of a phosphoric acid solution requires 34.9 mL of the sodium hydroxide solution for complete neutralization. Calculate the concentration of the phosphoric acid solution.
- 134.** Find the mass of sodium formate that must be dissolved in  $250.0 \text{ cm}^3$  of a 1.4 M solution of formic acid to prepare a buffer solution with pH = 3.36.
- 135.** What relative masses of dimethyl amine and dimethyl ammonium chloride do you need to prepare a buffer solution of pH = 10.43?
- 136.** You are asked to prepare 2.0 L of a HCN/NaCN buffer that has a pH of 9.8 and an osmotic pressure of 1.35 atm at 298 K. What masses of HCN and NaCN should you use to prepare the buffer? (Assume complete dissociation of NaCN.)
- 137.** What should the molar concentrations of benzoic acid and sodium benzoate be in a solution that is buffered at a pH of 4.55 and has a freezing point of  $-2.0^\circ\text{C}$ ? (Assume complete dissociation of sodium benzoate and a density of 1.01 g/mL for the solution.)

## CHALLENGE PROBLEMS

- 138.** Derive an equation similar to the Henderson-Hasselbalch equation for a buffer composed of a weak base and its conjugate acid. Instead of relating pH to  $pK_a$  and the relative concentrations of an acid and its conjugate base (as the Henderson-Hasselbalch equation does), the equation should relate pOH to  $pK_b$  and the relative concentrations of a base and its conjugate acid.
- 139.** Since soap and detergent action is hindered by hard water, laundry formulations usually include water softeners—called builders—designed to remove hard water ions (especially  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) from the water. A common builder used in North America is sodium carbonate. Suppose that the hard water used to do laundry contains 75 ppm  $\text{Ca}^{2+}$  (reported as  $\text{CaCO}_3$ ). What mass of  $\text{Na}_2\text{CO}_3$  is required to remove 90.0% of these ions from 10.0 L of laundry water?
- 140.** A 0.558-g sample of a diprotic acid with a molar mass of 255.8 g/mol is dissolved in water to a total volume of 25.0 mL. The solution is then titrated with a saturated calcium hydroxide solution.
- Assuming that the  $pK_a$  values for each ionization step are sufficiently different to see two equivalence points, determine the volume of added base for the first and second equivalence points.
  - The pH after adding 25.0 mL of the base is 3.82. Find the value of  $K_{a_1}$ .
  - The pH after adding 20.0 mL past the first equivalence point is 8.25. Find the value of  $K_{a_2}$ .
- 141.** When excess solid  $\text{Mg(OH)}_2$  is shaken with 1.00 L of 1.0 M  $\text{NH}_4\text{Cl}$  solution, the resulting saturated solution has pH = 9.00. Calculate the  $K_{sp}$  of  $\text{Mg(OH)}_2$ .
- 142.** What amount of solid NaOH must be added to 1.0 L of a 0.10 M  $\text{H}_2\text{CO}_3$  solution to produce a solution with  $[\text{H}^+] = 3.2 \times 10^{-11}$  M? There is no significant volume change as the result of the addition of the solid.
- 143.** Calculate the solubility of  $\text{Au(OH)}_3$  in (a) water and (b) 1.0 M nitric acid solution ( $K_{sp} = 5.5 \times 10^{-46}$ ).
- 144.** Calculate the concentration of  $\text{I}^-$  in a solution obtained by shaking 0.10 M KI with an excess of  $\text{AgCl}(s)$ .
- 145.** What volume of 0.100 M sodium carbonate solution is required to precipitate 99% of the Mg from 1.00 L of 0.100 M magnesium nitrate solution?
- 146.** Find the solubility of  $\text{CuI}$  in 0.40 M HCN solution. The  $K_{sp}$  of  $\text{CuI}$  is  $1.1 \times 10^{-12}$  and the  $K_f$  for the  $\text{Cu}(\text{CN})_2^-$  complex ion is  $1 \times 10^{24}$ .
- 147.** Find the pH of a solution prepared from 1.0 L of a 0.10 M solution of  $\text{Ba(OH)}_2$  and excess  $\text{Zn(OH)}_2(s)$ . The  $K_{sp}$  of  $\text{Zn(OH)}_2$  is  $3 \times 10^{-15}$  and the  $K_f$  of  $\text{Zn(OH)}_4^{2-}$  is  $2 \times 10^{15}$ .
- 148.** What amount of HCl gas must be added to 1.00 L of a buffer solution that contains [acetic acid] = 2.0 M and [acetate] = 1.0 M in order to produce a solution with pH = 4.00?

## CONCEPTUAL PROBLEMS

- 149.** Without doing any calculations, determine if  $\text{pH} = \text{p}K_a$ ,  $\text{pH} > \text{p}K_a$ , or  $\text{pH} < \text{p}K_a$ . Assume that HA is a weak monoprotic acid.
- 0.10 mol HA and 0.050 mol of  $\text{A}^-$  in 1.0 L of solution
  - 0.10 mol HA and 0.150 mol of  $\text{A}^-$  in 1.0 L of solution
  - 0.10 mol HA and 0.050 mol of  $\text{OH}^-$  in 1.0 L of solution
  - 0.10 mol HA and 0.075 mol of  $\text{OH}^-$  in 1.0 L of solution
- 150.** A buffer contains 0.10 mol of a weak acid and 0.20 mol of its conjugate base in 1.0 L of solution. Determine whether or not each addition exceeds the capacity of the buffer.
- adding 0.020 mol of NaOH
  - adding 0.020 mol of HCl
  - adding 0.10 mol of NaOH
  - adding 0.010 mol of HCl
- 151.** Consider three solutions:
- 0.10 M solution of a weak monoprotic acid
  - 0.10 M solution of strong monoprotic acid
  - 0.10 M solution of a weak diprotic acid
- Each solution is titrated with 0.15 M NaOH. Which quantity is the same for all three solutions?
- the volume required to reach the final equivalence point
  - the volume required to reach the first equivalence point
  - the pH at the first equivalence point
  - the pH at one-half the first equivalence point
- 152.** Two monoprotic acid solutions (A and B) are titrated with identical NaOH solutions. The volume to reach the equivalence point for solution A is twice the volume required to reach the equivalence point for solution B, and the pH at the equivalence point of solution A is higher than the pH at the equivalence point for solution B. Which statement is true?
- The acid in solution A is more concentrated than in solution B and is also a stronger acid than that in solution B.
  - The acid in solution A is less concentrated than in solution B and is also a weaker acid than that in solution B.
  - The acid in solution A is more concentrated than in solution B and is also a weaker acid than that in solution B.
  - The acid in solution A is less concentrated than in solution B and is also a stronger acid than that in solution B.
- 153.** Describe the solubility of  $\text{CaF}_2$  in each solution compared to its solubility in water.
- in a 0.10 M NaCl solution
  - in a 0.10 M NaF solution
  - in a 0.10 M HCl solution
- 154.** Why does the titration of a weak acid with a strong base always have a basic equivalence point?

## QUESTIONS FOR GROUP WORK

Discuss these questions with the group and record your consensus answer.

**155.** Name a compound that you could add to a solution of each of the compounds to make a buffer. Explain your reasoning in complete sentences.

- acetic acid
- sodium nitrite
- ammonia
- potassium formate
- $\text{Na}_2\text{HPO}_4$  (two possible answers)

**156.** Derive the Henderson–Hasselbalch equation as a group. Take turns having each group member write and explain the next step in the derivation.

**157.** With group members acting as atoms or ions, act out the reaction that occurs when HCl is added to a buffer solution composed of  $\text{HC}_2\text{H}_3\text{O}_2$  and  $\text{NaC}_2\text{H}_3\text{O}_2$ . Write out a script for a narrator that describes the processes that occur, including how the buffer keeps the pH approximately the same even though a strong acid is added.

Active Classroom Learning

**158.** A certain town gets its water from an underground aquifer that contains water in equilibrium with calcium carbonate limestone.

- What is the symbol for the equilibrium constant that describes calcium carbonate dissolving in water? What is the numerical value?
- Calculate the molar solubility of calcium carbonate.
- If an entire coffee cup of water (about 200 mL) evaporated on your desk over spring break, how many grams of calcium carbonate would be left behind?
- If you wanted to clean out your coffee cup, would it be better to use an acidic or a basic cleaning solution? Why?

**159.** Have each group member look up the  $K_{\text{sp}}$  for a different compound. Calculate the molar solubility. Do the numerical values suggest that the compound is soluble or insoluble? Compare answers with the solubility rules from Chapter 5, and have each group member present his or her findings to the group.



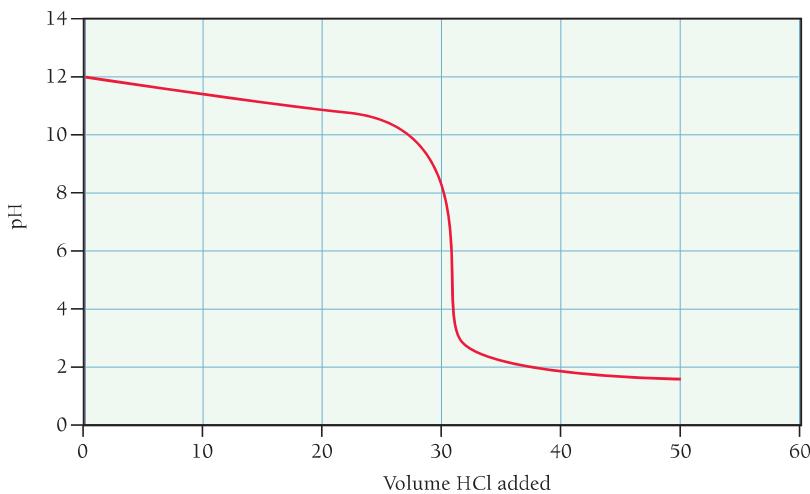
## DATA INTERPRETATION AND ANALYSIS

### Titration of an Unknown Base

**160.** A base is known to be one of the three listed in the table. You are given a sample of the base and asked to identify it. To do so, you dissolve 0.30 g of the base in enough water to make 25.0 mL of the basic solution. You then titrate the solution with 0.100 M HCl and record the pH as a function of the added acid resulting in the titration curve that follows. Examine the table and the titration curve and answer the questions.

### Possible Bases in Sample

Base	$K_b$
Pyridine ( $\text{C}_5\text{H}_5\text{N}$ )	$1.7 \times 10^{-9}$
Aniline ( $\text{C}_6\text{H}_5\text{NH}_2$ )	$3.9 \times 10^{-10}$
Triethylamine ( $\text{C}_6\text{H}_{15}\text{N}$ )	$5.6 \times 10^{-4}$



Titration Curve for 0.30 g of Unknown Base Dissolved in 25.0 mL of Solution

- What is the volume of added HCl at the equivalence point?
- What is the pH at the half-equivalence point?
- What is the molar mass of the unknown base?
- What are the  $pK_b$  and  $K_b$  of the unknown base?
- What is the most likely identity of the unknown base?



## ANSWERS TO CONCEPTUAL CONNECTIONS

### Buffers

**18.1 (d)** Only this solution contains significant amounts of a weak acid and its conjugate base. (Remember that  $\text{HNO}_3$  is a strong acid, but  $\text{HNO}_2$  is a weak acid.)

### pH of Buffer Solutions

**18.2 (a)** Since the pH of the buffer is less than the  $pK_a$  of the acid, the buffer must contain more acid than base ( $[\text{HA}] > [\text{A}^-]$ ).

### Buffering Action

**18.3 (a)** Since one HA molecule is converted to one ion of the conjugate base ( $\text{A}^-$  ion), one  $\text{OH}^-$  ion was added to the buffer solution.

### Adding Acid or Base to a Buffer

**18.4 (b)** Since acid is added to the buffer, the pH will become slightly lower (slightly more acidic). Answer **(a)** reflects too large a change in pH for a buffer, and answers **(c)** and **(d)** have the pH changing in the wrong direction.

### Buffer Capacity

**18.5 (a)** Adding 0.050 mol of HCl destroys the buffer because it will react with all of the  $\text{NaF}$ , leaving no conjugate base in the buffer mixture.

### Titration Equivalence Point

**18.6 (d)** Because the flask contains 7  $\text{H}^+$  ions, the equivalence point is reached when 7  $\text{OH}^-$  ions have been added.

### Weak Acid and Strong Base Titration

**18.7 (c)** Acid A is more concentrated (it took more NaOH to reach the equivalence point), and acid B has the larger  $K_a$  ( $pK_a$  is smaller so  $K_a$  is larger).

### The Half-Equivalence Point

**18.8 (c)** The pH at the half-equivalence point is the  $pK_a$  of the conjugate acid, which is equal to  $14.00 - 8.75 = 5.25$ .

### Acid–Base Titrations

**18.9 (c)** Since the volumes and concentrations of all three acids are the same, the volume of NaOH required to reach the first equivalence point (and the only equivalence point for titrations i and iii) is the same for all three titrations.

### Common Ion Effect

**18.10 (c)** The sodium nitrate solution is the only one that has no common ion with barium sulfate. The other two solutions have common ions with barium sulfate; therefore, the solubility of barium sulfate is lower in these solutions.

### Selective Precipitation

**18.11 (a)**  $\text{Ba}^{2+}$  has the smallest solubility product constant and, since the stoichiometry of dissolution is the same for all three ions, it will precipitate first.

### Solubility and Complex Ion Equilibria

**18.12 (c)** Only  $\text{NaCN}$  contains an anion ( $\text{CN}^-$ ) that forms a complex ion with  $\text{Cu}^{2+}$  [from Table 18.3 we can see that  $K_f = 1.0 \times 10^{25}$  for  $\text{Cu}(\text{CN})_4^{2-}$ ]. Therefore, the presence of  $\text{CN}^-$  will drive the dissolution reaction of  $\text{CuS}$ .