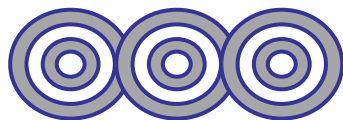




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Theodore L. Brown; H. Eugene LeMay, Jr.;  
Bruce E. Bursten; Catherine J. Murphy



# Chapter 17

## Additional Aspects of Aqueous Equilibria

**Ahmad Aqel Ifseisi**

Assistant Professor of Analytical Chemistry  
College of Science, Department of Chemistry  
King Saud University

P.O. Box 2455 Riyadh 11541 Saudi Arabia

Office: AA53

Tel. 014674198, Fax: 014675992

Web site: <http://fac.ksu.edu.sa/aifseisi>

E-mail: [ahmad3qel@yahoo.com](mailto:ahmad3qel@yahoo.com)

[aifseisi@ksu.edu.sa](mailto:aifseisi@ksu.edu.sa)



كرسي أبحاث  
المواد المتقدمة  
Advanced Materials  
Research Chair



The various aqueous solutions encountered in nature typically contain many solutes. For example, the aqueous solutions in hot springs and oceans.

The idea in this chapter is to consider not only solutions in which there is a single solute but also those containing a mixture of solutes.

In this chapter we take a step toward understanding such complex solutions by looking first at further applications of acid-base equilibria.

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**17.1**

**The Common Ion Effect**

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In chapter 16 we examined the equilibrium concentrations of ions in solutions containing a weak acid or a weak base. We now consider solutions that contain a weak acid, such as acetic acid ( $\text{CH}_3\text{COOH}$ ), and a soluble salt of that acid, such as sodium acetate ( $\text{CH}_3\text{COONa}$ ). Notice that these solutions contain two substances that share a common ion  $\text{CH}_3\text{COO}^-$ .

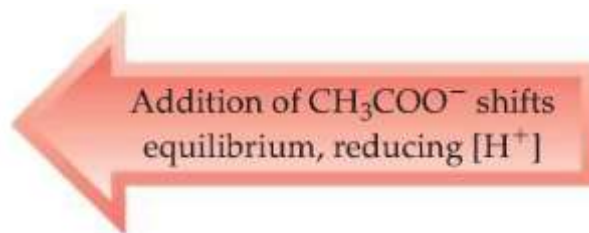
Sodium acetate is a soluble ionic compound and is therefore a strong electrolyte. Consequently, it dissociates completely in aqueous solution to form  $\text{Na}^+$  and  $\text{CH}_3\text{COO}^-$  ions:



In contrast,  $\text{CH}_3\text{COOH}$  is a weak electrolyte that ionizes as follows:



According to Le Chatelier's principle, the  $\text{CH}_3\text{COO}^-$  from  $\text{CH}_3\text{COONa}$  causes this equilibrium to shift to the left, thereby decreasing the equilibrium concentration of  $\text{H}^+(aq)$ .



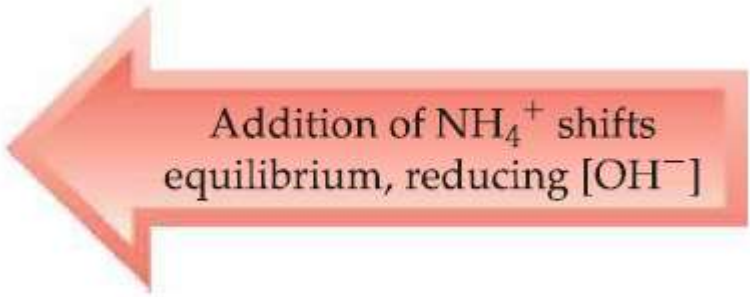
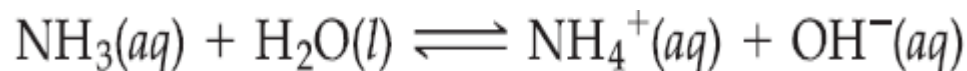
In other words, the presence of the added acetate ion causes the acetic acid to ionize less than it normally would.

Whenever a weak electrolyte and a strong electrolyte contain a common ion, the weak electrolyte ionizes less than it would if it were alone in solution. We call this observation the **common-ion effect**.

“The extent of ionization of a weak electrolyte is decreased by adding to the solution a strong electrolyte that has an ion in common with the weak electrolyte.”

Electrolyte and a strong electrolyte that have a common ion. The procedures are similar to those encountered for weak acids and weak bases.

The ionization of a weak base is also decreased by the addition of a common ion. For example, the addition of  $\text{NH}_4^+$  (as from the strong electrolyte  $\text{NH}_4\text{Cl}$ ) causes the base-dissociation equilibrium of  $\text{NH}_3$  to shift to the left, decreasing the equilibrium concentration of  $\text{OH}^-$  and lowering the pH:



Addition of  $\text{NH}_4^+$  shifts equilibrium, reducing  $[\text{OH}^-]$

## Sample Exercise 17.1 Calculating the pH When a Common Ion is Involved

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

### Solution

First, because  $\text{CH}_3\text{COOH}$  is a weak electrolyte and  $\text{CH}_3\text{COONa}$  is a strong electrolyte, the major species in the solution are  $\text{CH}_3\text{COOH}$  (a weak acid),  $\text{Na}^+$  (which is neither acidic nor basic and is therefore a spectator in the acid–base chemistry), and  $\text{CH}_3\text{COO}^-$  (which is the conjugate base of  $\text{CH}_3\text{COOH}$ ).

Second,  $[\text{H}^+]$  and, therefore, the pH are controlled by the dissociation equilibrium of  $\text{CH}_3\text{COOH}$ : (We have written the equilibrium Using  $\text{H}^+(\text{aq})$  rather than  $\text{H}_3\text{O}^+(\text{aq})$  but both representations of the hydrated hydrogen ion are equally valid).

Third, we tabulate the initial and equilibrium concentrations (as we did in solving other equilibrium problems):

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

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

Now we can use the equilibrium-constant expression:

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

(The dissociation constant for  $\text{CH}_3\text{COOH}$  at 25 °C is from Appendix D; addition of  $\text{CH}_3\text{COONa}$  does not change the value of this constant). Substituting the equilibrium-constant concentrations from our table into the equilibrium expression gives

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

Because  $K_a$  is small, we assume that  $x$  is small compared to the original concentrations of  $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COO}^-$  (0.30  $M$  each). Thus, we can ignore the very small  $x$  relative to 0.30  $M$ , giving

$$K_a = 1.8 \times 10^{-5} = \frac{x(0.30)}{0.30}$$
$$x = 1.8 \times 10^{-5} M = [\text{H}^+]$$

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

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

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

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

**Comment:** In Section 16.6 we calculated that a 0.30  $M$  solution of  $\text{CH}_3\text{COOH}$  has a pH of 2.64, corresponding to  $[\text{H}^+] = 2.3 \times 10^{-3} M$ . Thus, the addition of  $\text{CH}_3\text{COONa}$  has substantially decreased  $[\text{H}^+]$  as we would expect from Le Châtelier's principle.

## Sample Exercise 17.2 Calculating Ion Concentrations When a Common is Involved

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

### Solution

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



	HF(aq)	$\rightleftharpoons$	H <sup>+</sup> (aq)	+	F <sup>−</sup> (aq)
Initial	0.20 <i>M</i>		0.10 <i>M</i>		0
Change	− <i>x M</i>		+ <i>x M</i>		+ <i>x M</i>
Equilibrium	(0.20 − <i>x</i> ) <i>M</i>		(0.10 + <i>x</i> ) <i>M</i>		<i>x M</i>

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

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

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

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

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



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

This  $F^-$  concentration is substantially smaller than it would be in a 0.20  $M$  solution of HF with no added HCl.

The common ion,  $H^+$ , suppresses the ionization of HF. The concentration of  $H^+(aq)$  is

Thus,

$$[H^+] = (0.10 + x) M \simeq 0.10 M$$
$$pH = 1.00$$

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

# **17.2**

## **Buffered Solutions**

Buffers are solutions of a weak conjugate acid-base pair.

They are particularly resistant to pH changes, even when strong acid or base is added.

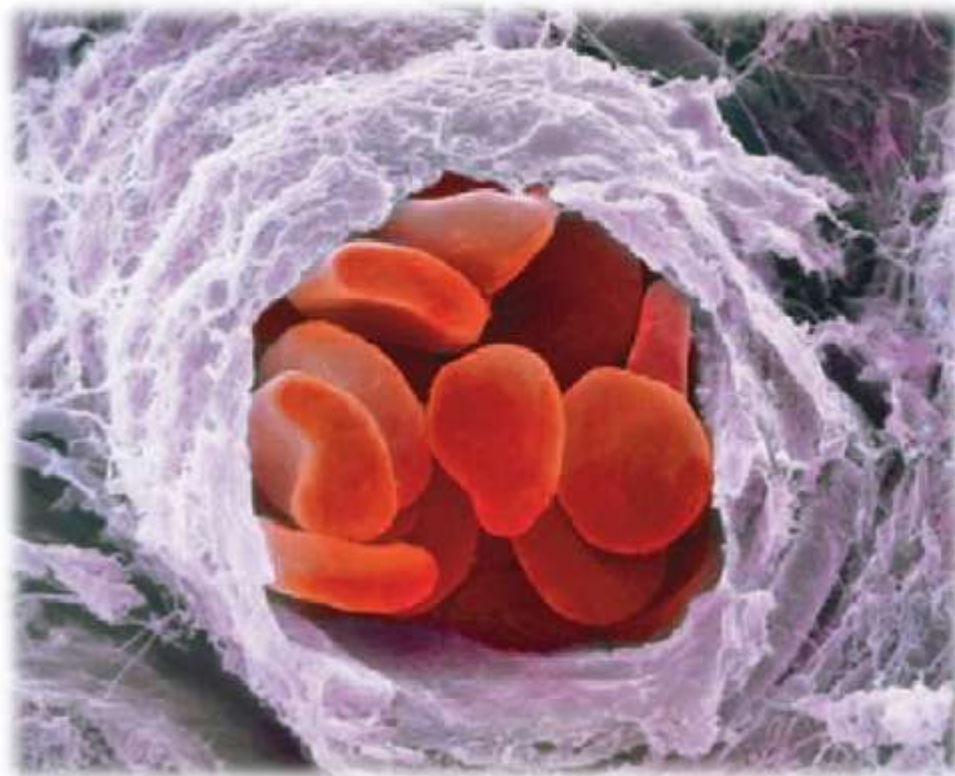
Solutions, which contain a weak conjugate acid-base pair, can resist drastic changes in pH upon the addition of small amounts of strong acid or base. These solutions are called **buffered solutions** (or merely buffers).



Human blood, is a complex aqueous mixture with a pH buffered at about 7.4. much of the chemical behavior of seawater is determined by its pH, buffered at about 8.1 to 8.3 near the surface. Buffered solutions find many important applications in the laboratory and in medicine.

Human blood is slightly basic with a normal pH of 7.35 to 7.45. death may result if the blood pH falls below 6.8 or rises above 7.8. when the pH falls below 7.35, the condition is called acidosis; when it rises above 7.45, the condition is called alkalosis.

The major buffer system that used to control the pH of blood is the carbonic acid-bicarbonate buffer system. The important equilibria in this buffer system are:



A scanning electromicrograph of a group red blood cells

# Composition and Action of Buffered Solutions

A buffer resists changes in pH because it contains both an acid to neutralize  $\text{OH}^-$  ions and a base to neutralize  $\text{H}^+$  ions.

The acid and base that make up the buffer, however, must not consume each other through a neutralization reaction. These requirements are fulfilled by a weak acid-base conjugate pair such as

$\text{CH}_3\text{COOH}-\text{CH}_3\text{COO}^-$  or  $\text{NH}_4^+-\text{NH}_3$ .

Thus, buffers are often prepared by mixing a weak acid or a weak base with a salt of that acid or base.

The  $\text{CH}_3\text{COOH}-\text{CH}_3\text{COO}^-$  buffer can be prepared, for example, by adding  $\text{CH}_3\text{COONa}$  to a solution of  $\text{CH}_3\text{COOH}$ . The  $\text{NH}_4^+-\text{NH}_3$  buffer can be prepared by adding  $\text{NH}_4\text{Cl}$  to a solution of  $\text{NH}_3$ . By choosing appropriate components and adjusting their relative concentrations, we can buffer a solution at virtually any pH.

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



The corresponding acid-dissociation-constant expression is

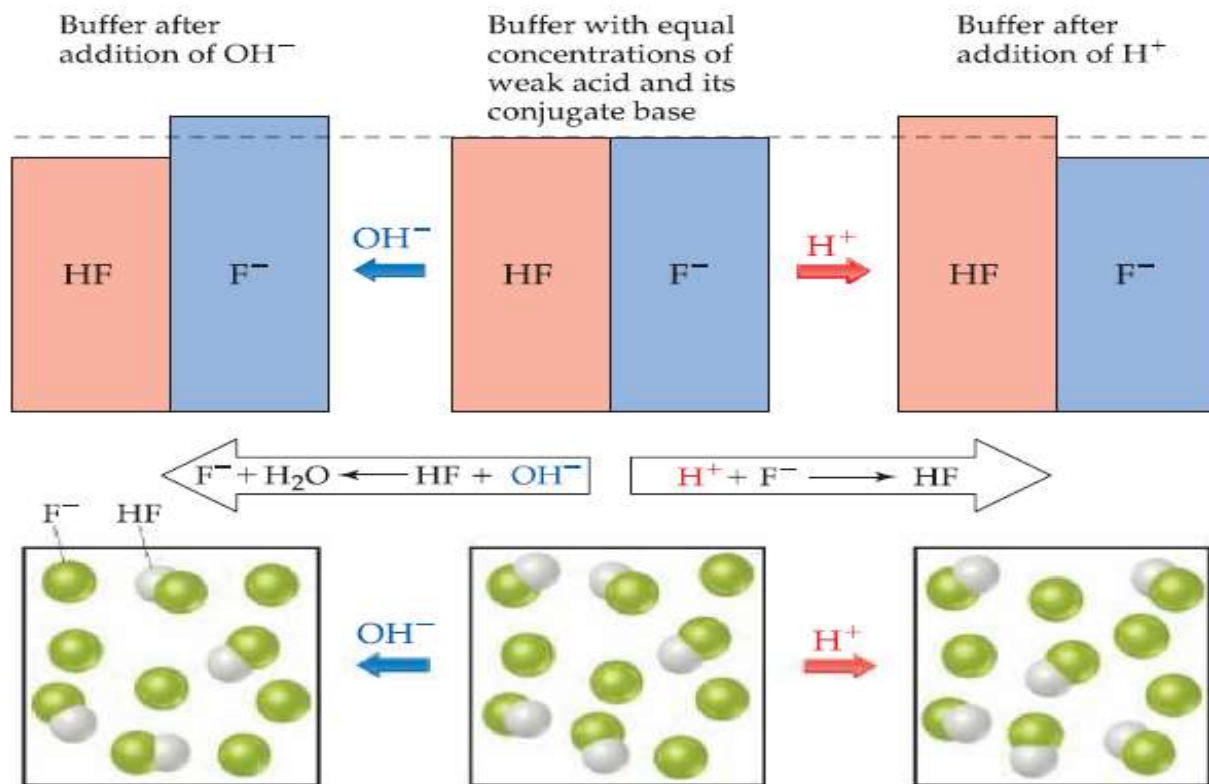
$$K_a = \frac{[H^+][X^-]}{[HX]}$$

Solving this expression for  $[H^+]$ , we have

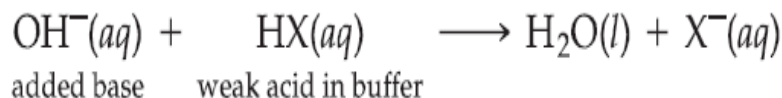
$$[H^+] = K_a \frac{[HX]}{[X^-]}$$

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

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

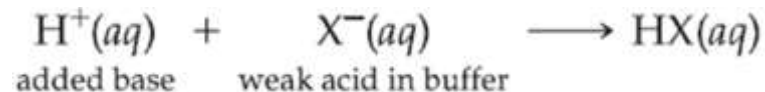


If  $\text{OH}^-$  ions are added to the buffered solution, they react with the acid component of the buffer to produce water and  $\text{X}^-$ :



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

If  $\text{H}^+$  ions are added, they react with the base component of the buffer:

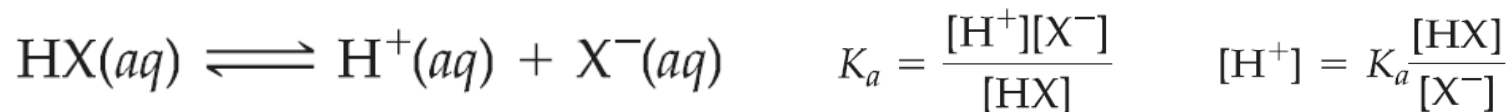


This reaction can also be represented using  $\text{H}_3\text{O}^+$ :



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

# Calculating the pH of a Buffer



Taking -log of both sides of equation, we have

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

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

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

In general,

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



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

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

Last Equation is known as the **Henderson-Hasselbalch equation**.

Biologists, biochemists, and others who work frequently with buffers often use this equation to calculate the pH of buffers.

In doing equilibrium calculations, we have seen that we can normally neglect the amounts of the acid and base of the buffer that ionize. Therefore, we can usually use the starting concentrations of the acid and base components of the buffer directly in the Henderson-Hasselbalch equation.

### Sample Exercise 17.3 Calculating the pH of a Buffer

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

#### Solution

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

	$\text{HC}_3\text{H}_5\text{O}_3(aq)$	$\rightleftharpoons$	$\text{H}^+(aq)$	+	$\text{C}_3\text{H}_5\text{O}_3^-(aq)$
Initial	0.12 <i>M</i>		0		0.10 <i>M</i>
Change	$-x$ <i>M</i>		$+x$ <i>M</i>		$+x$ <i>M</i>
Equilibrium	$(0.12 - x)$ <i>M</i>		$x$ <i>M</i>		$(0.10 + x)$ <i>M</i>

The equilibrium concentrations are governed by the equilibrium expression:

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

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

Solving for  $x$  gives a value that justifies our approximation:

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

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

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

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

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

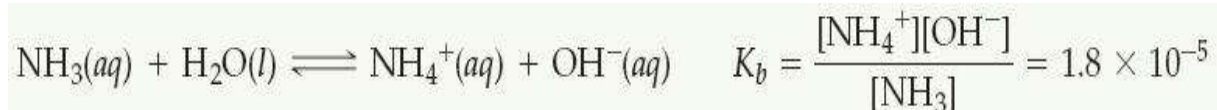
## Sample Exercise 17.4 Preparing a Buffer

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

### Solution

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

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



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

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

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

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

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

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

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

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

**Comment:** Because  $\text{NH}_4^+$  and  $\text{NH}_3$  are a conjugate acid–base pair, we could use the Henderson–Hasselbalch equation (Equation 17.9) to solve this problem. To do so requires first using Equation 16.41 to calculate  $\text{p}K_a$  for  $\text{NH}_4^+$  from the value of  $\text{p}K_b$  for  $\text{NH}_3$ . We suggest you try this approach to convince yourself that you can use the Henderson–Hasselbalch equation for buffers for which you are given  $K_b$  for the conjugate base rather than  $K_a$  for the conjugate acid.

# Buffer Capacity and pH Range

Two important characteristics of a buffer are its capacity and its effective pH range.

**Buffer capacity** is the amount of acid or base the buffer can neutralize before the pH begins to change to an appreciable degree. The buffer capacity depends on the amount of acid and base from which the buffer is made. The pH of the buffer depends on the  $K_a$  for the acid and on the relative concentrations of the acid and base that comprise the buffer.

According to the Equation below, for example,  $[H^+]$  for a 1-L solution that is 1 M in  $CH_3COOH$  and 1 M in  $CH_3COONa$  will be the same as for a 1-L solution that is 0.1 M in  $CH_3COOH$  and 1.0 M in  $CH_3COONa$ . The first solution has a greater buffering capacity, however, because it contains more  $CH_3COOH$  and  $CH_3COO^-$ . The greater the amounts of the conjugate acid-base pair, the more resistant is the ratio of their concentrations, and hence the pH, is to change.

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

The **pH range** of any buffer is the pH range over which the buffer system works or acts effectively.

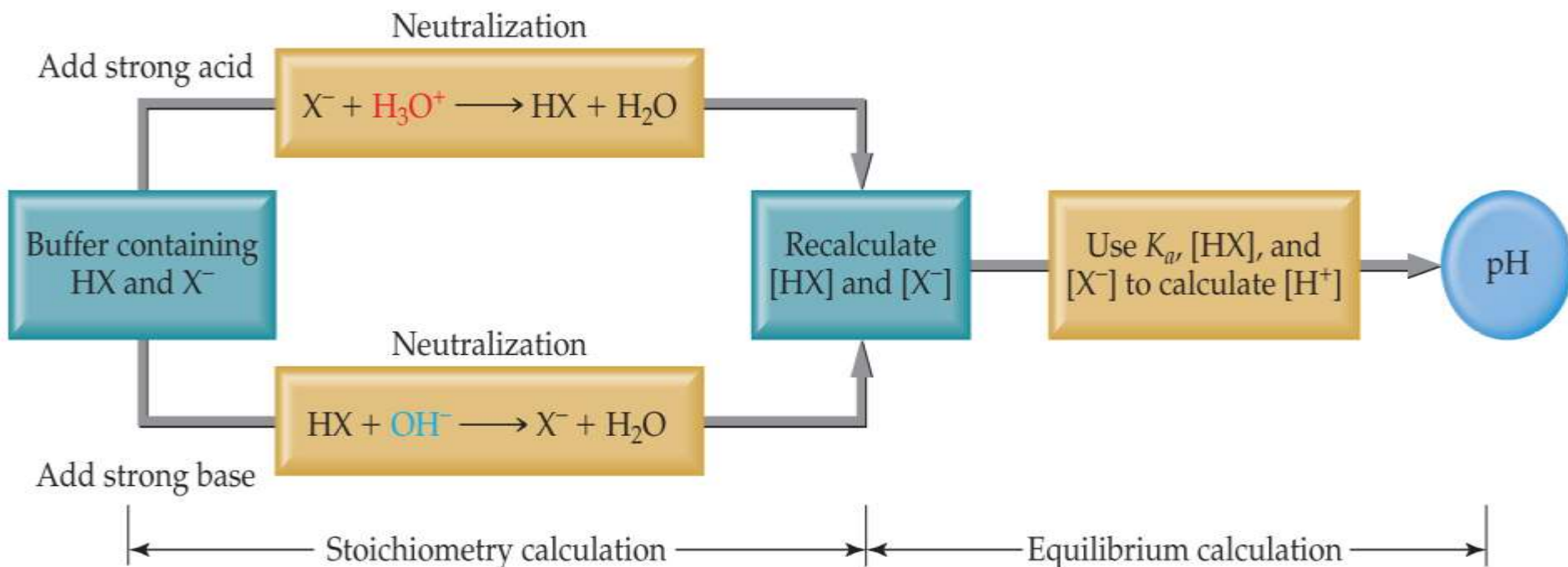
Buffers most effectively resist a change in pH in either direction when the concentrations of weak acid and conjugate base are about the same.

From Equation below, we see that when the concentrations of weak acid and conjugate base are equal,  $\text{pH} = \text{pK}_a$ . This relationship gives the optimal pH of any buffer. Thus, we usually try to select a buffer whose acid form has a  $\text{pK}_a$  close to the desired pH.

In practice, we find that if the concentration of one component of the buffer is more than 10 times the concentration of the other component, the buffering action is poor. Because  $\log 10 = 1$ , buffers usually have a usable range within  $\pm 1$  pH unit of  $\text{pK}_a$  (that is, a range of  $\text{pH} = \text{pK}_a \pm 1$ )

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

# Addition of Strong Acids or Bases to Buffers



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

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

It is important to understand that reactions between strong acids and weak bases proceed essentially to completion, as do those between strong bases and weak acids. Thus, as long as we do not exceed the buffering capacity of the buffer, we can assume that the strong acid or strong base is completely consumed by reaction with the buffer.

When a strong acid is added to the buffer, the added  $\text{H}^+$  is consumed by  $\text{X}^-$  to produce  $\text{HX}$ ; thus,  $[\text{HX}]$  increases and  $[\text{X}^-]$  decreases.

When a strong base is added to the buffer, the added  $\text{OH}^-$  is consumed by  $\text{HX}$  to produce  $\text{X}^-$ ; thus,  $[\text{HX}]$  decreases and  $[\text{X}^-]$  increases.

To calculate how the pH of the buffer responds to the addition of a strong acid or a strong base, we follow this strategy:

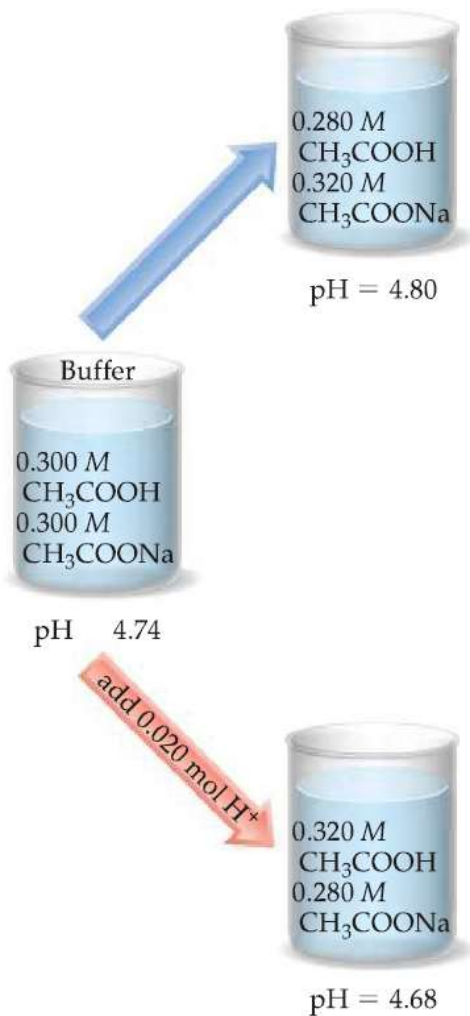
1. Determine how the neutralization reaction affects the amounts of the weak acid and its conjugate base in solution (**stoichiometry calculation**).
2. Use the Henderson–Hasselbalch equation to determine the new pH of the solution (**equilibrium calculation**).



## Sample Exercise 17.5 Calculating pH Changes in Buffers

A buffer is made by adding 0.300 mol  $\text{CH}_3\text{COOH}$  and 0.300 mol  $\text{CH}_3\text{COONa}$  to enough water to make 1.00 L of solution. The pH of the buffer is 4.74 (Sample Exercise 17.1). **(a)** Calculate the pH of this solution after 0.020 mol of  $\text{NaOH}$  is added. **(b)** For comparison, calculate the pH that would result if 0.020 mol of  $\text{NaOH}$  were added to 1.00 L of pure water (neglect any volume changes).

### Solution



**Stoichiometry Calculation:** The  $\text{OH}^-$  provided by  $\text{NaOH}$  reacts with  $\text{CH}_3\text{COOH}$ , the weak acid component of the buffer. Prior to this neutralization reaction, there are 0.300 mol each of  $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COO}^-$ . Neutralizing the 0.020 mol  $\text{OH}^-$  requires 0.020 mol of  $\text{CH}_3\text{COOH}$ . Consequently, the amount of  $\text{CH}_3\text{COOH}$  *decreases* by 0.020 mol, and the amount of the product of the neutralization,  $\text{CH}_3\text{COO}^-$ , *increases* by 0.020 mol. We can create a table to see how the composition of the buffer changes as a result of its reaction with  $\text{OH}^-$ :

	$\text{CH}_3\text{COOH}(aq) + \text{OH}^-(aq) \longrightarrow \text{H}_2\text{O}(l) + \text{CH}_3\text{COO}^-(aq)$			
Buffer before addition	0.300 mol	0	—	0.300 mol
Addition	—	0.020 mol		—
Buffer after addition	0.280 mol	0	—	0.320 mol

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



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

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



**Comment** Notice that we could have used mole amounts in place of concentrations in the Henderson–Hasselbalch equation and gotten the same result. The volumes of the acid and base are equal and cancel. If 0.020 mol of  $\text{H}^+$  was added to the buffer, we would proceed in a similar way to calculate the resulting pH of the buffer. In this case the pH decreases by 0.06 units, giving  $\text{pH} = 4.68$ , as shown in the figure in the margin.

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

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

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

# **17.3**

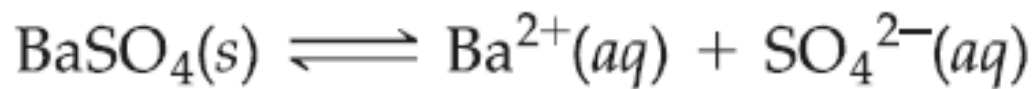
## **Solubility Equilibria**

The equilibria that we have considered thus far in this chapter have involved acids and bases. Furthermore, they have been homogeneous; that is, all the species have been in the same phase.

Through the rest of this chapter we will consider the equilibria involved in the dissolution or precipitation of ionic compounds. These reactions are heterogeneous.

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

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



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

Solids do not appear in the equilibrium-constant expressions for heterogeneous equilibria. The equilibrium constant expression for this equilibrium is

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

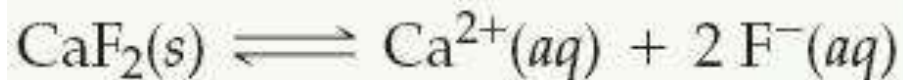
In general, the solubility product of a compound equals the product of the concentration of the ions involved in the equilibrium, each raised to the power of its coefficient in the equilibrium equation. The coefficient for each ion in the equilibrium equation also equals its subscript in the compound's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

The value of  $K_{sp}$  for  $\text{BaSO}_4$  is  $1.1 \times 10^{-10}$ , a very small number, indicating that only a very small amount of the solid will dissolve in water.

## Sample Exercise 17.9 Writing Solubility-Product ( $K_{sp}$ ) Expressions

Write the expression for the solubility-product constant  $K_{sp}$  for  $\text{CaF}_2$ .

### Solution



Following the italicized rule stated previously, the expression for is

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

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

# Solubility and $K_{sp}$

It is important to distinguish carefully between solubility and the solubility-product constant. The solubility of a substance is the quantity that dissolves to form a saturated solution. Solubility is often expressed as grams of solute per liter of solution (g/L). Molar solubility is the number of moles of the solute that dissolve in forming a liter of saturated solution of the solute (mol/L). The solubility-product constant ( $K_{sp}$ ) is the equilibrium constant for the equilibrium between an ionic solid and its saturated solution and is a unitless number. Thus, the magnitude of  $K_{sp}$  is a measure of how much of the solid dissolves to form a saturated solution.

## Relationships between solubility and $K_{sp}$



$K_{sp}$  is *not* the same as solubility.

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

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

The concentrations of ions calculated from  $K_{sp}$  sometimes deviate appreciably from those found experimentally. In part, these deviations are due to electrostatic interactions between ions in solution which can lead to ion pairs.



### Sample Exercise 17.10 Calculating $K_{sp}$ from Solubility

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

#### Solution

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



To calculate  $K_{sp}$ , we need the equilibrium concentrations of  $\text{Ag}^+$  and  $\text{CrO}_4^{2-}$ . We know that at equilibrium  $[\text{Ag}^+] = 1.3 \times 10^{-4} M$ . All the  $\text{Ag}^+$  and  $\text{CrO}_4^{2-}$  ions in the solution come from the  $\text{Ag}_2\text{CrO}_4$  that dissolves. Thus, we can use  $[\text{Ag}^+]$  to calculate  $[\text{CrO}_4^{2-}]$ .

From the chemical formula of silver chromate, we know that there must be 2  $\text{Ag}^+$  ions in solution for each  $\text{CrO}_4^{2-}$  ion in solution. Consequently, the concentration of  $\text{CrO}_4^{2-}$  is half the concentration of  $\text{Ag}^+$ :

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

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

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

### Sample Exercise 17.11 Calculating Solubility from $K_{sp}$

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

#### Solution

Assume initially that none of the salt has dissolved, and then allow  $x$  moles/liter of  $\text{CaF}_2$  to dissociate completely when equilibrium is achieved.

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

(Remember that  $\sqrt[3]{y} = y^{1/3}$  to calculate the cube root of a number, you can use the  $y\sqrt{x}$  function on your calculator. Thus, the molar solubility of  $\text{CaF}_2$  is  $2.1 \times 10^{-4}$  mol/L. The mass of  $\text{CaF}_2$  that dissolves in water to form a liter of solution is

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

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

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

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

**Comment:** Because  $\text{F}^-$  is the anion of a weak acid, you might expect that the hydrolysis of the ion would affect the solubility of  $\text{CaF}_2$ . The basicity of  $\text{F}^-$  is so small ( $K_b = 1.5 \times 10^{-11}$ ), however, that the hydrolysis occurs to only a slight extent and does not significantly influence the solubility. The reported solubility is  $0.017\text{ g/L}$  at  $25^\circ\text{C}$ , in good agreement with our calculation



Q & A



The addition of bromide ion will decrease the water solubility of which of the following salts?

- a.  $\text{BaSO}_4$
- b.  $\text{Li}_2\text{CO}_3$
- c.  $\text{PbS}$
- d.  $\text{AgBr}$

Which pair of compounds will form a buffer solution when dissolved in water in equimolar amounts?

- a. HCl and KCl
- b.  $\text{HNO}_3$  and  $\text{NaNO}_3$
- c. HCl and  $\text{NH}_4\text{Cl}$
- d.  $\text{NH}_3$  and  $\text{NH}_4\text{Cl}$

The  $K_a$  of HCN is  $4.9 \times 10^{-10}$ . What is the pH of a buffer solution that is 0.100 M in both HCN and KCN?

- a. 4.7
- b. 7.0
- c. 9.3
- d. 14.0

The  $K_a$  of HCN is  $4.9 \times 10^{-10}$ . What is the pH of a buffer solution that is 0.100  $M$  in HCN and 0.200  $M$  in KCN?

- a. 7.0
- b. 9.0
- c. 9.3
- d. 9.6

The  $K_a$  of HCN is  $4.9 \times 10^{-10}$ . What is the pH of a buffer solution that is 1.00 M in HCN and 0.100 M in KCN?

- a. 7.0
- b. 8.3
- c. 9.0
- d. 9.3



In titrating a weak base with a strong acid, the best indicator to use would be:

- a. methyl red (changes color at  $\text{pH} = 5$ ).
- b. bromothymol blue (changes at  $\text{pH} = 7$ ).
- c. phenolphthalein (changes at  $\text{pH} = 9$ ).
- d. none of the above.

In titrating a weak acid with a strong base, the best indicator to use would be:

- a. methyl red (changes color at  $\text{pH} = 5$ ).
- b. bromothymol blue (changes at  $\text{pH} = 7$ ).
- c. phenolphthalein (changes at  $\text{pH} = 9$ ).
- d. none of the above.

The  $K_{sp}$  of  $\text{BaCO}_3$  is  $5.0 \times 10^{-9}$ .  
What is the concentration of barium ion in a saturated aqueous solution of  $\text{BaCO}_3$ ?

- a.  $7.1 \times 10^{-5} \text{ M}$
- b.  $2.5 \times 10^{-9} \text{ M}$
- c.  $5.0 \times 10^{-9} \text{ M}$
- d.  $1.0 \times 10^{-8} \text{ M}$

The  $K_{sp}$  of  $\text{BaF}_2$  is  $1.7 \times 10^{-6}$ . What is the concentration of barium ion in a saturated aqueous solution of  $\text{BaF}_2$ ?

- a.  $1.7 \times 10^{-6} \text{ M}$
- b.  $3.4 \times 10^{-6} \text{ M}$
- c.  $7.6 \times 10^{-3} \text{ M}$
- d.  $1.5 \times 10^{-2} \text{ M}$

The  $K_{sp}$  of  $\text{BaF}_2$  is  $1.7 \times 10^{-6}$ . What is the concentration of fluoride ion in a saturated aqueous solution of  $\text{BaF}_2$ ?

- a.  $1.7 \times 10^{-6} \text{ M}$
- b.  $5.7 \times 10^{-5} \text{ M}$
- c.  $7.6 \times 10^{-3} \text{ M}$
- d.  $1.5 \times 10^{-2} \text{ M}$

# Which of the following will produce a buffer solution?

- $\text{HCl}/\text{NaCl}$
- $\text{HC}_2\text{H}_3\text{O}_2/\text{NH}_3$
- $\text{NaH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4$
- $\text{HNO}_3/\text{Ca}(\text{OH})_2$
- $\text{KNO}_3/\text{NaOH}$











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In an  $\text{NH}_4^+/\text{NH}_3$  buffer, what concentration changes will occur if a small amount of  $\text{OH}^-$  is added?

	$[\text{NH}_4^+]$	$[\text{NH}_3]$	pH
1.	Increase	Increase	Increase
2.	Decrease	Increase	Increase
3.	Increase	Decrease	Increase
4.	Increase	Decrease	Decrease
5.	Decrease	Increase	Decrease

Which indicator would best determine the endpoint of the titration of  $\text{NaC}_2\text{H}_3\text{O}_2$  with  $\text{HNO}_3$ ?

- Methyl violet
- **Methyl orange**
- Bromthymol blue
- Phenolphthalein
- Alizarin yellow R

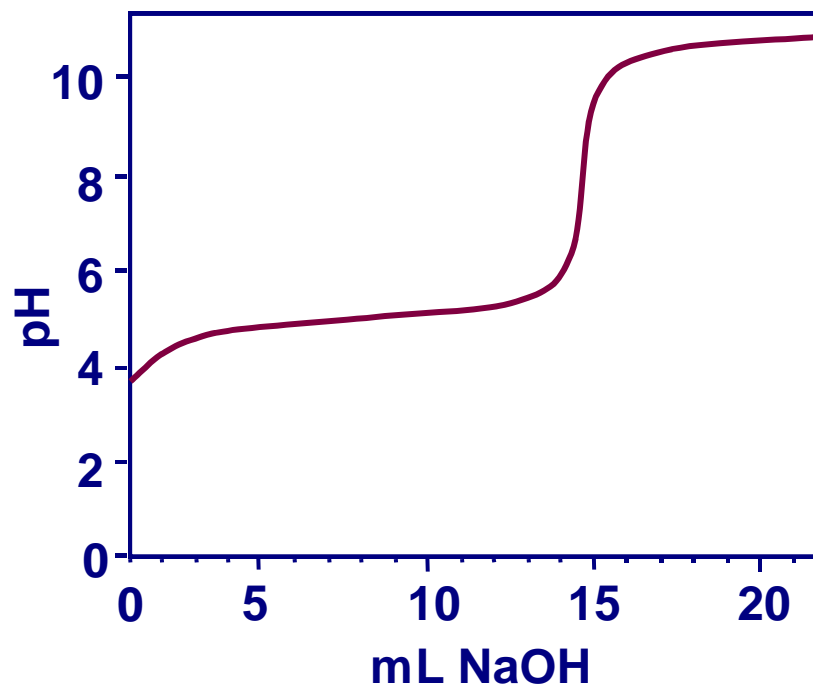
	pH range for color change									
	0	2	4	6	8	10	12	14		
Methyl violet	Yellow		Violet							
Thymol blue		Red		Yellow		Yellow		Blue		
Methyl orange			Red		Yellow					
Methyl red				Red		Yellow				
Bromthymol blue					Yellow		Blue			
Phenolphthalein						Colorless		Pink		
Alizarin yellow R							Yellow		Red	

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This titration curve was obtained in the titration of an unknown acid with 0.10 M NaOH. What is the  $pK_a$  of the acid?

- ~2
- ~4
- ~5
- ~7
- ~8



Addition of \_\_\_\_\_ will increase the solubility of  $\text{MgCO}_3$ .



- $\text{MgCl}_2$
- $\text{Na}_2\text{CO}_3$
- $\text{NaOH}$
- $\text{HCl}$
- $\text{KHCO}_3$

Which of the following conjugate acid-base pairs will not function as a buffer:

$\text{C}_2\text{H}_5\text{COOH}$  and  $\text{C}_2\text{H}_5\text{COO}^-$

$\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$

$\text{HNO}_3$  and  $\text{NO}_3^-$

***Answer:*** The  $\text{HNO}_3$  will not work as buffer because it is strong acid.

Predict which of the following compounds will have the greatest molar solubility in water: AgCl ( $K_{sp} = 1.8 \times 10^{-10}$ ),  
AgBr ( $K_{sp} = 5.0 \times 10^{-13}$ ),  
AgI ( $K_{sp} = 8.3 \times 10^{-17}$ ).

***Answer.*** AgCl > AgBr > AgI

Calculate the pH of a solution containing 0.085 *M* nitrous acid ( $\text{HNO}_2$ ;  $K_a = 4.5 \times 10^{-4}$ ) and 0.10 *M* potassium nitrite ( $\text{KNO}_2$ ).

***Answer: 3.42***

Calculate the formate ion concentration and pH of a solution that is 0.050  $M$  in formic acid ( $\text{HCOOH}$ ;  $K_a = 1.8 \times 10^{-4}$ ) and 0.10  $M$  in  $\text{HNO}_3$ .

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

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

***Answer: 4.42***

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

***Answer: 0.13 M***



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

***Answers: (a) 4.68, (b) 1.70***

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

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

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

***Answer:***  $1.6 \times 10^{-12}$

The  $K_{sp}$  for  $\text{LaF}_3$  is  $2 \times 10^{-19}$ . What is the solubility of  $\text{LaF}_3$  in water in moles per liter?

***Answer:***  $9 \times 10^{-6} \text{ mol/L}$

