



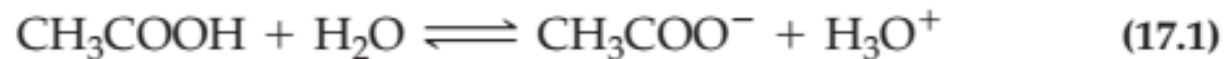
## Additional Aspects of Acid–Base Equilibria

In this section, we will consider the acid-base properties of a solution with two dissolved solutes that contain the same ion (cation or anion), called the common ion.

## The Common Ion Effect:

### Solutions of Weak Acids and Strong Acids

Consider a solution that is at the same time 0.100 M  $\text{CH}_3\text{COOH}$  and 0.100 M  $\text{HCl}$ . We can write separate equations for the ionizations of the acids, one weak and the other strong. The ionization of  $\text{CH}_3\text{COOH}$  produces  $\text{CH}_3\text{COO}^-$  ions:



The ionization of  $\text{HCl}$  produces  $\text{H}_3\text{O}^+$  and  $\text{Cl}^-$  ions.



Because  $\text{H}_3\text{O}^+$  is formed in both ionization processes, we say that  $\text{H}_3\text{O}^+$  is a *common ion*. An important point concerning the common ion,  $\text{H}_3\text{O}^+$ , is that  $[\text{H}_3\text{O}^+]$  appears in the equilibrium constant expressions for both reactions. Therefore, the ionization of  $\text{HCl}$  affects the equilibrium position of reaction (17.1), and, in principle, the ionization of  $\text{CH}_3\text{COOH}$  affects the equilibrium position of reaction (17.2). We will now investigate the extent to which the ionization of each acid is affected by the other acid.

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

**EXAMPLE 17-1**     **Demonstrating the Common-Ion Effect: A Solution of a Weak Acid and a Strong Acid**

- (a) Determine  $[\text{H}_3\text{O}^+]$  and  $[\text{CH}_3\text{COO}^-]$  in 0.100 M  $\text{CH}_3\text{COOH}$ . (b) Then determine these same quantities in a solution that is 0.100 M in both  $\text{CH}_3\text{COOH}$  and  $\text{HCl}$ .

### EXAMPLE 17-1    Demonstrating the Common-Ion Effect: A Solution of a Weak Acid and a Strong Acid

- (a) Determine  $[\text{H}_3\text{O}^+]$  and  $[\text{CH}_3\text{COO}^-]$  in 0.100 M  $\text{CH}_3\text{COOH}$ . (b) Then determine these same quantities in a solution that is 0.100 M in both  $\text{CH}_3\text{COOH}$  and  $\text{HCl}$ .

#### Solve

- (a) This calculation was done in Example 16-8 (page 754). We found that in 0.100 M  $\text{CH}_3\text{COOH}$ ,  $[\text{H}_3\text{O}^+] = [\text{CH}_3\text{COO}^-] = 1.3 \times 10^{-3} \text{ M}$ .
- (b) Because  $\text{HCl}$  ionizes completely, the ionization of  $\text{CH}_3\text{COOH}$  is the only equilibrium we need to consider. However, the  $\text{H}_3\text{O}^+$  produced by the ionization of  $\text{HCl}$  cannot be ignored. To account for the  $\text{H}_3\text{O}^+$  produced by the ionization of  $\text{HCl}$ , we use 0.100 M for the initial concentration of  $\text{H}_3\text{O}^+$  in the following equilibrium summary.

	$\text{CH}_3\text{COOH}$	+	$\text{H}_2\text{O}$	$\rightleftharpoons$	$\text{CH}_3\text{COO}^-$	+	$\text{H}_3\text{O}^+$
initial concns:	0.100 M				0 M		0.100 M
changes:	$-x \text{ M}$				$+x \text{ M}$		$+x \text{ M}$
equil concns:	$(0.100 - x) \text{ M}$				$x \text{ M}$		$(0.100 + x) \text{ M}$

We begin by assuming that  $x$  is very small compared with 0.100. Thus,  $0.100 - x \approx 0.100$  and  $0.100 + x \approx 0.100$ .

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{(0.100 + x) \cdot x}{0.100 - x} \approx \frac{0.100 \cdot x}{0.100} = 1.8 \times 10^{-5}$$

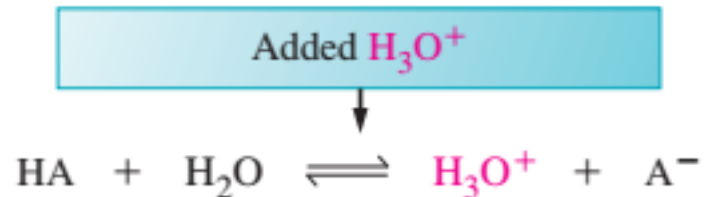
We see that  $x = 1.8 \times 10^{-5}$ . Since  $[\text{CH}_3\text{COO}^-] = x \text{ M}$  and  $[\text{CH}_3\text{COOH}] = (0.100 + x) \text{ M}$ , then

$$[\text{CH}_3\text{COO}^-] = 1.8 \times 10^{-5} \text{ M} \quad \text{and} \quad [\text{CH}_3\text{COOH}] = 0.100 \text{ M}$$

Notice that  $x$  is only 0.018% of 0.100, and so the assumption that  $x$  is small compared with 0.100 is valid.

Example 17-1 illustrates that the ionization of a weak acid is significantly suppressed by the presence (or addition) of a strong acid. It is also the case that the ionization of a weak base is significantly suppressed by the presence or addition of a strong base. These statements can be justified by applying Le Châtelier's principle. Let's first consider a solution of a weak acid, HA, that has reached equilibrium. The effect of adding strong acid is illustrated below. For a solution of a weak base, B, that has reached equilibrium, the effect of adding a strong base can be described similarly.

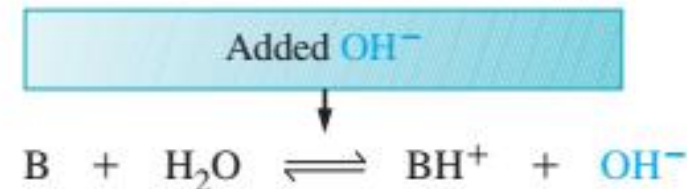
When a strong acid supplies the common ion  $\text{H}_3\text{O}^+$ ,  
the equilibrium shifts to form more HA



The equilibrium shifts to the left.  
The ionization of HA is suppressed.



When a strong base supplies the common ion  $\text{OH}^-$ ,  
the equilibrium shifts to form more B.

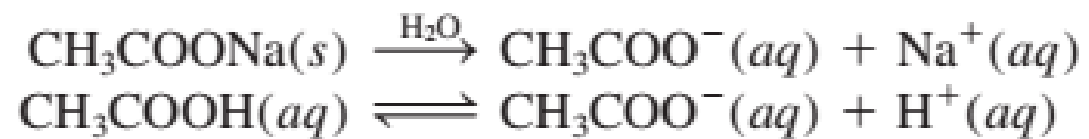


The equilibrium shifts to the left.  
The ionization of B is suppressed.

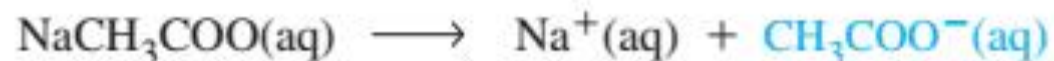


## Solutions of Weak Acids and Their Salts

If sodium acetate and acetic acid are dissolved in the same solution, for example, they both dissociate and ionize to produce  $\text{CH}_3\text{COO}^-$  ions:



When a salt supplies the common anion  $\text{CH}_3\text{COO}^-$ ,  
the equilibrium shifts to form more  $\text{CH}_3\text{COOH}$ .



Added  $\text{CH}_3\text{COO}^-$



The equilibrium shifts to the left.  
The ionization of  $\text{CH}_3\text{COOH}$  is suppressed.



The common ion effect is the shift in equilibrium caused by the addition of a compound having an ion in common with the dissolved substance. The common ion effect plays an important role in determining the pH of a solution. Here we will study the common ion effect as it relates to the pH of a solution. Keep in mind that despite its distinctive name, the common ion effect is simply a special case of Le Châtelier's principle.



The ionization of a weak electrolyte is suppressed by the addition of an ion that is the product of the ionization and is known as [the common-ion effect](#).

## EXAMPLE 16.1

(a) Calculate the pH of a 0.20 *M* CH<sub>3</sub>COOH solution. (b) What is the pH of a solution containing both 0.20 *M* CH<sub>3</sub>COOH and 0.30 *M* CH<sub>3</sub>COONa? The *K*<sub>a</sub> of CH<sub>3</sub>COOH is  $1.8 \times 10^{-5}$ .

### EXAMPLE 16.1

(a) Calculate the pH of a 0.20 M  $\text{CH}_3\text{COOH}$  solution. (b) What is the pH of a solution containing both 0.20 M  $\text{CH}_3\text{COOH}$  and 0.30 M  $\text{CH}_3\text{COONa}$ ? The  $K_a$  of  $\text{CH}_3\text{COOH}$  is  $1.8 \times 10^{-5}$ .

**Solution** (a) In this case, the changes are

	$\text{CH}_3\text{COOH}(aq) \rightleftharpoons \text{H}^+(aq) + \text{CH}_3\text{COO}^-(aq)$		
Initial (M):	0.20	0	0
Change (M):	$-x$	$+x$	$+x$
Equilibrium (M):	$0.20 - x$	$x$	$x$

$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$
$$1.8 \times 10^{-5} = \frac{x^2}{0.20 - x}$$

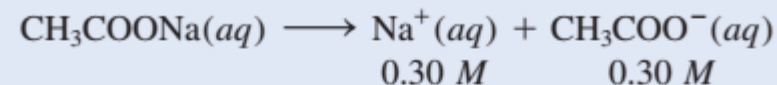
Assuming  $0.20 - x \approx 0.20$ , we obtain

$$1.8 \times 10^{-5} = \frac{x^2}{0.20 - x} \approx \frac{x^2}{0.20}$$

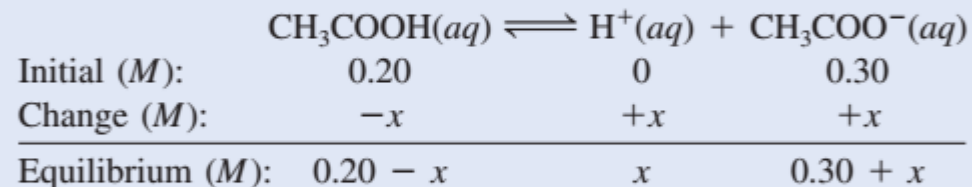
or 
$$x = [\text{H}^+] = 1.9 \times 10^{-3} \text{ M}$$

Thus, 
$$\text{pH} = -\log(1.9 \times 10^{-3}) = 2.72$$

(b) Sodium acetate is a strong electrolyte, so it dissociates completely in solution:



The initial concentrations, changes, and final concentrations of the species involved in the equilibrium are



From Equation (16.1),

$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$
$$1.8 \times 10^{-5} = \frac{(x)(0.30 + x)}{0.20 - x}$$

Assuming that  $0.30 + x \approx 0.30$  and  $0.20 - x \approx 0.20$ , we obtain

$$1.8 \times 10^{-5} = \frac{(x)(0.30 + x)}{0.20 - x} \approx \frac{(x)(0.30)}{0.20}$$

or  $x = [\text{H}^+] = 1.2 \times 10^{-5}\text{ M}$

Thus,  $\text{pH} = -\log [\text{H}^+]$   
 $= -\log (1.2 \times 10^{-5}) = 4.92$

## Buffer Solutions

A buffer solution is a solution of (1) a weak acid or a weak base and (2) its salt; both components must be present. The solution has the ability to resist changes in pH upon the addition of small amounts of either acid or base. Buffers are very important to chemical and biological systems.

The pH in the human body varies greatly from one fluid to another; for example, the pH of blood is about 7.4, whereas the gastric juice in our stomachs has a pH of about 1.5. These pH values, which are crucial for proper enzyme function and the balance of osmotic pressure, are maintained by buffers in most cases.

A buffer solution must contain a relatively large concentration of acid to react with any  $\text{OH}^-$  ions that are added to it, and it must contain a similar concentration of base to react with any added  $\text{H}^+$  ions. Furthermore, the acid and the base components of the buffer must not consume each other in a neutralization reaction. These requirements are satisfied by an acid-base conjugate pair, for example, a weak acid and its conjugate base (supplied by a salt) or a weak base and its conjugate acid (supplied by a salt).

A simple buffer solution can be prepared by adding comparable molar amounts of acetic acid ( $\text{CH}_3\text{COOH}$ ) and its salt sodium acetate ( $\text{CH}_3\text{COONa}$ ) to water. The equilibrium concentrations of both the acid and the conjugate base (from  $\text{CH}_3\text{COONa}$ ) are assumed to be the same as the starting concentrations. A solution containing these two substances has the ability to neutralize either added acid or added base. Sodium acetate, a strong electrolyte, dissociates completely in water:

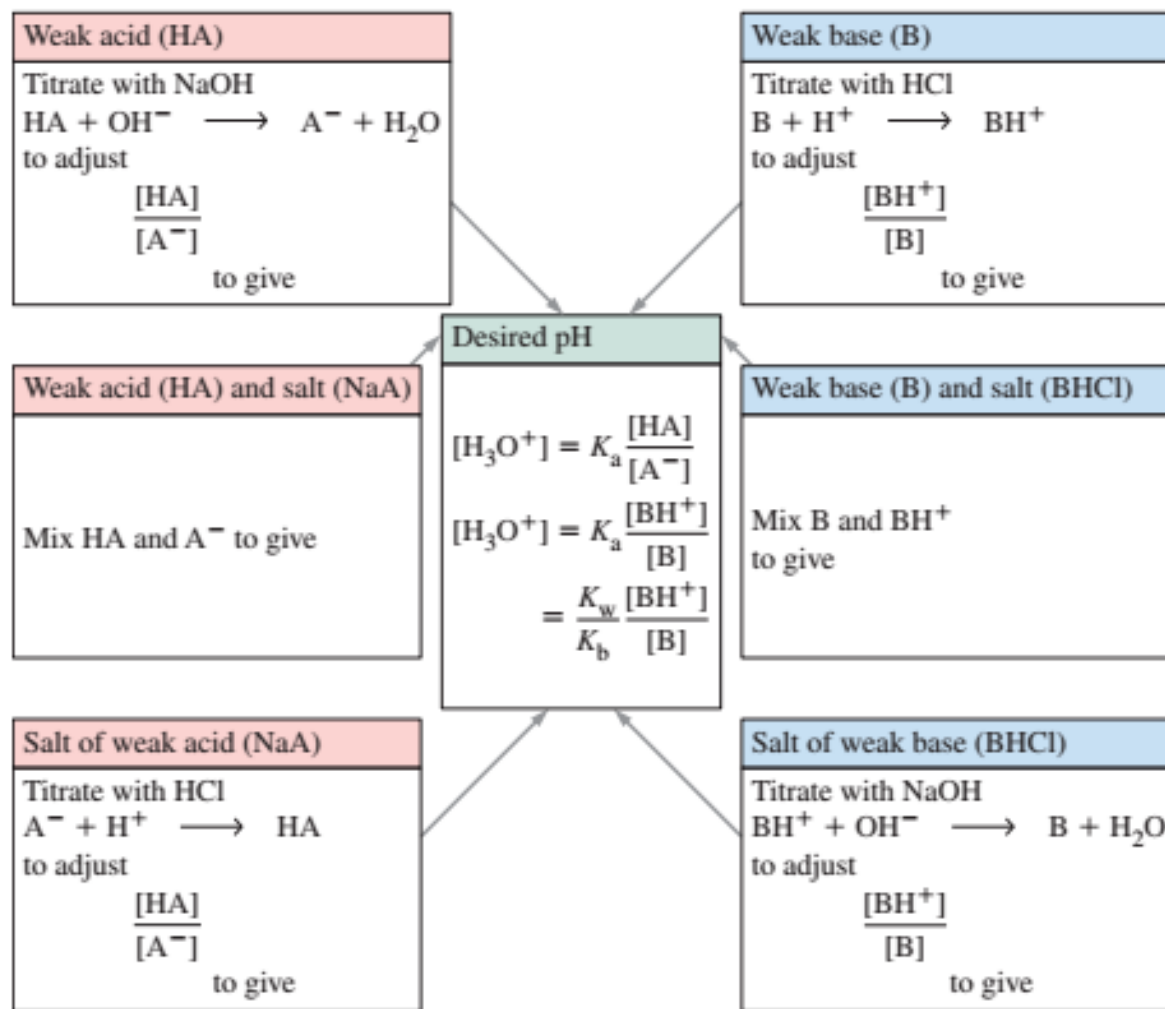


If a base is added to the buffer system, the  $\text{OH}^-$  ions will be neutralized by the acid in the buffer:



If an acid is added, the  $\text{H}^+$  ions will be consumed by the conjugate base in the buffer,





▲ FIGURE 17-5

**Six methods for preparing buffer solutions**

Depending on the pH range required and the type of experiment the buffer is to be used for, either a weak acid or a weak base can be used to prepare a buffer solution.

## EXAMPLE 16.2

Which of the following solutions can be classified as buffer systems? (a)  $\text{KH}_2\text{PO}_4/\text{H}_3\text{PO}_4$ , (b)  $\text{NaClO}_4/\text{HClO}_4$ , (c)  $\text{C}_5\text{H}_5\text{N}/\text{C}_5\text{H}_5\text{NHCl}$  ( $\text{C}_5\text{H}_5\text{N}$  is pyridine; its  $K_b$  is given in Table 15.4). Explain your answer.



## EXAMPLE 16.2

Which of the following solutions can be classified as buffer systems? (a)  $\text{KH}_2\text{PO}_4/\text{H}_3\text{PO}_4$ , (b)  $\text{NaClO}_4/\text{HClO}_4$ , (c)  $\text{C}_5\text{H}_5\text{N}/\text{C}_5\text{H}_5\text{NHCl}$  ( $\text{C}_5\text{H}_5\text{N}$  is pyridine; its  $K_b$  is given in Table 15.4). Explain your answer.

**Solution** The criteria for a buffer system is that we must have a weak acid and its salt (containing the weak conjugate base) or a weak base and its salt (containing the weak conjugate acid).

- (a)  $\text{H}_3\text{PO}_4$  is a weak acid, and its conjugate base,  $\text{H}_2\text{PO}_4^-$ , is a weak base (see Table 15.5). Therefore, this is a buffer system.
- (b) Because  $\text{HClO}_4$  is a strong acid, its conjugate base,  $\text{ClO}_4^-$ , is an extremely weak base. This means that the  $\text{ClO}_4^-$  ion will not combine with a  $\text{H}^+$  ion in solution to form  $\text{HClO}_4$ . Thus, the system cannot act as a buffer system.
- (c) As Table 15.4 shows,  $\text{C}_5\text{H}_5\text{N}$  is a weak base and its conjugate acid,  $\text{C}_5\text{H}_5\text{NH}^+$  (the cation of the salt  $\text{C}_5\text{H}_5\text{NHCl}$ ), is a weak acid. Therefore, this is a buffer system.

### EXAMPLE 16.3

(a) Calculate the pH of a buffer system containing 1.0 *M* CH<sub>3</sub>COOH and 1.0 *M* CH<sub>3</sub>COONa. (b) What is the pH of the buffer system after the addition of 0.10 mole of gaseous HCl to 1.0 L of the solution? Assume that the volume of the solution does not change when the HCl is added.

### EXAMPLE 16.3

(a) Calculate the pH of a buffer system containing 1.0 M  $\text{CH}_3\text{COOH}$  and 1.0 M  $\text{CH}_3\text{COONa}$ . (b) What is the pH of the buffer system after the addition of 0.10 mole of gaseous  $\text{HCl}$  to 1.0 L of the solution? Assume that the volume of the solution does not change when the  $\text{HCl}$  is added.

**Solution** (a) We summarize the concentrations of the species at equilibrium as follows:

	$\text{CH}_3\text{COOH}(aq)$	$\rightleftharpoons$	$\text{H}^+(aq)$	+	$\text{CH}_3\text{COO}^-(aq)$
Initial ( $M$ ):	1.0		0		1.0
Change ( $M$ ):	$-x$		$+x$		$+x$
Equilibrium ( $M$ ):	$1.0 - x$		$x$		$1.0 + x$

$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$
$$1.8 \times 10^{-5} = \frac{(x)(1.0 + x)}{(1.0 - x)}$$

Assuming  $1.0 + x \approx 1.0$  and  $1.0 - x \approx 1.0$ , we obtain

$$1.8 \times 10^{-5} = \frac{(x)(1.0 + x)}{(1.0 - x)} \approx \frac{x(1.0)}{1.0}$$

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

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

(b) When HCl is added to the solution, the initial changes are

	$\text{HCl}(aq) \longrightarrow \text{H}^+(aq) + \text{Cl}^-(aq)$		
Initial (mol):	0.10	0	0
Change (mol):	-0.10	+0.10	+0.10
Final (mol):	0	0.10	0.10

The  $\text{Cl}^-$  ion is a spectator ion in solution because it is the conjugate base of a strong acid.

The  $\text{H}^+$  ions provided by the strong acid HCl react completely with the conjugate base of the buffer, which is  $\text{CH}_3\text{COO}^-$ . At this point it is more convenient to work with moles rather than molarity. The reason is that in some cases the volume of the solution may change when a substance is added. A change in volume will change the molarity, but not the number of moles. The neutralization reaction is summarized next:

	$\text{CH}_3\text{COO}^-(aq) + \text{H}^+(aq) \longrightarrow \text{CH}_3\text{COOH}(aq)$		
Initial (mol):	1.0	0.10	1.0
Change (mol):	-0.10	-0.10	+0.10
Final (mol):	0.90	0	1.1

Finally, to calculate the pH of the buffer after neutralization of the acid, we convert back to molarity by dividing moles by 1.0 L of solution.

	$\text{CH}_3\text{COOH}(aq) \rightleftharpoons \text{H}^+(aq) + \text{CH}_3\text{COO}^-(aq)$		
Initial ( <i>M</i> ):	1.1	0	0.90
Change ( <i>M</i> ):	- <i>x</i>	+ <i>x</i>	+ <i>x</i>
Equilibrium ( <i>M</i> ):	$1.1 - x$	<i>x</i>	$0.90 + x$

$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$
$$1.8 \times 10^{-5} = \frac{(x)(0.90 + x)}{1.1 - x}$$

Assuming  $0.90 + x \approx 0.90$  and  $1.1 - x \approx 1.1$ , we obtain

$$1.8 \times 10^{-5} = \frac{(x)(0.90 + x)}{1.1 - x} \approx \frac{x(0.90)}{1.1}$$

or

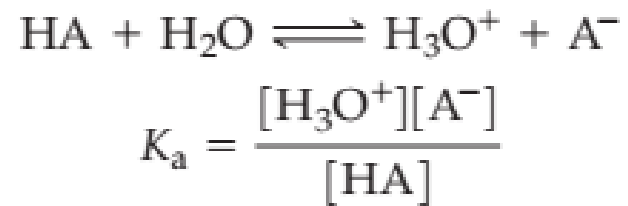
$$x = [\text{H}^+] = 2.2 \times 10^{-5} \text{ M}$$

Thus,

$$\text{pH} = -\log(2.2 \times 10^{-5}) = 4.66$$

## An Equation for Buffer Solutions: The Henderson–Hasselbalch Equation

For buffer calculations, it is often useful to describe a buffer solution by means of an equation known as the Henderson–Hasselbalch equation. Biochemists and molecular biologists commonly use this equation. To derive this variation of the ionization constant expression, let's consider a mixture of a hypothetical weak acid, HA and its salt, NaA. We start with the familiar expressions



and rearrange the right side of the  $K_a$  expression to obtain

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

Next, we take the *negative logarithm* of each side of this equation.

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

Now, recall that  $\text{pH} = -\log[\text{H}_3\text{O}^+]$  and that  $\text{p}K_a = -\log K_a$ , which gives

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

Solve for pH by rearranging the equation.

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

$\text{A}^-$  is the conjugate base of the weak acid HA, so we can write the more general equation (17.7), the Henderson–Hasselbalch equation.

$$\text{pH} = \text{p}K_a + \log \frac{[\text{conjugate base}]}{[\text{acid}]} \quad (17.7)$$

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

### EXAMPLE 17-5      Preparing a Buffer Solution of a Desired pH

What mass of  $\text{NaCH}_3\text{COO}$  must be dissolved in 0.300 L of 0.25 M  $\text{CH}_3\text{COOH}$  to produce a solution with  $\text{pH} = 5.09$ ? Assume that the solution volume remains constant at 0.300 L.

### EXAMPLE 17-5 Preparing a Buffer Solution of a Desired pH

What mass of  $\text{NaCH}_3\text{COO}$  must be dissolved in 0.300 L of 0.25 M  $\text{CH}_3\text{COOH}$  to produce a solution with  $\text{pH} = 5.09$ ? Assume that the solution volume remains constant at 0.300 L.

#### Solve

The relevant concentration terms, then, are

$$\begin{aligned}[\text{H}_3\text{O}^+] &= 10^{-\text{pH}} = 10^{-5.09} = 8.1 \times 10^{-6} \text{ M} \\ [\text{CH}_3\text{COOH}] &= 0.25 \text{ M} \\ [\text{CH}_3\text{COO}^-] &= ?\end{aligned}$$

The required acetate ion concentration in the buffer solution is

$$[\text{CH}_3\text{COO}^-] = K_a \times \frac{[\text{CH}_3\text{COOH}]}{[\text{H}_3\text{O}^+]} = 1.8 \times 10^{-5} \times \frac{0.25}{8.1 \times 10^{-6}} = 0.56 \text{ M}$$

We complete the calculation of the mass of sodium acetate with some familiar ideas of solution stoichiometry.

$$\begin{aligned}\text{mass} &= 0.300 \text{ L} \times \frac{0.56 \text{ mol CH}_3\text{COO}^-}{1 \text{ L}} \times \frac{1 \text{ mol NaCH}_3\text{COO}}{1 \text{ mol CH}_3\text{COO}^-} \\ &\quad \times \frac{82.0 \text{ g NaCH}_3\text{COO}}{1 \text{ mol NaCH}_3\text{COO}} = 14 \text{ g NaCH}_3\text{COO}\end{aligned}$$

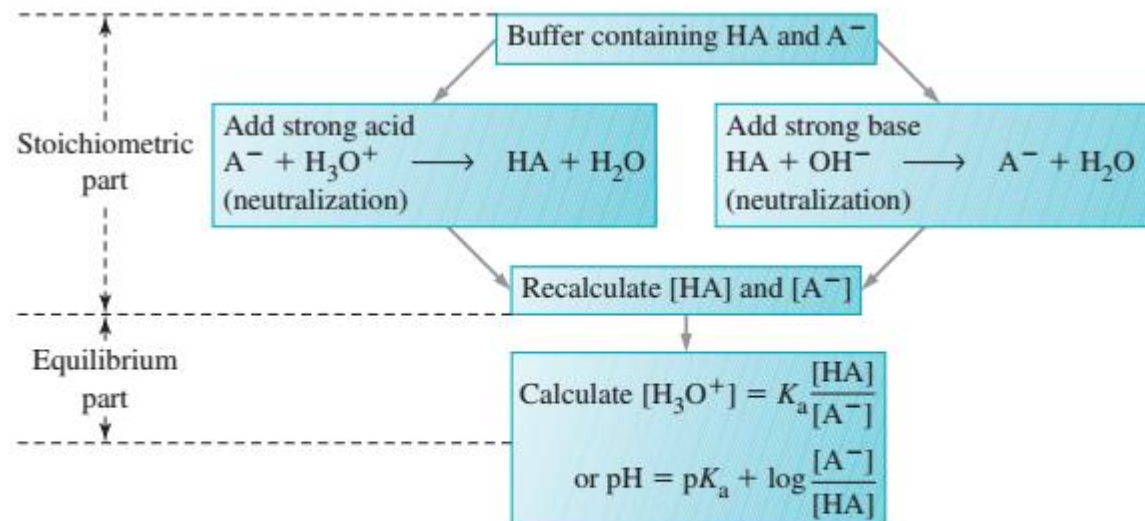


## Calculating pH Changes in Buffer Solutions

To calculate how the pH of a buffer solution changes when small amounts of a strong acid or base are added, we must first use stoichiometric principles to establish how much of one buffer component is consumed and how much of the other component is produced. Then the new concentrations of weak acid (or weak base) and its salt can be used to calculate the pH of the buffer solution. Essentially, this problem is solved in two steps.

First, we assume that the neutralization reaction proceeds to completion and determine new stoichiometric concentrations.

Then these new stoichiometric concentrations are substituted into the equilibrium constant expression and the expression is solved for which is converted to pH. This method is applied in Example 17-6 and illustrated in Figure 17-6.



▲ FIGURE 17-6  
**Calculation of the new pH of a buffer after strong acid or base is added**  
The stoichiometric and equilibrium parts of the calculation are indicated. This scheme can also be applied to the conjugate acid–base pair  $BH^+/B$ , where B is a base.

### EXAMPLE 17-6      Calculating pH Changes in a Buffer Solution

What are the effects on the pH of adding **(a)** 0.0060 mol HCl and **(b)** 0.0060 mol NaOH to 0.300 L of a buffer solution that is 0.250 M  $\text{CH}_3\text{COOH}$  and 0.560 M  $\text{NaCH}_3\text{COO}$ ?

## Solve

To judge the effect of adding either (a) acid or (b) base on the pH of the buffer, the value we must keep in mind is the pH of the original buffer. Because the initial (or stoichiometric) concentrations of  $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COO}^-$  are large and not too different, the initial pH of the buffer can be obtained by substituting the initial concentrations into equation (17.7). (See the discussion following equation (17.7) on page 799.)

$$\begin{aligned}\text{pH} &= \text{p}K_a + \log \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} \\ &= 4.74 + \log \frac{0.560}{0.250} = 4.74 + 0.35 = 5.09\end{aligned}$$

- (a) **Stoichiometric Calculation:** Let's calculate amounts in moles, and assume that the neutralization goes to completion. Essentially, this is a limiting reactant calculation, but perhaps simpler than many of those in Chapter 4. In neutralizing the added  $\text{H}_3\text{O}^+$ , 0.0060 mol  $\text{CH}_3\text{COO}^-$  is converted to 0.0060 mol  $\text{CH}_3\text{COOH}$ .

	$\text{CH}_3\text{COO}^-$	+	$\text{H}_3\text{O}^+$	$\longrightarrow$	$\text{CH}_3\text{COOH}$	+	$\text{H}_2\text{O}$
original buffer:	$\frac{0.300 \text{ L} \times 0.560 \text{ M}}{0.168 \text{ mol}}$				$\frac{0.300 \text{ L} \times 0.250 \text{ M}}{0.0750 \text{ mol}}$		
add:			0.0060 mol				
changes:	-0.0060 mol		-0.0060 mol		+0.0060 mol		
final buffer:							
amounts:	0.162 mol		$\approx 0$		0.0810 mol		
concns:	$\frac{0.162 \text{ mol}/0.300 \text{ L}}{0.540 \text{ M}}$		$\approx 0$		$\frac{0.0810 \text{ mol}/0.300 \text{ L}}{0.270 \text{ M}}$		

**Equilibrium Calculation:** We can calculate the pH with equation (17.7), using the new equilibrium concentrations.

$$\begin{aligned}\text{pH} &= \text{p}K_a + \log \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} \\ &= 4.74 + \log \frac{0.540}{0.270} = 4.74 + 0.30 = 5.04\end{aligned}$$

**(b) Stoichiometric Calculation:** In neutralizing the added  $\text{OH}^-$ , 0.0060 mol  $\text{CH}_3\text{COOH}$  is converted to 0.0060 mol  $\text{CH}_3\text{COO}^-$ . The calculation of the new stoichiometric concentrations is shown on the last line of the following table.

	$\text{CH}_3\text{COOH}$	+	$\text{OH}^-$	$\longrightarrow$	$\text{CH}_3\text{COO}^-$	+	$\text{H}_2\text{O}$
original buffer:	$\frac{0.300 \text{ L} \times 0.250 \text{ M}}{0.0750 \text{ mol}}$				$\frac{0.300 \text{ L} \times 0.560 \text{ M}}{0.168 \text{ mol}}$		
add:			0.0060 mol				
changes:	-0.0060 mol		-0.0060 mol		+0.0060 mol		
final buffer:							
amounts:	0.0690 mol		$\approx 0$		0.174 mol		
concns:	$\frac{0.0690 \text{ mol}/0.300 \text{ L}}{0.230 \text{ M}}$		$\approx 0$		$\frac{0.174 \text{ mol}/0.300 \text{ L}}{0.580 \text{ M}}$		

**Equilibrium Calculation:** This is the same type of calculation as in part (a), but with slightly different concentrations.

$$\text{pH} = 4.74 + \log \frac{0.580}{0.230} = 4.74 + 0.40 = 5.14$$

**Buffer capacity** refers to the amount of acid or base that a buffer can neutralize before its pH changes appreciably. In general, the maximum buffer capacity exists when the concentrations of a weak acid and its conjugate base are kept *large* and *approximately equal to each other*.

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

when the ratio  $[\text{conjugate base}]/[\text{acid}] = 1$ ,  $\text{pH} = \text{p}K_a$ . When the ratio falls to 0.10, the pH *decreases* by 1 pH unit from  $\text{p}K_a$  because  $\log 0.10 = -1$ . If the ratio increases to a value of 10, the pH *increases* by 1 unit because  $\log 10 = 1$ . For practical purposes, this range of 2 pH units is the maximum range to which a buffer solution should be exposed. For acetic acid–sodium acetate buffers, the effective range is about pH 3.7–5.7; for ammonia–ammonium chloride buffers, it is about pH 8.3–10.3.