19 Ionic Equilibria II: Buffers and Titration Curves

OUTLINE

The red anthocyanin pigment in the common geranium is a naturally occurring acid–base indicator.

OBJECTIVES

After you have studied this chapter, you should be able to

- *Explain the common ion effect and give illustrations of its operation*

- *Recognize buffer solutions and describe their chemistry*

- *Describe how to prepare a buffer solution of a specified pH*

- *Carry out calculations related to buffer solutions and their action*

- *Explain what acid–base indicators are and how they function*

- *Describe what species are present at various stages of titration curves for (a) strong acids and strong bases, (b) weak acids and strong bases, and (c) weak acids and weak bases*

- *Carry out calculations based on titration curves for (a) strong acids and strong bases and (b) weak acids and strong bases*

I n the previous chapter we calculated the acidity or basicity of aqueous solutions of strong acids, strong bases, weak acids, weak bases, and their salts. In this chapter we will study (1) solutions that have both weak acids and weak bases present, (2) indicators, and (3) titration curves.

It can be a challenge to recognize the type of solution present. Recognition can be even more difficult if the solution is formed by a partial or total neutralization reaction. To help you to recognize the various solutions, a summary table (Table 19-7) is included in Section 19.8. We encourage you to look at the table often as you progress through this chapter and as you review this and the previous chapter.

19-1 THE COMMON ION EFFECT AND BUFFER SOLUTIONS

In laboratory reactions, in industrial processes, and in the bodies of plants and animals, it is often necessary to keep the pH nearly constant despite the addition of acids or bases.

The oxygen-carrying capacity of the hemoglobin in your blood and the activity of the enzymes in your cells are very sensitive to the pH of your body fluids. Our bodies use a combination of compounds known as a *buffer system* to keep the pH within a narrow range.

Buffer systems resist changes in pH.

> A buffer solution contains a conjugate acid–base pair with both the acid and base in reasonable concentrations. The acidic component reacts with added strong bases. The basic component reacts with added strong acids.

The operation of a buffer solution depends on the *common ion effect*, a special case of LeChatelier's Principle.
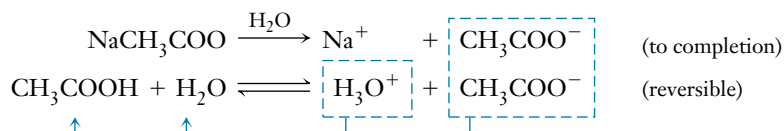
> When a solution of a weak electrolyte is altered by adding one of its ions from another source, the ionization of the weak electrolyte is suppressed. This behavior is termed the **common ion effect.**

Many types of solutions exhibit this behavior. Two of the most frequently encountered kinds are

1. A solution of a weak acid *plus* a soluble ionic salt of the weak acid (e.g., CH_3COOH plus $NaCH_3COO$)

2. A solution of a weak base *plus* a soluble ionic salt of the weak base (e.g., NH_3 plus NH_4Cl)

Weak Acids Plus Salts of Weak Acids

Consider a solution that contains acetic acid *and* sodium acetate, a soluble ionic salt of CH_3COOH. The $NaCH_3COO$ is completely dissociated into its constituent ions, but CH_3COOH is only slightly ionized.

$$NaCH_3COO \xrightarrow{H_2O} Na^+ \quad + \boxed{CH_3COO^-} \quad \text{(to completion)}$$

$$CH_3COOH + H_2O \rightleftharpoons \boxed{H_3O^+} + \boxed{CH_3COO^-} \quad \text{(reversible)}$$

LeChatelier's Principle (Section 17-6) is applicable to equilibria in aqueous solution.

Both CH_3COOH and $NaCH_3COO$ are sources of CH_3COO^- ions. The completely dissociated $NaCH_3COO$ provides a high $[CH_3COO^-]$. This shifts the ionization equilibrium of CH_3COOH far to the left as CH_3COO^- combines with H_3O^+ to form nonionized CH_3COOH and H_2O. The result is a drastic decrease in $[H_3O^+]$ in the solution.

> Solutions that contain a weak acid plus a salt of the weak acid are always less acidic than solutions that contain the same concentration of the weak acid alone.

EXAMPLE 19-1   *Weak Acid/Salt of Weak Acid Buffer Solution*

Calculate the concentration of H_3O^+ and the pH of a buffer solution that is 0.10 *M* in CH_3COOH and 0.20 *M* in $NaCH_3COO$.

Plan

Write the appropriate equations for *both* NaCH₃COO *and* CH₃COOH and the ionization constant expression for CH₃COOH. Then, represent the *equilibrium* concentrations algebraically and substitute into the K_a expression.

Solution

The appropriate equations and ionization constant expression are

$$\text{rxn 1} \qquad \text{NaCH}_3\text{COO} \longrightarrow \text{Na}^+ + \text{CH}_3\text{COO}^- \qquad \text{(to completion)}$$

$$\text{rxn 2} \qquad \text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{CH}_3\text{COO}^- \qquad \text{(reversible)}$$

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

This K_a expression is valid for *all solutions* that contain CH₃COOH. In solutions that contain both CH₃COOH and NaCH₃COO, CH₃COO⁻ ions come from two sources. The ionization constant is satisfied by the *total* CH₃COO⁻ concentration.

Because NaCH₃COO is completely dissociated, the [CH₃COO⁻] *from NaCH₃COO* will be 0.20 mol/L. Let $x = $ [CH₃COOH] that ionizes; then x is also equal to [H₃O⁺] *and* equal to [CH₃COO⁻] *from CH₃COOH.* The *total* concentration of CH₃COO⁻ is $(0.20 + x)$ *M.* The concentration of nonionized CH₃COOH is $(0.10 - x)$ *M.*

$$\text{rxn 1} \qquad \begin{array}{cccc} \text{NaCH}_3\text{COO} & \longrightarrow & \text{Na}^+ + & \text{CH}_3\text{COO}^- \\ 0.20\,M & \rightleftharpoons & 0.20\,M & 0.20\,M \end{array}$$

$$\text{rxn 2} \qquad \begin{array}{cccc} \text{CH}_3\text{COOH} + \text{H}_2\text{O} & \rightleftharpoons & \text{H}_3\text{O}^+ + & \text{CH}_3\text{COO}^- \\ (0.10 - x)\,M & & x\,M & x\,M \end{array}$$

$$\longrightarrow \text{Total } [\text{CH}_3\text{COO}^-] = (0.20 + x)\,M$$

Substitution into the ionization constant expression for CH₃COOH gives

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{(x)(0.20 + x)}{(0.10 - x)} = 1.8 \times 10^{-5}$$

The small value of K_a suggests that x is very small. This leads to two assumptions.

Assumption	Implication
$x \ll 0.20$, so $(0.20 + x) \approx 0.20$	Most of the CH₃COO⁻ comes from NaCH₃COO (rxn 1) and very little CH₃COO⁻ comes from ionization of CH₃COOH (rxn 2)
$x \ll 0.10$, so $(0.10 - x) \approx 0.10$	Very little of the CH₃COOH ionizes (rxn 2)

It is reasonable to assume that x (from the ionization of CH₃COOH) is small, because CH₃COOH is a weak acid (rxn 2), and its ionization is further suppressed by the high concentration of CH₃COO⁻ formed by the soluble salt, NaCH₃COO (rxn 1).

Introducing these assumptions gives

$$\frac{0.20\,x}{0.10} = 1.8 \times 10^{-5} \qquad \text{and} \qquad x = 9.0 \times 10^{-6}$$

$$x\,M = \boxed{[\text{H}_3\text{O}^+] = 9.0 \times 10^{-6}\,M} \qquad \text{so} \qquad \boxed{\text{pH} = 5.05}$$

You should now work Exercise 8.

The general equations

$$\text{NaA} \longrightarrow \text{Na}^+ + \text{A}^-$$

and

$$\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$$

may be used in place of these equations.

You can verify the validity of the assumption by substituting the value for x, 9.0×10^{-6}, into the original equation.

To see how much the acidity of the 0.10 M CH_3COOH solution is reduced by making it also 0.20 M in $NaCH_3COO$, refer back to Example 18-11. There we found that in 0.10 M CH_3COOH the H_3O^+ concentration is 1.3×10^{-3} mol/L (pH = 2.89).

Let us calculate the percent ionization in the solution of Example 19-1.

$$\% \text{ ionization} = \frac{[CH_3COOH]_{ionized}}{[CH_3COOH]_{initial}} \times 100\%$$

$$= \frac{9.0 \times 10^{-6} \ M}{0.10 \ M} \times 100\% = 0.0090\% \text{ ionized}$$

This compares with 1.3% ionization in 0.10 M CH_3COOH (Example 18-11). Table 19-1 compares these solutions. The third column shows that $[H_3O^+]$ is *140 times greater* in 0.10 M CH_3COOH than in the solution to which 0.20 mol/L $NaCH_3COO$ has been added (common ion effect).

The calculation of the pH of a solution containing significant amounts of both a weak acid and the salt of the weak acid may be carried out as we have done in Example 19-1. Alternatively, one may proceed as follows. We can start by writing the equation for the ionization of the *weak monoprotic acid* and its K_a as we did previously.

$$HA + H_2O \rightleftharpoons H_3O^+ + A^- \quad \text{and} \quad \frac{[H_3O^+][A^-]}{[HA]} = K_a$$
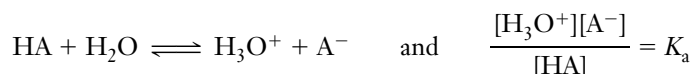
Solving this expression for $[H_3O^+]$ gives

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

Consider a solution in which the concentrations of both the weak acid and its anion (from an added salt) are some reasonable values, such as greater than 0.050 M. Under these conditions the concentration of the anion, $[A^-]$, in the solution can be assumed to be entirely due to the dissolved salt. With these restrictions, the preceding expression becomes

These are the kinds of assumptions we made in Example 19-1.

$$[H_3O^+] = K_a \times \frac{[HA]}{[\text{conjugate base}]}$$

$[HA]$ is the concentration of nonionized weak acid (in most cases this is the total acid concentration) and [conjugate base] is the concentration of the anion from the dissolved salt.

If we take the logarithm of both sides of the preceding equation, we obtain

$$\log [H_3O^+] = \log K_a + \log \frac{[\text{acid}]}{[\text{salt}]}$$

The two solutions of Table 19-1, in the presence of universal indicator. The CH_3COOH solution is on the left.

TABLE 19-1	*Comparison of $[H_3O^+]$ and pH in Acetic Acid and Sodium Acetate–Acetic Acid Solutions*			
Solution	% CH_3COOH Ionized	$[H_3O^+]$	pH	
0.10 M CH_3COOH	1.3%	1.3×10^{-3} M	2.89	
0.10 M CH_3COOH and 0.20 M $NaCH_3COO$	0.0090%	9.0×10^{-6} M	5.05	ΔpH = 2.16

Multiplying by -1 gives

$$-\log [H_3O^+] = -\log K_a - \log \frac{[acid]}{[salt]}$$

Recalling that in Chapter 18 we defined $-\log [H_3O^+]$ (or for the general expression $-\log [H^+]$) as pH and $-\log K_a$ as pK_a, the preceding equation becomes

$$pH = pK_a + \log \frac{[salt]}{[acid]} \qquad \text{where} \qquad pK_a = -\log K_a \qquad \text{(acid/salt buffer)}$$

The relationship is valid *only* for solutions that contain a weak *monoprotic* acid and a soluble, ionic salt of the weak acid with a *univalent* cation, both in reasonable concentrations.

This equation is known as the **Henderson–Hasselbalch equation.** Workers in the biological sciences use it frequently. In general terms, we write

$$pH = pK_a + \log \frac{[conjugate\ base]}{[acid]} \qquad \text{(acid/salt buffer)}$$

See the *Saunders Interactive General Chemistry CD-ROM,* Screen 18.9, pH of Buffer Solutions.

EXAMPLE 19-2 *Weak Acid/Salt of Weak Acid Buffer Solution (via the Henderson–Hasselbalch Equation)*

Use the Henderson–Hasselbalch equation to calculate the pH of the buffer solution in Example 19-1.

Plan

The Henderson–Hasselbalch equation is $pH = pK_a + \log \dfrac{[conjugate\ base]}{[acid]}$. The value for pK_a for acetic acid can be calculated from the value of K_a found in Example 19-1 and many other places. The solution in Example 19-1 is 0.10 M in CH_3COOH and 0.20 M in $NaCH_3COO$. The values used for [conjugate base] and [acid] are their initial concentrations after mixing but before reaction.

Solution

The appropriate values needed for the Henderson–Hasselbalch equation are

$$pK_a = -\log K_a = -\log 1.8 \times 10^{-5} = 4.74$$

$$[conjugate\ base] = [CH_3COO^-] = [NaCH_3COO]_{initial} = 0.20\ M$$

$$[acid] = [CH_3COOH]_{initial} = 0.10\ M$$

$$pH = pK_a + \log \frac{[conjugate\ base]}{[acid]} = 4.74 + \log \frac{(0.20)}{(0.10)}$$

$$= 4.74 + \log 2.0 = 4.74 + 0.30 = \boxed{5.04}$$

The values $pK_a = 4.74$, the log of 2.0, and pH = 5.04 all have two significant figures.

You should now work Exercise 9.

Weak Bases Plus Salts of Weak Bases

Let us consider the second common kind of buffer solution, containing a weak base and its salt. A solution that contains aqueous NH_3 and ammonium chloride, NH_4Cl, a soluble ionic salt of NH_3, is typical. The NH_4Cl is completely dissociated, but aqueous NH_3 is only slightly ionized.

rxn 1 $\quad\quad$ $NH_4Cl \xrightarrow{H_2O} \boxed{NH_4^+} + Cl^-$ $\quad\quad$ (to completion)

rxn 2 $\quad\quad$ $NH_3 + H_2O \rightleftharpoons \boxed{NH_4^+} + \boxed{OH^-}$ $\quad\quad$ (reversible)

Both NH_4Cl and aqueous NH_3 are sources of NH_4^+ ions. The completely dissociated NH_4Cl provides a high $[NH_4^+]$. This shifts the ionization equilibrium of aqueous NH_3 far to the left, as NH_4^+ ions combine with OH^- ions to form nonionized NH_3 and H_2O. The result is that $[OH^-]$ is decreased significantly.

> Solutions that contain a weak base plus a salt of the weak base are always less basic than solutions that contain the same concentration of the weak base alone.

EXAMPLE 19-3 *Weak Base/Salt of Weak Base Buffer Solution*

Calculate the concentration of OH^- and the pH of a solution that is 0.20 M in aqueous NH_3 *and* 0.10 M in NH_4Cl.

Plan

Write the appropriate equations for *both* NH_4Cl and NH_3 and the ionization constant expression for NH_3. Then, represent the *equilibrium* concentrations algebraically, and substitute into the K_b expression.

Solution

The appropriate equations and algebraic representations of concentrations are

rxn 1 $\quad\quad$ $\underset{0.10\,M}{NH_4Cl}$ $\quad\quad\quad \longrightarrow \underset{0.10\,M}{NH_4^+} + \underset{0.10\,M}{Cl^-}$

rxn 2 $\quad\quad$ $\underset{(0.20-x)\,M}{NH_3} + H_2O \rightleftharpoons \underset{x\,M}{NH_4^+} + \underset{x\,M}{OH^-}$

$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad$ Total $[NH_4^+] = (0.10 + x)\,M$

Substitution into the K_b expression for aqueous NH_3 gives

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8 \times 10^{-5} = \frac{(0.10 + x)(x)}{(0.20 - x)}$$

The small value of K_b suggests that x is very small. This leads to two assumptions.

Assumption	Implication
$x \ll 0.10$, so $(0.10 + x) \approx 0.10$	Most of the NH_4^+ comes from NH_4Cl (rxn 1) and very little NH_4^+ comes from ionization of NH_3 (rxn 2)
$x \ll 0.20$, so $(0.20 - x) \approx 0.20$	Very little of the NH_3 ionizes (rxn 2)

It is reasonable to assume that x (from the ionization of NH_3) is small, because NH_3 is a weak base (rxn 2), and its ionization is further suppressed by the high concentration of NH_4^+ formed by the soluble salt, NH_4Cl (rxn 1).

Introducing these assumptions gives

$$\frac{0.10x}{0.20} = 1.8 \times 10^{-5} \, M \qquad \text{and} \qquad x = 3.6 \times 10^{-5} \, M$$

$$x \, M = \boxed{[OH^-] = 3.6 \times 10^{-5} \, M} \qquad \text{so} \qquad pOH = 4.44 \qquad \text{and} \qquad \boxed{pH = 9.56}$$

You should now work Exercise 10.

The percent ionization of NH_3 in this solution is

$$\frac{3.6 \times 10^{-5} \, M_{ionized}}{0.20 \, M_{original}} \times 100\% = 0.018\%.$$

In Example 18-14 we calculated $[OH^-]$ and pH for 0.20 M aqueous NH_3. Compare those results with the values obtained in Example 19-3 (Table 19-2). The concentration of OH^- is *53 times greater* in the solution containing only 0.20 M aqueous NH_3 than in the solution to which 0.10 mol/L NH_4Cl has been added. This is another demonstration of the common ion effect.

We can derive a relationship for $[OH^-]$ in a solution containing a weak base, B, *plus* a salt that contains the cation, BH^+, of the weak base, just as we did for weak acids. In general terms the equation for the ionization of a monoprotic weak base and its K_b expression are

$$B + H_2O \rightleftharpoons BH^+ + OH^- \qquad \text{and} \qquad \frac{[BH^+][OH^-]}{[B]} = K_b$$
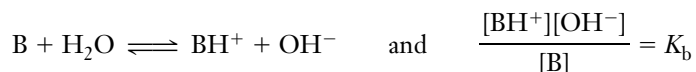
Solving the K_b expression for $[OH^-]$ gives

$$[OH^-] = K_b \times \frac{[B]}{[BH^+]}$$

B and BH^+ represent the weak base and its conjugate acid, respectively — for example, NH_3 and NH_4^-.

Taking the logarithm of both sides of the equation gives

$$\log [OH^-] = \log K_b + \log \frac{[B]}{[BH^+]}$$

Multiplication by -1 and rearrangement gives another form of the *Henderson–Hasselbalch equation* for solutions containing a weak base plus a salt of the weak base.

$$pOH = pK_b + \log \frac{[BH^+]}{[B]} \qquad \text{where} \qquad pK_b = -\log K_b \qquad \text{(base/salt buffer)}$$

TABLE 19-2 *Comparison of $[OH^-]$ and pH in Ammonia and Ammonium Chloride—Ammonia Solutions*

Solution	% NH_3 Ionized	$[OH^-]$	pH
0.20 M aq NH_3	0.95%	$1.9 \times 10^{-3} \, M$	11.28 ⎫
0.20 M aq NH_3 and 0.10 M aq NH_4Cl	0.018%	$3.6 \times 10^{-5} \, M$	9.56 ⎬ $\Delta pH = -1.72$

The two solutions in Table 19-2, in the presence of universal indicator. The NH_3 solution is on the left. Can you calculate the percentage of NH_3 that is ionized in these two solutions?

The Henderson–Hasselbalch equation is valid for solutions of weak bases plus salts of weak bases with univalent anions in reasonable concentrations. In general terms we can also write this equation as

$$pOH = pK_b + \log \frac{[\text{conjugate acid}]}{[\text{base}]} \qquad \text{(base/salt buffer)}$$

19-2 BUFFERING ACTION

A buffer solution is able to react with either H_3O^+ or OH^- ions, whichever is added.

Thus, a buffer solution resists changes in pH. When we add a modest amount of a strong base or a strong acid to a buffer solution, the pH changes very little.

The two common kinds of buffer solutions are the ones we have just discussed—namely, solutions containing (1) a weak acid plus a soluble ionic salt of the weak acid and (2) a weak base plus a soluble ionic salt of the weak base.

Solutions of a Weak Acid and a Salt of the Weak Acid

Three common examples of buffers. Many medications are buffered to minimize digestive upset. Most body fluids, including blood plasma, contain very efficient natural buffer systems. Buffer capsules are used in laboratories to prepare solutions of specified pH.

A solution containing acetic acid, CH_3COOH, and sodium acetate, $NaCH_3COO$, is an example of this kind of buffer solution. The acidic component is CH_3COOH. The basic component is $NaCH_3COO$ because the CH_3COO^- ion is the conjugate base of CH_3COOH. The operation of this buffer depends on the equilibrium

$$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$$
$$\text{\textit{high} conc} \qquad\qquad\qquad \text{\textit{high} conc (from salt)}$$
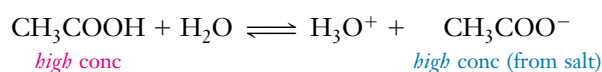
If we add a strong acid such as HCl to this solution, it produces H_3O^+. As a result of the added H_3O^+, the reaction occurs to the *left*, to use up most of the added H_3O^+ and reestablish equilibrium. Because the $[CH_3COO^-]$ in the buffer solution is high, this can occur to a great extent. The net reaction is

$$H_3O^+ + CH_3COO^- \longrightarrow CH_3COOH + H_2O \qquad (\approx 100\%)$$

or, as a formula unit equation,

$$\underset{\text{added acid}}{HCl} + \underset{\text{base}}{NaCH_3COO} \longrightarrow \underset{\text{weak acid}}{CH_3COOH} + \underset{\text{salt}}{NaCl} \qquad (\approx 100\%)$$

The net effect is to neutralize most of the H_3O^+ from HCl by forming nonionized CH_3COOH molecules. This slightly decreases the ratio $[CH_3COO^-]/[CH_3COOH]$, which governs the pH of the solution.
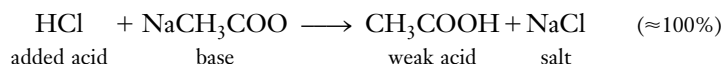
This reaction goes nearly to completion because CH_3COOH is a *weak* acid; even when mixed from separate sources, its ions have a strong tendency to form nonionized CH_3COOH molecules rather than remain separate.

When a strong base, such as NaOH, is added to the CH_3COOH–$NaCH_3COO$ buffer solution, it is consumed by the acidic component, CH_3COOH. This occurs in the following way. The additional OH^- causes the water autoionization reaction to proceed to the *left*.

$$2H_2O \rightleftharpoons H_3O^+ + OH^- \qquad \text{(shifts \textit{left})}$$

This uses up some H_3O^+, causing more CH_3COOH to ionize.

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+ \qquad \text{(shifts } \textit{right)}$$
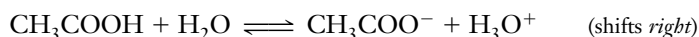
Because the $[CH_3COOH]$ is high, this can occur to a great extent. The net result is the neutralization of OH^- by CH_3COOH.

$$\underset{\text{added base}}{OH^-} + \underset{\text{acid}}{CH_3COOH} \longrightarrow \underset{\text{weaker base}}{CH_3COO^-} + \underset{\text{water}}{H_2O} \qquad (\approx 100\%)$$
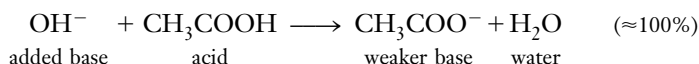
> The net effect is to neutralize most of the OH^- from NaOH. This slightly increases the ratio $[CH_3COO^-]/[CH_3COOH]$, which governs the pH of the solution.

EXAMPLE 19-4 *Buffered Solutions*

If we add 0.010 mol of solid NaOH to 1.00 liter of a buffer solution that is 0.100 M in CH_3COOH and 0.100 M in $NaCH_3COO$, how much will $[H_3O^+]$ and pH change? Assume that there is no volume change due to the addition of solid NaOH.

Plan

Calculate $[H_3O^+]$ and pH for the original buffer solution. Then, write the reaction summary that shows how much of the CH_3COOH is neutralized by NaOH. Calculate $[H_3O^+]$ and pH for the resulting buffer solution. Finally, calculate the change in pH.

Solution

For the 0.100 M CH_3COOH and 0.100 M $NaCH_3COO$ solution, we can write

$$[H_3O^+] = K_a \times \frac{[\text{acid}]}{[\text{salt}]} = 1.8 \times 10^{-5} \times \frac{0.100}{0.100} = 1.8 \times 10^{-5} \; M; \; \text{pH} = 4.74$$

When solid NaOH is added, it reacts with CH_3COOH to form more $NaCH_3COO$.

	NaOH	+ CH_3COOH	$\longrightarrow$ $NaCH_3COO$ + H_2O
start	0.010 mol	0.100 mol	0.100 mol
change due to rxn	−0.010 mol	−0.010 mol	+0.010 mol
after rxn	0 mol	0.090 mol	0.110 mol

The volume of the solution is 1.00 liter, so we now have a solution that is 0.09 M in CH_3COOH and 0.110 M in $NaCH_3COO$. In this solution,

$$[H_3O^+] = K_a \times \frac{[\text{acid}]}{[\text{salt}]} = 1.8 \times 10^{-5} \times \frac{0.090}{0.110} = 1.5 \times 10^{-5} \; M; \; \text{pH} = 4.82$$

> The addition of 0.010 mol of solid NaOH to 1.00 liter of this buffer solution decreases $[H_3O^+]$ from 1.8×10^{-5} M to 1.5×10^{-5} M and increases pH from 4.74 to 4.82, a change of 0.08 pH unit, which is a very slight change.

> This is enough NaOH to neutralize 10% of the acid.

You should now work Exercise 22.

Addition of 0.010 mole of solid NaOH to one liter of 0.100 M CH_3COOH (pH = 2.89 from Table 19-1) would give a solution that is 0.090 M in CH_3COOH and 0.010 M in $NaCH_3COO$. The pH of this solution is 3.78, which is 0.89 pH unit higher than that of the 0.100 M CH_3COOH solution.

By contrast, adding 0.010 mole of NaOH to enough pure H_2O to give one liter produces a 0.010 M solution of NaOH: $[OH^-] = 1.0 \times 10^{-2}$ M and pOH = 2.00. The pH of this solution is 12.00, an increase of 5.00 pH units above that of pure H_2O.

> pH + pOH = 14

In summary, 0.010 mole of NaOH

added to 1.00 L of the $CH_3COOH/NaCH_3COO$ buffer, pH 4.74 $\longrightarrow$ 4.82
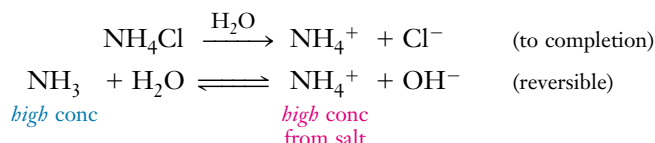
added to 1.00 L of 0.100 M CH_3COOH, pH 2.89 $\longrightarrow$ 3.78

added to 1.00 L of pure H_2O, pH 7.00 $\longrightarrow$ 12.00

In similar fashion we could calculate the effects of adding 0.010 mole of pure HCl(g) instead of pure NaOH to 1.00 liter of each of these three solutions. This would result in the following changes in pH.

added to 1.00 L of the $CH_3COOH/NaCH_3COO$ buffer, pH 4.74 $\longrightarrow$ 4.66

added to 1.00 L of 0.100 M CH_3COOH, pH 2.89 $\longrightarrow$ 2.00

added to 1.00 L of pure H_2O, pH 7.00 $\longrightarrow$ 2.00

The results of adding NaOH or HCl to these solutions (Table 19-3) demonstrate the efficiency of the buffer solution. We recall that each change of 1 pH unit means that the $[H_3O^+]$ and $[OH^-]$ change by a *factor* of 10. In these terms, the effectiveness of the buffer solution in controlling pH is even more dramatic.

Solutions of a Weak Base and a Salt of the Weak Base

An example of this type of buffer solution is one that contains the weak base ammonia, NH_3, and its soluble ionic salt ammonium chloride, NH_4Cl. The reactions responsible for the operation of this buffer are

$$NH_4Cl \xrightarrow{H_2O} NH_4^+ + Cl^- \qquad \text{(to completion)}$$

$$\underset{\textit{high} \text{ conc}}{NH_3} + H_2O \rightleftharpoons \underset{\substack{\textit{high} \text{ conc} \\ \text{from salt}}}{NH_4^+} + OH^- \qquad \text{(reversible)}$$

If a strong acid such as HCl is added to this buffer solution, the resulting H_3O^+ shifts the equilibrium reaction

$$2H_2O \rightleftharpoons H_3O^+ + OH^- \qquad \text{(shifts \textit{left})}$$
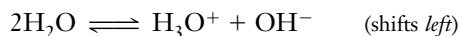
TABLE 19-3	*Changes in pH Caused by Addition of Pure Acid or Base to One Liter of Solution*				
	When We Add 0.010 mol NaOH(s)		**When We Add 0.010 mol HCl(g)**		
We Have 1.00 L of Original Solution	**pH Changes by**	**$[H_3O^+]$ Decreases by a factor of**	**pH Changes by**	**$[H_3O^+]$ Increases by a factor of**	
buffer solution (0.10 M $NaCH_3COO$ and 0.10 M CH_3COOH)	+0.08 pH unit	1.2	−0.08 pH unit	1.2	
0.10 M CH_3COOH	+0.91	8.1	−0.89	7.8	
pure H_2O	+5.00	100,000	−5.00	100,000	

strongly to the *left*. As a result of the diminished OH^- concentration, the reaction

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \quad \text{(shifts } right\text{)}$$
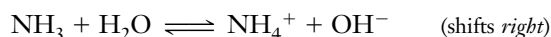
shifts markedly to the *right*. Because the $[NH_3]$ in the buffer solution is high, this can occur to a great extent. The net reaction is

$$\underset{\text{added acid}}{H_3O^+} + \underset{\text{base}}{NH_3} \longrightarrow \underset{\text{weak acid}}{NH_4^+} + \underset{\text{water}}{H_2O} \quad (\approx 100\%)$$

The net effect is to neutralize most of the H_3O^+ from HCl. This slightly increases the ratio $[NH_4^+]/[NH_3]$, which governs the pH of the solution.
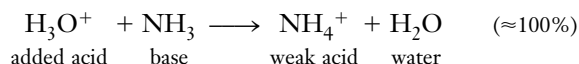
When a strong base such as NaOH is added to the *original* buffer solution, it is neutralized by the more acidic component, NH_4Cl, or NH_4^+, the conjugate acid of ammonia.

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \quad \text{(shifts } left\text{)}$$
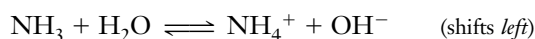
Because the $[NH_4^+]$ is high, this can occur to a great extent. The result is the neutralization of OH^- by NH_4^+.

$$OH^- + NH_4^+ \longrightarrow NH_3 + H_2O \quad (\approx 100\%)$$

The net effect is to neutralize most of the OH^- from NaOH. This slightly decreases the ratio $[NH_4^+]/[NH_3]$, which governs the pH of the solution.

or, as a formula unit equation,

$$\underset{\text{added base}}{NaOH} + \underset{\text{acid}}{NH_4Cl} \longrightarrow \underset{\text{weak base}}{NH_3} + \underset{\text{water}}{H_2O} + NaCl \quad (\approx 100\%)$$

> **Summary** Changes in pH are minimized in buffer solutions because the basic component can react with H_3O^+ ions and the acidic component can react with OH^- ions.

19-3 PREPARATION OF BUFFER SOLUTIONS

Buffer solutions can be prepared by mixing other solutions. When solutions are mixed, the volume in which each solute is contained increases, so solute concentrations change. These changes in concentration must be considered. If the solutions are dilute, we may assume that their volumes are additive.

EXAMPLE 19-5 *Preparation of Buffer Solutions*

Calculate the concentration of H_3O^+ and the pH of a buffer solution prepared by mixing 200. mL of 0.10 *M* NaF and 100. mL of 0.050 *M* HF. $K_a = 7.2 \times 10^{-4}$ for HF.

Plan

Calculate the number of millimoles (or moles) of NaF and HF and then the molarity of each solute in the solution after mixing. Write the appropriate equations for both NaF and HF, represent the equilibrium concentrations algebraically, and substitute into the K_a expression for HF.

Alternatively, one could substitute into the Henderson–Hasselbalch equation and solve for pH, then $[H_3O^+]$.

Solution

When two dilute solutions are mixed, we assume that their volumes are additive. The volume of the new solution will be 300. mL. Mixing a solution of a weak acid with a solution of its salt does not form any new species. So we have a straightforward buffer calculation. We calculate the number of millimoles (or moles) of each compound and the molarities in the new solution.

$$\left. \begin{array}{l} \underline{?} \text{ mmol NaF} = 200. \text{ mL} \times \dfrac{0.10 \text{ mmol NaF}}{\text{mL}} = 20. \text{ mmol HF} \\[2mm] \underline{?} \text{ mmol HF} = 100. \text{ mL} \times \dfrac{0.050 \text{ mmol HF}}{\text{mL}} = 5.0 \text{ mmol HF} \end{array} \right\} \text{in 300. mL}$$

The molarities of NaF and HF in the solution are

$$\dfrac{20. \text{ mmol NaF}}{300. \text{ mL}} = 0.067 \ M \text{ NaF} \qquad \text{and} \qquad \dfrac{5.0 \text{ mmol HF}}{300. \text{ mL}} = 0.017 \ M \text{ HF}$$

The appropriate equations and algebraic representations of concentrations are

$$
\begin{array}{ccccc}
\text{NaF} & \longrightarrow & \text{Na}^+ & + & \text{F}^- \\
0.067 \ M & \Longrightarrow & 0.067 \ M & & 0.067 \ M \\
\text{HF} & + \text{H}_2\text{O} \rightleftharpoons & \text{H}_3\text{O}^+ & + & \text{F}^- \\
(0.017 - x) \ M & & x \ M & & x \ M
\end{array}
$$

$$\longrightarrow \text{Total } [\text{F}^-] = (0.067 + x) \ M$$
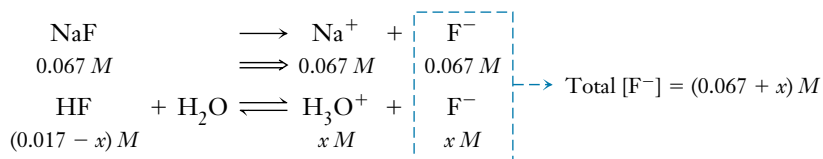
Substituting into the K_a expression for hydrofluoric acid gives

$$K_a = \dfrac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]} = \dfrac{(x)(0.067 + x)}{(0.017 - x)} = 7.2 \times 10^{-4}$$

Can we assume that x is negligible compared with 0.067 and 0.017 in this expression? When in doubt, solve the equation using the simplifying assumption. Then decide whether the assumption was valid. Assume that $(0.067 + x) \approx 0.067$ and $(0.017 - x) \approx 0.017$.

Our assumption is valid.

$$\dfrac{0.067x}{0.017} = 7.2 \times 10^{-4} \qquad x = \boxed{1.8 \times 10^{-4} \ M = [\text{H}_3\text{O}^+]}$$

$$\text{pH} = \boxed{3.74}$$

You should now work Exercise 34.

See the *Saunders Interactive General Chemistry CD-ROM*, Screen 18.10, Preparing Buffer Solutions.

We often need a buffer solution of a given pH. One method by which such solutions can be prepared involves adding a salt of a weak base (or weak acid) to a solution of the weak base (or weak acid).

EXAMPLE 19-6 *Preparation of Buffer Solutions*

Calculate the numbers of moles and grams of NH_4Cl that must be used to prepare 500. mL of a buffer solution that is 0.10 M in aqueous NH_3 and has a pH of 9.15.

Plan

Convert the given pH to the desired $[OH^-]$ by the usual procedure. Write the appropriate equations for the reactions of NH_4Cl and NH_3 and represent the equilibrium concentrations. Then, substitute into the K_b expression, and solve for the concentration of NH_4Cl required.

Solution

Because the desired pH = 9.15, pOH = 14.00 − 9.15 = 4.85. So $[OH^-] = 10^{-pOH} = 10^{-4.85} = 1.4 \times 10^{-5} \ M \ OH^-$ desired. Let x mol/L be the necessary molarity of NH_4Cl. Because $[OH^-] = 1.4 \times 10^{-5} \ M$, this must be the $[OH^-]$ produced by ionization of NH_3. The equations and representations of equilibrium concentrations follow.

$$\begin{array}{ccccc}
NH_4Cl & \xrightarrow{100\%} & NH_4^+ & + & Cl^- \\
x\,M & \Longrightarrow & x\,M & & x\,M \\
NH_3 & + \quad H_2O \quad \rightleftharpoons & NH_4^+ & + & OH^- \\
(0.10 - 1.4 \times 10^{-5})\,M & & 1.4 \times 10^{-5}\,M & & 1.4 \times 10^{-5}\,M
\end{array}$$

$$\text{Total } [NH_4^+] = (x + 1.4 \times 10^{-5})\,M$$
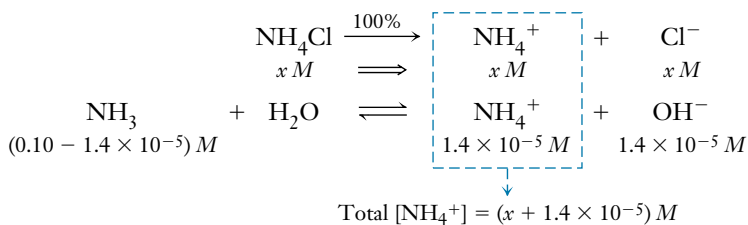
Substitution into the K_b expression for aqueous ammonia gives

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8 \times 10^{-5} = \frac{(x + 1.4 \times 10^{-5})(1.4 \times 10^{-5})}{0.10 - 1.4 \times 10^{-5}}$$

NH_4Cl is 100% dissociated, so $x \gg 1.4 \times 10^{-5}$. Then $(x + 1.4 \times 10^{-5}) \approx x$.

Here x does *not* represent a *change* in concentration, but rather the initial concentration of NH_4Cl. We do *not* assume that $x \ll 1.4 \times 10^{-5}$, but rather the reverse.

$$\frac{(x)(1.4 \times 10^{-5})}{0.10} = 1.8 \times 10^{-5} \qquad x = 0.13\,M = [NH_4^+] = M_{NH_4Cl}$$

Now we calculate the number of moles of NH_4Cl that must be added to prepare 500. mL (0.500 L) of buffer solution.

$$\underline{?}\ \text{mol } NH_4Cl = 0.500\ L \times \frac{0.13\ \text{mol } NH_4Cl}{L} = \boxed{0.065\ \text{mol } NH_4Cl}$$

$$\underline{?}\ \text{g } NH_4Cl = 0.065\ \text{mol} \times \frac{53.5\ \text{g } NH_4Cl}{\text{mol } NH_4Cl} = \boxed{3.5\ \text{g } NH_4Cl}$$

You should now work Exercise 37.

_____

We have used K_a or K_b expressions or the Henderson–Hasselbalch equation in its acid–salt or base–salt form to find the pH of buffered solutions. Each of these approaches involves a *ratio* of concentrations, for instance $\dfrac{[\text{conjugate base}]}{[\text{acid}]}$. Although the ratios are

Preparation of the buffer solution in Example 19-6. We add 3.5 grams of NH_4Cl to a 500-mL volumetric flask and dissolve it in a little of the 0.10 M NH_3 solution. We then dilute to 500 mL with the 0.10 M NH_3 solution.
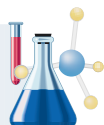
Fun with Carbonates

Carbonates react with acids to produce carbon dioxide. This property of carbonates has been exploited in many ways, both serious and silly.

One of the giddiest applications of this behavior of carbonates is in Mad Dawg, a foaming bubble gum developed in the early 1990s. If you chew a piece of this gum, large quantities of foam are produced so that it is difficult to keep the colorful lather from oozing out of your mouth. The froth begins to form as your teeth mix saliva with the gum's ingredients (sodium hydrogen carbonate, citric acid, malic acid, food coloring, and flavoring).

How is this foam produced? When citric acid and malic acid dissolve in saliva, they produce hydrogen ions which decompose the sodium hydrogen carbonate (baking soda) to produce carbon dioxide, a gas. These bubbles of carbon dioxide produce the foam. Large quantities of foam are produced because citric and malic acids taste sour, which stimulates salivation.

A common medical recipe for a similar combination of ingredients is found in Alka Seltzer tablets; these contain sodium hydrogen carbonate, citric acid, and aspirin. The acid and carbonate react in water to produce carbon dioxide, which gives the familiar fizz of Alka Seltzer.

Makeup artists add baking soda to cosmetics to produce monster-flesh makeup. When the hero throws acid (which is actually vinegar, a dilute solution of acetic acid) into the monster's face, the acetic acid reacts with sodium hydrogen carbonate to produce the disgustingly familiar scenes of "dissolving flesh" that we see in horror movies. The ability of baking soda to produce carbon dioxide delights children of all ages as it creates monsters in the movies.

Many early fire extinguishers utilized the reaction of sodium hydrogen carbonate with acids. A metal cylinder was filled with a solution of sodium hydrogen carbonate and water; a bottle filled with sulfuric acid was placed above the water layer. Inverting the extinguisher activated it by causing
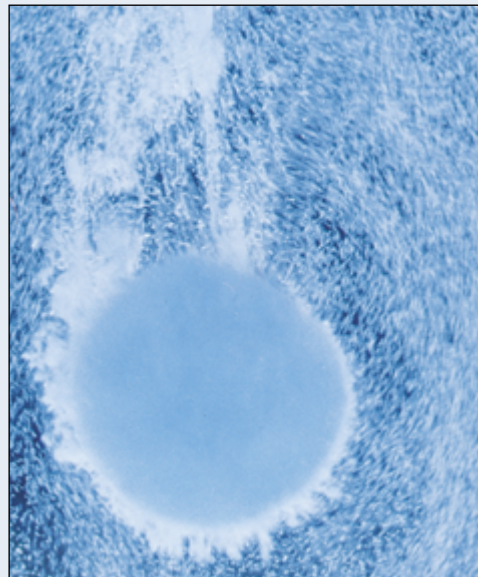
Alka Seltzer™.

the acid to spill into the carbonate solution. The pressure produced by gaseous carbon dioxide gas pushed the liquid contents out through a small hose.

Kitchen oven fires can usually be extinguished by throwing baking soda onto the flame. When heated, carbonates decompose to produce carbon dioxide, which smothers fires by depriving them of oxygen.

Chefs frequently use the heat-sensitive nature of carbonates to test the freshness of a box of baking soda. Pouring some boiling water over a little fresh baking soda results in active bubbling. Less active bubbling means the baking soda is unlikely to work well in a baking recipe.

Ronald DeLorenzo
Middle Georgia College

written in terms of molarities, it is not always necessary to use concentrations in the calculation. Both reagents are present in *a single* buffer solution, so the solution volume cancels from the molarity ratio. For example:

$$\frac{[\text{conjugate base}]}{[\text{acid}]} = \frac{\dfrac{\text{mol conjugate base}}{\text{L soln}}}{\dfrac{\text{mol acid}}{\text{L soln}}} = \frac{\text{mol conjugate base}}{\text{mol acid}}$$

Thus we see that a molarity ratio in the acid–salt Henderson–Hasselbalch equation can be treated as a mole (or millimole) ratio. A similar conclusion can be reached for the base–salt version of the Henderson–Hasselbalch equation or for the K_a or K_b expressions that were used in previous buffer calculations.

In practice, a common method of preparing a buffer solution is by *partial* neutralization of a weak acid solution by adding a strong base solution. For example,

$$HA + NaOH \longrightarrow NaA + H_2O \qquad \text{(partial)}$$
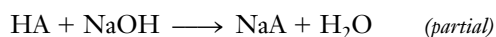
If an appreciable amount of the weak acid remains unneutralized, then this solution contains significant concentrations of a *weak acid* and *its conjugate base*, just as though we had added the salt from a separate solution; thus, it is a buffer solution. Example 19-7 illustrates the preparation of a buffer by this method.

EXAMPLE 19-7   *Buffer Preparation by Partial Neutralization*

Calculate the pH of a solution obtained by mixing 400. mL of a 0.200 M acetic acid solution and 100. mL of a 0.300 M sodium hydroxide solution.

Plan

Sodium hydroxide, NaOH, is a strong base, so it reacts with acetic acid, CH_3COOH, to form sodium acetate, $NaCH_3COO$. If an appreciable amount of excess acetic acid is still present after the sodium hydroxide has reacted, the excess acetic acid and the newly formed sodium acetate solution form a buffered solution.

Solution

We first calculate how much of the weak acid has been neutralized. The numbers of millimoles of CH_3COOH and NaOH mixed are calculated as

$$\text{mmol } CH_3COOH = (0.200 \text{ mmol/mL}) \times 400. \text{ mL} = 80.0 \text{ mmol}$$

$$\text{mmol NaOH} = (0.300 \text{ mmol/mL}) \times 100. \text{ mL} = 30.0 \text{ mmol}$$

Not enough NaOH is present to neutralize all of the CH_3COOH, so NaOH is the *limiting reactant*.

	NaOH	+ CH_3COOH	$\longrightarrow$	$NaCH_3COO$	+ H_2O
start	30.0 mol	80.0 mmol		0	—
change	−30.0 mmol	−30.0 mmol		+30.0 mmol	—
after rxn	0.0 mmol	50.0 mmol		30.0 mmol	

Because $NaCH_3COO$ is a soluble salt, it provides 30.0 mmol CH_3COO^- to the solution. This solution contains a significant amount of CH_3COOH not yet neutralized *and* a significant amount of its conjugate base, CH_3COO^-. We recognize this as a buffer solution and can use the Henderson–Hasselbalch equation to find the pH.

We could solve this problem using the K_a expression as we did in Example 19-5.

$$pH = pK_a + \log \frac{\text{mmol conjugate base}}{\text{mmol acid}} = pK_a + \log \frac{\text{mmol } CH_3COO^-}{\text{mmol } CH_3COOH}$$

$$= 4.74 + \log \frac{30.0}{50.0} = 4.74 + \log(0.600) = 4.74 + (-0.222)$$

$$= \boxed{4.52}$$

You should now work Exercises 52b to 52f.

19-4 ACID–BASE INDICATORS

In Section 11-2 we described acid–base titrations and the use of indicators to tell us when to stop a titration. Detection of the end point in an acid–base titration is only one of the important uses of indicators.

An indicator is an organic dye; its color depends on the concentration of H_3O^+ ions, or pH, in the solution. By the color an indicator displays, it "indicates" the acidity or basicity of a solution. Figure 19-1 displays solutions that contain three common indicators in solutions over the pH range 3 to 11. Carefully study Figure 19-1 and its legend.

The first indicators used were vegetable dyes. Litmus is a familiar example. Most of the indicators that we use in the laboratory today are synthetic compounds; that is, they have been made in laboratories by chemists. Phenolphthalein is the most common acid–base indicator. It is colorless in solutions of pH less than 8 ($[H_3O^+] > 10^{-8}\,M$) and turns bright pink as pH approaches 10.

Many acid–base indicators are weak organic acids, HIn, where "In" represents various complex organic groups. Bromthymol blue is such an indicator. Its ionization constant is

Phenolphthalein was the active component of the laxative Ex-Lax. It is sometimes added to laboratory ethyl alcohol to discourage consumption.

(a)

(b)
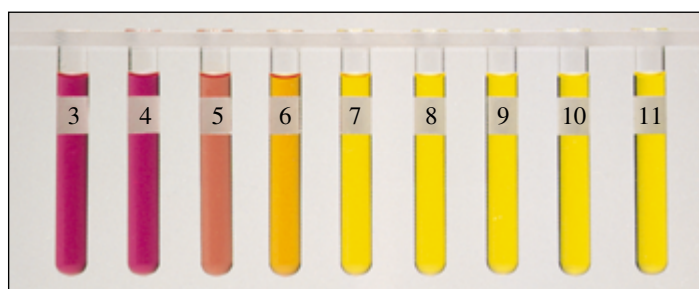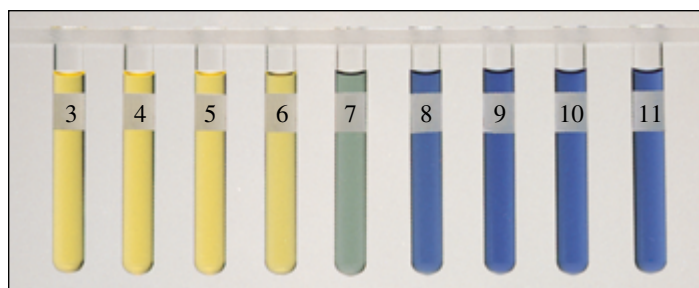
Figure 19-1 Three common indicators in solutions that cover the pH range 3 to 11 (the black numbers). (a) Methyl red is red at pH 4 and below; it is yellow at pH 7 and above. Between pH 4 and pH 7 it changes from red to red-orange, to orange, to yellow. (b) Bromthymol blue is yellow at pH 6 and below; it is blue at pH 8 and above. Between pH 6 and 8 it changes from yellow to yellow-green, to green, to blue-green, to blue. (c) Phenolphthalein is colorless below pH 8 and bright pink above pH 10. It changes from colorless to pale pink, to pink, to bright pink in the pH range 8 to 10.

(c)

7.9×10^{-8}. We can represent its ionization in dilute aqueous solution and its ionization constant expression as

$$HIn + H_2O \rightleftharpoons H_3O^+ + In^- \qquad K_a = \frac{[H_3O^+][In^-]}{[HIn]} = 7.9 \times 10^{-8}$$
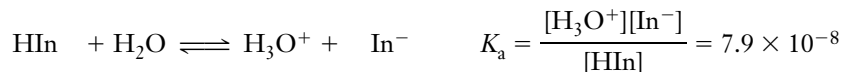
color 1
yellow   ← for bromthymol blue →   color 2
blue

HIn represents nonionized acid molecules, and In^- represents the anion (conjugate base) of HIn. The essential characteristic of an acid–base indicator is that HIn and In^- *must* have quite different colors. The relative amounts of the two species determine the color of the solution. Adding an acid favors the reaction to the left and gives more HIn molecules (color 1). Adding a base favors the reaction to the right and gives more In^- ions (color 2). The ionization constant expression can be rearranged.

$$\frac{[H_3O^+][In^-]}{[HIn]} = K_a \qquad so \qquad \frac{[In^-]}{[HIn]} = \frac{K_a}{[H_3O^+]}$$

This shows clearly how the $[In^-]/[HIn]$ ratio depends on $[H_3O^+]$ (or on pH) and the K_a value for the indicator. As a rule of thumb, when $[In^-]/[HIn] \geq 10$, color 2 is observed; conversely, when $[In^-]/[HIn] \leq \frac{1}{10}$, color 1 is observed.

Universal indicators are mixtures of several acid–base indicators that display a continuous range of colors over a wide range of pH values. Figure 18-2 shows concentrated solutions of a universal indicator in flat dishes so that the colors are very intense. The juice of red (purple) cabbage is a universal indicator. Figure 19-2 shows the color of red cabbage juice in solutions within the pH range 1 to 13.

One important use of universal indicators is in commercial indicator papers, which are small strips of paper impregnated with solutions of universal indicators. A strip of the paper is dipped into the solution of interest, and the color of the indicator on the paper indicates the pH of the solution. The photographs on page 757 (solutions of universal indicators) and page 763 (an indicator paper) illustrate the use of universal indicators to estimate pH. We shall describe the use of indicators in titrations more fully in Sections 19-5 and 19-6.

Bromthymol blue indicator is yellow in acidic solutions and blue in basic solutions.

Figure 19-2 The juice of the red (purple) cabbage is a naturally occurring universal indicator. From left to right are solutions of pH 1, 4, 7, 10, and 13.

TITRATION CURVES

19-5 STRONG ACID/STRONG BASE TITRATION CURVES

A **titration curve** is a plot of pH versus the amount (usually volume) of acid or base added. It displays graphically the change in pH as acid or base is added to a solution and shows how pH changes near the equivalence point.

The point at which the color of an indicator changes in a titration is known as the **end point.** It is determined by the K_a value for the indicator (Section 19-4). Table 19-4 shows a few acid–base indicators and the pH ranges over which their colors change. Typically, color changes occur over a range of 1.5 to 2.0 pH units.

The **equivalence point** is the point at which chemically equivalent amounts of acid and base have reacted.

> Ideally, the end point and the equivalence point in a titration should coincide.

In practice, we try to select an indicator whose range of color change includes the equivalence point. We use the same procedures in both standardization and analysis to minimize any error arising from a difference between end point and equivalence point.

Titrations are usually done with 50-mL or smaller burets. We have used 100. mL of solution in this example to simplify the arithmetic.

Review Section 11-2 before you consider the titration of 100.0 mL of a 0.100 M solution of HCl with a 0.100 M solution of NaOH. As we know, NaOH and HCl react in a 1:1 ratio. We calculate the pH of the solution at several stages as NaOH is added.

1. Before any NaOH is added to the 0.100 M HCl solution:

$$HCl + H_2O \xrightarrow{100\%} H_3O^+ + Cl^-$$

$$[H_3O^+] = 0.100 \; M \qquad \text{so} \qquad pH = 1.00$$

2. After 20.0 mL of 0.100 M NaOH has been added:

If one prefers, these calculations can be done using moles and liters in the place of millimoles and milliliters.
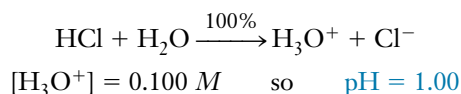
	HCl	+	NaOH	$\longrightarrow$	NaCl	+ H$_2$O
start	10.0 mmol		2.0 mmol		0 mmol
change	−2.0 mmol		−2.0 mmol		+2.0 mmol
after rxn	8.0 mmol		0 mmol		2.0 mmol

TABLE 19-4	*Range and Color Changes of Some Common Acid–Base Indicators*

pH Scale

Indicators	1	2	3	4	5	6	7	8	9	10	11	12	13
methyl orange	←—— red ——→3.1 —— 4.4 ←——————————— yellow ———————————→
methyl red	←———— red ————→ 4.4 ———————— 6.2 ←——————— yellow ———————→
bromthymol blue	←————— yellow —————→ 6.2 —— 7.6 ←————— blue —————→
neutral red	←————— red —————→ 6.8 —— 8.0 ←——————— yellow ———————→
phenolphthalein	←—————— colorless —————→ 8.0 ———— 10.0 ←— bright pink —→ colorless beyond 13.0

The concentration of unreacted HCl in the total volume of 120. mL is

$$M_{HCl} = \frac{8.00 \text{ mmol HCl}}{120. \text{ mL}} = 0.067 \text{ M HCl}$$

$$[H_3O^+] = 6.7 \times 10^{-2} \text{ M} \quad \text{so} \quad pH = 1.17$$

3. After 50.0 mL of 0.100 M NaOH has been added (midpoint of the titration):

	HCl	+	NaOH	⟶	NaCl	+ H₂O
start	10.0 mmol		5.0 mmol		0 mmol	
change	−5.0 mmol		−5.0 mmol		+5.0 mmol	
after rxn	5.0 mmol		0 mmol		5.0 mmol	

$$M_{HCl} = \frac{5.00 \text{ mmol HCl}}{150. \text{ mL}} = 0.033 \text{ M HCl}$$

$$[H_3O^+] = 3.3 \times 10^{-2} \text{ M} \quad \text{so} \quad pH = 1.48$$

4. After 100. mL of 0.100 M NaOH has been added:

	HCl	+	NaOH	⟶	NaCl	+ H₂O
start	10.0 mmol		10.0 mmol		0 mmol	
change	−10.0 mmol		−10.0 mmol		+10.0 mmol	
after rxn	0 mmol		0 mmol		10.0 mmol	

We have added enough NaOH to neutralize the HCl exactly so this is the equivalence point. A strong acid and a strong base react to give a neutral salt solution so pH = 7.00.

5. After 110.0 mL of 0.100 M NaOH has been added:

	HCl	+	NaOH	⟶	NaCl	+ H₂O
start	10.0 mmol		11.0 mmol		0 mmol	
change	−10.0 mmol		−10.0 mmol		+10.0 mmol	
after rxn	0 mmol		1.0 mmol		10.0 mmol	

The pH is determined by the excess NaOH.

Some household products. Each solution contains a few drops of a universal indicator. A color of yellow or red indicates a pH less than 7. A green to purple color indicates a pH greater than 7.

The end point of the titration of 0.100 M HCl with 0.100 M NaOH using another indicator, bromthymol blue.

$$M_{NaOH} = \frac{1.0 \text{ mmol NaOH}}{210. \text{ mL}} = 0.0048 \text{ } M \text{ NaOH}$$

$$[OH^-] = 4.8 \times 10^{-3} \text{ } M \quad \text{so} \quad pOH = 2.32 \quad \text{and} \quad pH = 11.68$$

Table 19-5 displays the data for the titration of 100.0 mL of 0.100 M HCl by 0.100 M NaOH solution. A few additional points have been included to show the shape of the curve better. These data are plotted in Figure 19-3a. This titration curve has a long "vertical section" over which the pH changes very rapidly with the addition of very small amounts of base. The pH changes from 3.60 (99.5 mL NaOH added) to 10.40 (100.5 mL of NaOH added) in the vicinity of the equivalence point (100.0 mL NaOH added). The midpoint of the vertical section (pH = 7.00) is the equivalence point. We can separate the calculations on this kind of titration into four distinct types that correspond to four regions of the titration curves.

1. Before any strong base is added, the pH depends on the strong acid alone.
2. After some strong base has been added, but before the equivalence point, the remaining (excess) strong acid determines the pH.
3. At the equivalence point, the solution is neutral.
4. Beyond the equivalence point, excess strong base determines the pH.

Ideally, the indicator color change should occur at pH = 7.00. For practical purposes, indicators with color changes in the pH range 4 to 10 can be used in the titration of strong acids and strong bases because the vertical portion of the titration curve is so long. Figure 19-3 shows the ranges of color changes for methyl red and phenolphthalein, two widely used indicators. Both fall within the vertical section of the NaOH/HCl titration curve. When a strong acid is added to a solution of a strong base, the titration curve is inverted, but its essential characteristics are the same (Figure 19-3b).

In Figure 19-3a we see that the curve rises very slowly before the equivalence point. It then rises very rapidly near the equivalence point because there is no hydrolysis. The curve becomes almost flat beyond the equivalence point.

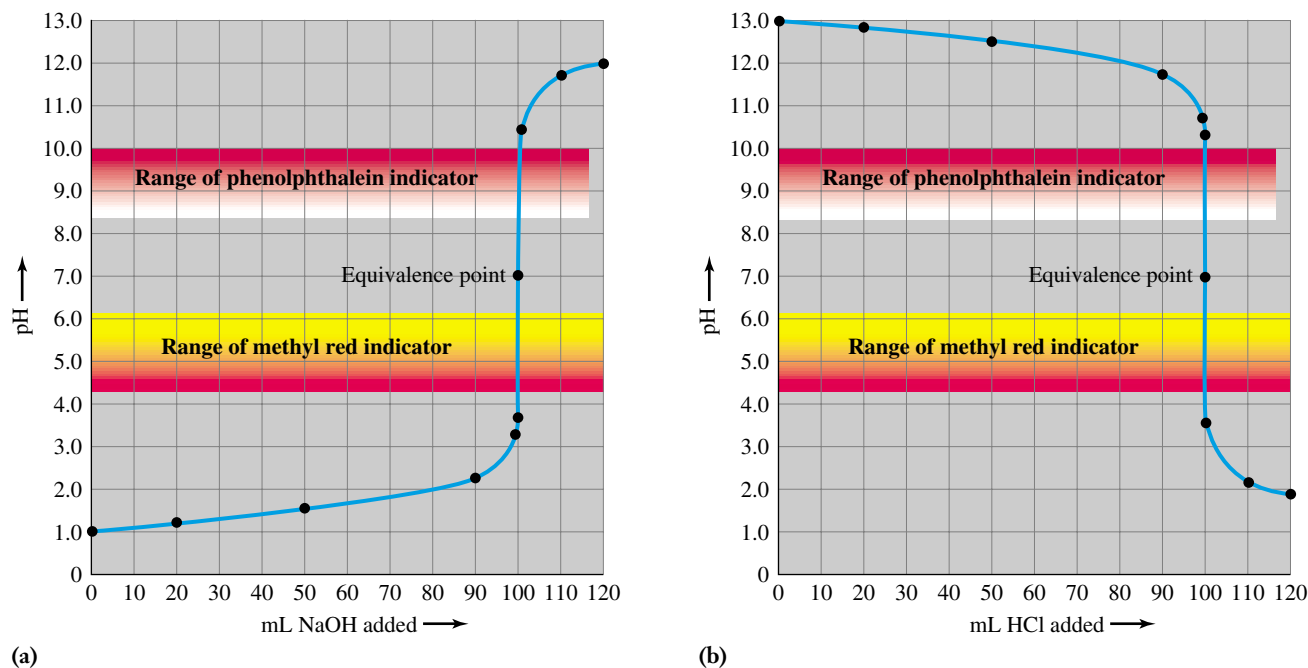| TABLE 19-5	*Titration Data for 100.0 mL of 0.100 M HCl versus NaOH*		
mL of 0.100 M NaOH Added	mmol NaOH Added	mmol Excess Acid or Base	pH
0.0	0.00	10.0 H_3O^+	1.00
20.0	2.00	8.0	1.17
50.0	5.00	5.0	1.48
90.0	9.00	1.0	2.28
99.0	9.90	0.10	3.30
99.5	9.95	0.05	3.60
100.0	10.00	0.00 (eq. pt.)	7.00
100.5	10.05	0.05 OH^-	10.40
110.0	11.00	1.00	11.68
120.0	12.00	2.00	11.96

Figure 19-3 (a) The titration curve for 100. mL of 0.100 *M* HCl with 0.100 *M* NaOH. Note that the "vertical" section of the curve is quite long. The titration curves for other strong acids and bases are identical with this one *if* the same concentrations of acid and bases are used *and if* both are monoprotic. (b) The titration curve for 100. mL of 0.100 *M* NaOH with 0.100 *M* HCl. This curve is similar to that in part (a), but inverted.
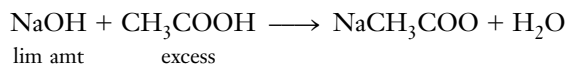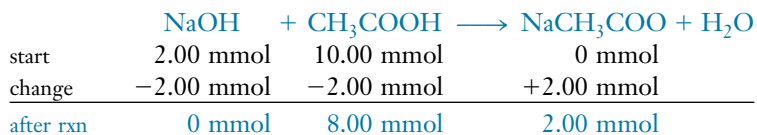
19-6 WEAK ACID/STRONG BASE TITRATION CURVES

When a weak acid is titrated with a strong base, the curve is quite different. The solution is buffered *before* the equivalence point. It is basic *at* the equivalence point because salts of weak acids and strong bases hydrolyze to give basic solutions. So, we can separate the calculations on this kind of titration into four distinct types, which correspond to four regions of the titration curves.

1. Before any base is added, the pH depends on the weak acid alone.
2. After some base has been added, but before the equivalence point, a series of weak acid/salt buffer solutions determines the pH.
3. At the equivalence point, hydrolysis of the anion of the weak acid determines the pH.
4. Beyond the equivalence point, excess strong base determines the pH.

Consider the titration of 100.0 mL of 0.100 *M* CH_3COOH with 0.100 *M* NaOH solution. (The strong electrolyte is added to the weak electrolyte.)

1. Before any base is added, the pH is 2.89 (Example 18-11 and Table 18-5).
2. As soon as some NaOH is added, but before the equivalence point, the solution is buffered because it contains both CH_3COOH and $NaCH_3COO$.

$$NaOH + CH_3COOH \longrightarrow NaCH_3COO + H_2O$$

$$\text{lim amt} \qquad \text{excess}$$

For instance, after 20.0 mL of 0.100 M NaOH solution has been added, we have

	NaOH	+ CH₃COOH	⟶ NaCH₃COO + H₂O
start	2.00 mmol	10.00 mmol	0 mmol
change	−2.00 mmol	−2.00 mmol	+2.00 mmol
after rxn	0 mmol	8.00 mmol	2.00 mmol

We recognize that this is a buffer solution, so we can use the ratio (mmol conjugate base)/(mmol acid) in the Henderson–Hasselbalch equation as we did in Example 19-7.

We could use the K_a expression for these calculations as we did in Example 19-5.

$$pH = pK_a + \log \frac{\text{mmol conjugate base}}{\text{mmol acid}} = pK_a + \log \frac{\text{mmol CH}_3\text{COO}^-}{\text{mmol CH}_3\text{COOH}}$$

$$= 4.74 + \log \frac{2.00}{8.00} = 4.74 + \log(0.250) = 4.74 + (-0.602) = 4.14$$

After some NaOH has been added, the solution contains both NaCH₃COO and CH₃COOH, and so it is buffered until the equivalence point is reached. All points before the equivalence point are calculated in the same way.

Just *before* the equivalence point, the solution contains relatively high concentrations of NaCH₃COO and relatively low concentrations of CH₃COOH. Just *after* the equivalence point, the solution contains relatively high concentrations of NaCH₃COO and relatively low concentrations of NaOH, both basic components. In both regions our calculations are only approximations. Exact calculations of pH in these regions are beyond the scope of this text.

3. At the equivalence point, the solution is 0.0500 M in NaCH₃COO.

	NaOH	+ CH₃COOH	⟶ NaCH₃COO + H₂O
start	10.0 mmol	10.0 mmol	0 mmol
change	−10.0 mmol	−10.0 mmol	+10.0 mmol
after rxn	0 mmol	0 mmol	10.0 mmol

$$M_{\text{NaCH}_3\text{COO}} = \frac{10.0 \text{ mmol NaCH}_3\text{COO}}{200. \text{ mL}} = 0.0500 \ M \text{ NaCH}_3\text{COO}$$
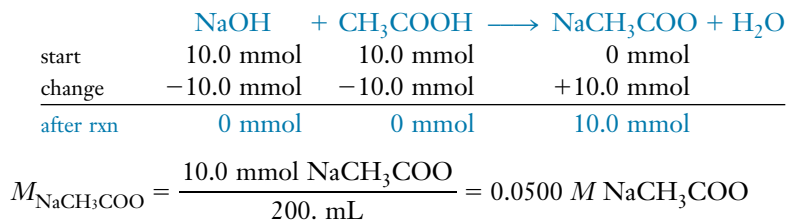
The pH of a 0.0500 M solution of NaCH₃COO is 8.72 (Example 18-19 shows a similar calculation). The solution is distinctly basic at the equivalence point because of the hydrolysis of the acetate ion.

4. Beyond the equivalence point, the concentration of the excess NaOH determines the pH of the solution just as it did in the titration of a strong acid.

Table 19-6 lists several points on the titration curve, and Figure 19-4 shows the titration curve for 100.0 mL of 0.100 M CH₃COOH titrated with a 0.100 M solution of NaOH. This titration curve has a short vertical section (pH ≈ 7 to 10), and the indicator range is limited. Phenolphthalein is the indicator commonly used to titrate weak acids with strong bases (see Table 19-4).

The titration curves for weak bases and strong acids are similar to those for weak acids and strong bases except that they are inverted (recall that strong is added to weak). Figure 19-5 displays the titration curve for 100.0 mL of 0.100 M aqueous ammonia titrated with 0.100 M HCl solution.

TABLE 19-6	Titration Data for 100.0 mL of 0.100 M CH₃COOH with 0.100 M NaOH		

mL 0.100 *M* NaOH Added		mmol Base Added	mmol Excess Acid or Base	pH
0.0 mL		0	10.0 CH_3COOH	2.89
20.0 mL		2.00	8.00	4.14
50.0 mL		5.00	5.00	4.74
75.0 mL	buffered	7.50	2.50	5.22
90.0 mL	region	9.00	1.00	5.70
95.0 mL		9.50	0.50	6.02
99.0 mL		9.90	0.10	6.74
100.0 mL		10.0	0 (equivalence point)	8.72
101.0 mL		10.1	0.10 OH^-	10.70
110.0 mL		11.0	1.0	11.68
120.0 mL		12.0	2.0	11.96
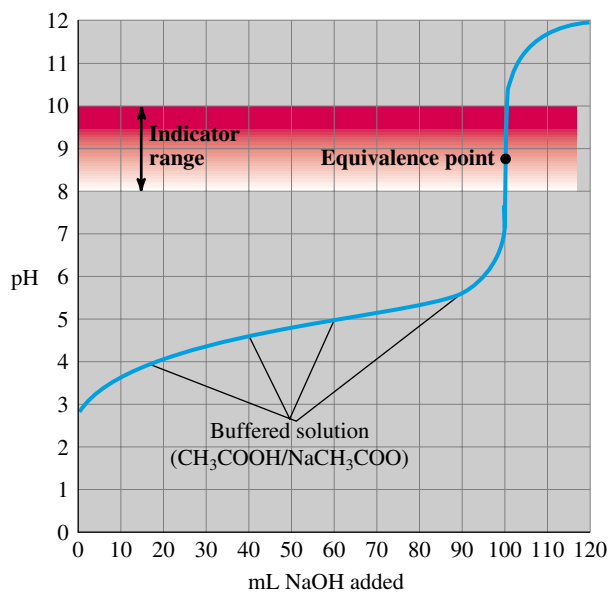
Figure 19-4 The titration curve for 100. mL of 0.100 *M* CH_3COOH with 0.100 *M* NaOH. The "vertical" section of this curve is much shorter than those in Figure 19-3 because the solution is buffered before the equivalence point.
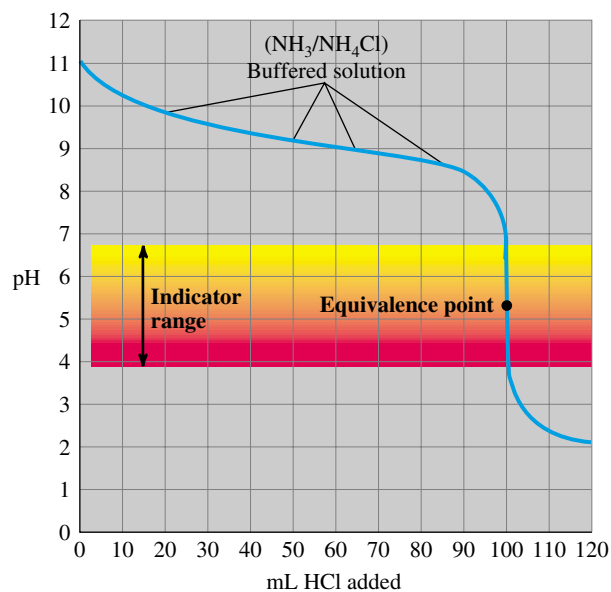
Figure 19-5 The titration curve for 100. mL of 0.100 *M* aqueous ammonia with 0.100 *M* HCl. The vertical section of the curve is relatively short because the solution is buffered before the equivalence point. The curve is very similar to that in Figure 19-4, but inverted.

Figure 19-6 The titration curve for 100. mL of 0.100 M CH_3COOH with 0.100 M aqueous NH_3. Because the solution is buffered before and after the equivalence point, the vertical section of the curve is too short to be noticed. Color indicators cannot be used in such titrations. Instead, physical methods such as conductivity measurements can be used to detect the end point.
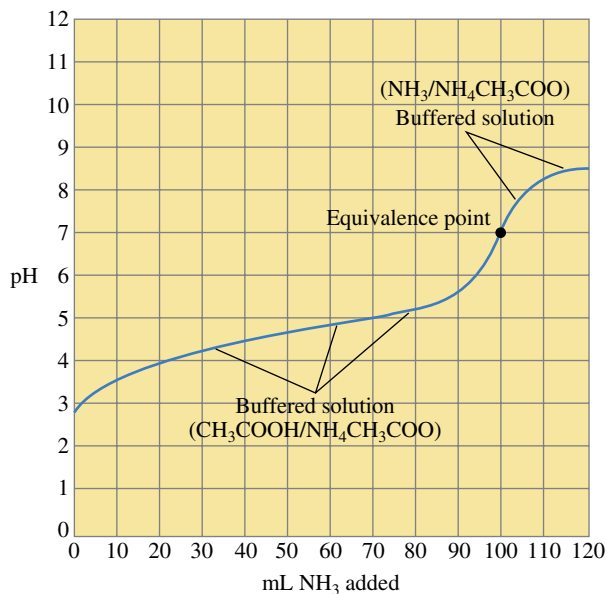
19-7 WEAK ACID/WEAK BASE TITRATION CURVES

In titration curves for weak acids and weak bases, pH changes near the equivalence point are too small for color indicators to be used. The solution is buffered both before and after the equivalence point. Figure 19-6 shows the titration curve for 100.0 mL of 0.100 M CH_3COOH solution titrated with 0.100 M aqueous NH_3. The calculation of values on the curve in Figure 19-6 other than the initial pH and the pH at the equivalence point is beyond the scope of this text.

> ✓ **Problem-Solving Tip:** *Titration Curves*
>
> You can consider a titration curve in four parts.
>
> 1. **Initial solution** (before any titrant is added).
> 2. **Region before the equivalence point.** This may or may not be buffered. The solution is buffered in this region if the substance being titrated is a weak acid or weak base.
> 3. **Equivalence point.** Its location depends on the concentrations of the acid and the base solutions; its pH depends on the strengths of the acid and base.
> 4. **Region beyond the equivalence point.** This becomes nearly flat as more and more excess reactant is added. We often calculate only one or two points in this region.
>
> Recognizing the four regions of a titration curve allows you to decide which kind of calculation is required.

19-8 SUMMARY OF ACID–BASE CALCULATIONS

In this and the previous chapter we have discussed several different types of acidic or alkaline solutions. Table 19-7 summarizes those many different types of solutions.

TABLE 19-7   *A Review of Our Understanding of Nonneutral Aqueous Solutions*

Type of Aq. Solution	Example(s)	Resulting Chemistry or Type of Solution; Calculation	Section
strong acid (represented as HX)	HNO_3 or HCl	*Complete* ionization; reaction goes to completion to form H_3O^+ $$HX + H_2O \longrightarrow H_3O^+ + X^-$$	18-1
strong base [represented as MOH or $M(OH)_2$]	NaOH or $Ba(OH)_2$	*Complete* ionization; reaction goes to completion to form OH^- $$MOH \longrightarrow M^+ + OH^-$$ $$M(OH)_2 \longrightarrow M^{2+} + 2OH^-$$	18-1
weak acid (represented as HA)	CH_3COOH or HCN	*Partial* ionization; $HA + H_2O \rightleftharpoons H_3O^+ + A^-$ Must solve equilibrium expression involving K_a for the acid using *equilibrium* concentrations: $K_a = \dfrac{[H_3O^+][A^-]}{[HA]}$	18-4
weak base (represented as B)	NH_3	*Partial* ionization; $B + H_2O \rightleftharpoons BH^+ + OH^-$ Must solve equilibrium expression involving K_b for the base, using *equilibrium* concentrations: $K_b = \dfrac{[BH^+][OH^-]}{[B]}$	18-4
Salt of *strong base* & *strong acid* (represented as MX)	$NaNO_3$ (salt of NaOH and HNO_3)	No hydrolysis—*neutral solution*	18-7
Salt of *strong base* & *weak acid* (represented as MA)	NaCN (salt of NaOH and HCN)	*Hydrolysis* of conjugate base (A^-) of *weak acid* $\Longrightarrow$ *basic* solution $$A^- + H_2O \rightleftharpoons HA + OH^-$$ Solve weak base equilibrium for A^- using $K_{b \text{ for } A^-} = \dfrac{K_w}{K_{a \text{ for HA}}}$	18-8
Salt of *weak base* & *strong acid* (represented as BHX)	NH_4NO_3 (salt of NH_3 and HNO_3)	*Hydrolysis* of conjugate acid (BH^+) of *weak base* $\Longrightarrow$ *acidic* solution $$BH^+ + H_2O \rightleftharpoons B + H_3O^+$$ Solve weak acid equilibrium for BH^+ using $K_{a \text{ for } BH^+} = \dfrac{K_w}{K_{b \text{ for } B}}$	18-9
Salt of *weak base* & *weak acid* (represented as BHA)	NH_4CN (salt of NH_3 and HCN)	*Hydrolysis* of conjugate base (A^-) of *weak acid* $\Longrightarrow$ *basic* solution and *Hydrolysis* of conjugate acid (BH^+) of *weak base* $\Longrightarrow$ *acidic* solution. This solution can be *basic, neutral,* or *acidic,* depending on which hydrolysis occurs to a greater extent; use K_b and K_a values for the *hydrolysis reactions* to tell which ion will be the dominant factor. (We did not do calculations for this type of salt.)	18-10
Weak acid & *salt* of its conjugate base (represented as HA & MA)	$CH_3COOH + NaCH_3COO$ (or the product of the partial neutralization in a titration of a *weak acid* with a *strong base*	Salt ionizes completely; $MA \longrightarrow M^+ + A^-$ Mixture of weak acid (HA) and its conjugate base (A^-) in significant concentrations gives a *buffer*. Use Henderson–Hasselbalch equation for acid–salt buffer (with initial concentrations or mole ratio): $$pH = pK_a + \log \frac{[\text{conjugate base}]}{[\text{acid}]}$$	19-1, 19-2, 19-3
Weak base & *salt* of its conjugate acid (represented as B & BHX)	$NH_3 + NH_4Cl$ (or the product of the partial neutralization in a titration of a *weak base* with a *strong acid*)	Salt ionizes completely; $NH_4Cl \longrightarrow NH_4^+ + Cl^-$ Mixture of weak base (NH_3) and its conjugate acid (NH_4^+) in significant concentrations gives a *buffer*. Use Henderson–Hasselbalch equation for base–salt buffer (with initial concentrations or mole ratio): $$pOH = pK_b + \log \frac{[\text{conjugate acid}]}{[\text{base}]}$$	19-1, 19-2, 19-3

Key Terms

Buffer solution   A solution that resists changes in pH when strong acids or strong bases are added. A buffer solution contains an acid and its conjugate base, so it can react with added base or acid. Common buffer solutions contain either (1) a weak acid and a soluble ionic salt of the weak acid *or* (2) a weak base and a soluble ionic salt of the weak base.

Common ion effect   Suppression of ionization of a weak electrolyte by the presence in the same solution of a strong electrolyte containing one of the same ions as the weak electrolyte.

End point   The point at which an indicator changes color and a titration should be stopped.

Equivalence point   The point at which chemically equivalent amounts of reactants have reacted.

Henderson–Hasselbalch equation   An equation that enables us to calculate the pH or pOH of a buffer solution directly.

For acid–salt buffer $pH = pK_a + \log \dfrac{[\text{conj. base}]}{[\text{acid}]}$

For base–salt buffer $pOH = pK_b + \log \dfrac{[\text{conj. acid}]}{[\text{base}]}$

Indicator (for acid–base titrations)   An organic compound that exhibits different colors in solutions of different acidities; used to indicate the point at which reaction between an acid and a base is complete.

Titration   A procedure in which one solution is added to another solution until the chemical reaction between the two solutes is complete; usually the concentration of one solution is known and that of the other is unknown.

Titration curve (for acid–base titration)   A plot of pH versus volume of acid or base solution added.

Exercises

Note *All exercises in this chapter assume a temperature of 25°C unless they specify otherwise. Values of K_a and K_b can be found in Appendix F or will be specified in the exercise.*

Basic Ideas

1. (a) What is the relationship between pH and pOH? (b) What is the relationship between K_a and pH? (c) What is the relationship between K_a and pOH?

2. Write the balanced equation for an acid–base reaction that would produce each of the following salts; predict whether an aqueous solution of each salt is acidic, basic, or neutral. (a) $NaNO_3$; (b) KCN; (c) $Al_2(SO_4)_3$; (d) $Mg(CH_3COO)_2$; (e) $(NH_4)_2SO_4$.

3. Write the balanced equation for an acid–base reaction that would produce each of the following salts; predict whether an aqueous solution of each salt is acidic, basic, or neutral. (a) CaF_2; (b) ZnS; (c) $AsCl_3$; (d) $Sr_3(PO_4)_2$; (e) NH_4NO_3.

4. Under what circumstances can it be predicted that a neutral solution is produced by an acid–base reaction? (*Hint:* This question has more than one answer.)
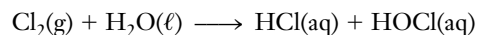
The Common Ion Effect and Buffer Solutions

5. Which of the following solutions are buffered? Each solution was prepared by mixing and diluting appropriate quantities of the two solutes to yield the concentrations indicated. Explain your decision for each solution. (a) 0.10 *M* HCN and 0.10 *M* NaCN; (b) 0.10 *M* NaOH and 0.10 *M* NaCl; (c) 0.10 *M* NH_3 and 0.10 *M* NH_4Br; (d) 0.10 *M* NaOH and 0.90 *M* KOH.

6. Which of the following solutions are buffered? Each solution was prepared by mixing and diluting appropri-

ate quantities of the two solutes to yield the concentrations indicated. Explain your decision for each solution. (a) 1.0 *M* HCN and 0.20 *M* NaCN; (b) 0.10 *M* NaF and 0.10 *M* HF; (c) 0.10 *M* NH_4Cl and 0.90 *M* NH_4Br; (d) 0.10 *M* NaCl and 0.20 *M* HF.

7. Suppose that you have a solution that is 0.50 *M* in methylamine, CH_3NH_2, and 0.00050 *M* in the salt methyl-ammonium chloride, CH_3NH_3Cl. Would you expect this to be an effective buffer solution? Why or why not?

8. Calculate pH for each of the following buffer solutions. (a) 0.10 *M* HF and 0.25 *M* KF; (b) 0.050 *M* CH_3COOH and 0.025 *M* $Ba(CH_3COO)_2$.

9. The pK_a of HOCl is 7.45. Calculate the pH of a solution that is 0.0444 *M* HOCl and 0.0888 *M* NaOCl.

10. Calculate the concentration of OH^- and the pH for the following buffer solutions. (a) 0.30 *M* $NH_3(aq)$ and 0.20 *M* NH_4NO_3; (b) 0.15 *M* $NH_3(aq)$ and 0.20 *M* $(NH_4)_2SO_4$.

11. Calculate the concentration of OH^- and the pH for the following solutions. (a) 0.45 *M* $NH_3(aq)$ and 0.25 *M* NH_4NO_3; (b) 0.10 *M* aniline, $C_6H_5NH_2$, and 0.20 *M* anilinium chloride, $C_6H_5NH_3Cl$.

*12. Buffer solutions are especially important in our body fluids and metabolism. Write net ionic equations to illustrate the buffering action of (a) the $H_2CO_3/NaHCO_3$ buffer system in blood and (b) the NaH_2PO_4/Na_2HPO_4 buffer system inside cells.

13. Calculate the ratio of $[NH_3]/[NH_4^+]$ concentrations that gives (a) solutions of pH = 9.75 and (b) solutions of pH = 9.10.

14. We prepare two solutions as follows. In solution A 0.50 mole of potassium acetate is added to 0.25 mole of acetic acid and diluted to a final volume of 1.00 liter. In solution

B 0.25 mole of potassium acetate is added to 0.50 mole of acetic acid and diluted to 1.00 liter. (a) Which solution is expected to have the lower pH? (b) Explain how you can reach your conclusion without calculating the pH of each solution.

15. Compare the pH of a 0.15 M acetic acid solution to the pH of a solution composed of 0.15 M acetic acid to which 0.15 mole of sodium acetate per liter has been added.

16. Calculate the mass of sodium acetate that must be added to one liter of a 0.125 M acetic acid solution to produce a buffer with the pH of 4.75. Assume that there is no volume change.

17. A solution is produced by dissolving 0.075 mole of formic acid and 0.075 mole of sodium formate in sufficient water to produce 1.00 L of solution. (a) Calculate the pH of this buffer solution. (b) Calculate the pH of the solution after an additional 0.010 mole of sodium formate is dissolved.

Buffering Action

18. Consider the ionization of formic acid, HCOOH.

$$HCOOH + H_2O \rightleftharpoons HCOO^- + H_3O^+$$

What effect does the addition of sodium formate, NaHCOO, have on the fraction of formic acid molecules that undergo ionization in aqueous solution?

19. Briefly describe why the pH of a buffer solution remains nearly constant when small amounts of acid or base are added. Over what pH range do we observe the best buffering action (nearly constant pH)?

20. What is the pH of a solution that is 0.10 M in $HClO_4$ and 0.10 M $KClO_4$? Is this a buffer solution?

21. (a) Find the pH of a solution that is 0.50 M in formic acid and 0.40 M in sodium formate. (b) Find the pH after 0.050 mol HCl has been added to 1.0 liter of the solution.

22. One liter of 0.400 M NH_3 solution also contains 12.78 g of NH_4Cl. How much will the pH of this solution change if 0.142 mole of gaseous HCl is bubbled into it?

23. (a) Find the pH of a solution that is 0.12 M in nitrous acid and 0.15 M in sodium nitrite. (b) Find the pH after 0.15 mol of NaOH has been added to 1.0 liter of the solution.

24. (a) Find the pH of a solution that is 1.00 M in NH_3 and 0.80 M in NH_4Cl. (b) Find the pH of the solution after 0.10 mol of HCl has been added to 1.0 liter of the solution. (c) A solution was prepared by adding NaOH to pure water to give 1.00 liter of solution whose pH = 9.34. Find the pH of this solution after 0.10 mol of HCl has been added to it.

25. (a) Calculate the concentrations of CH_3COOH and CH_3COO^- in a solution in which their total concentration is 0.200 mol/L and the pH is 4.50. (b) If 0.0100 mol of solid NaOH is added to 1.00 L of this solution, how much does the pH change?

26. A solution contains bromoacetic acid, $BrCH_2COOH$, and sodium bromoacetate, $NaBrCH_2COO$, with a total concentration of 0.30 mol/L. If the pH is 3.10, what are the concentrations of the acid and the salt? $K_a = 2.0 \times 10^{-3}$ for $BrCH_2COOH$.

27. Calculate the concentration of propionate ion, $CH_3CH_2COO^-$, in equilibrium with 0.020 M CH_3CH_2COOH (propionic acid) and 0.10 M H^+ from hydrochloric acid. $K_a = 1.3 \times 10^{-5}$ for CH_3CH_2COOH.

28. Calculate the concentration of $C_2H_5NH_3^+$ in equilibrium with 0.015 M $C_2H_5NH_2$ (ethylamine) and 0.0010 M OH^- ion from sodium hydroxide. $K_b = 4.7 \times 10^{-4}$ for ethylamine.

29. When chlorine gas is dissolved in water to make "chlorine water," HCl (a strong acid) and HOCl (a weak acid) are produced in equal amounts.

$$Cl_2(g) + H_2O(\ell) \longrightarrow HCl(aq) + HOCl(aq)$$

What is the concentration of OCl^- ion in a solution containing 0.010 mol of each acid in 1.00 L of solution?

Preparation of Buffer Solutions

30. A buffer solution of pH 5.30 is to be prepared from propionic acid and sodium propionate. The concentration of sodium propionate must be 0.50 mol/L. What should be the concentration of the acid? $K_a = 1.3 \times 10^{-5}$ for CH_3CH_2COOH.

31. We need a buffer with pH 9.00. It can be prepared from NH_3 and NH_4Cl. What must be the $[NH_4^+]/[NH_3]$ ratio?

32. What volumes of 0.150 M acetic acid and 0.100 M NaOH solutions must be mixed to prepare 1.00 L of a buffer solution of pH 4.50 at 25°C?

33. One liter of a buffer solution is prepared by dissolving 0.150 mol of $NaNO_2$ and 0.070 mol of HCl in water. What is the pH of this solution? If the solution is diluted twofold with water, what is the pH?

34. One liter of a buffer solution is made by mixing 500. mL of 1.25 M acetic acid and 500. mL of 0.500 M calcium acetate. What is the concentration of each of the following in the buffer solution? (a) CH_3COOH; (b) Ca^{2+}; (c) CH_3COO^-; (d) H^+. (e) What is the pH?

35. What must be the concentration of benzoate ion, $C_6H_5COO^-$, in a 0.045 M benzoic acid, C_6H_5COOH, solution so that the pH is 5.00?

36. What must be the concentration of chloroacetic acid, $ClCH_2COOH$, in a 0.015 M $NaCH_2ClCOO$ solution so that the pH is 3.00? $K_a = 1.4 \times 10^{-3}$ for $ClCH_2COOH$.

37. What must be the concentration of NH_4^+ in a 0.075 M NH_3 solution so that the pH is 8.80?

Acid–Base Indicators

38. (a) What are acid–base indicators? (b) What are the essential characteristics of acid–base indicators? (c) What

determines the color of an acid–base indicator in an aqueous solution?

39. K_a is 7.9×10^{-8} for bromthymol blue, an indicator that can be represented as HIn. HIn molecules are yellow, and In⁻ ions are blue. What color will bromthymol blue be in a solution in which (a) $[H_3O^+] = 1.0 \times 10^{-4}$ M and (b) pH = 10.30?

*40. The indicator metacresol purple changes from yellow to purple at pH 8.2. At this point it exists in equal concentrations as the conjugate acid and the conjugate base. What are K_a and pK_a for metacresol purple, a weak acid represented as HIn?

41. A series of acid–base indicators can be used to estimate the pH of an unknown solution. Use the values given in Table 19-4 to determine the possible range of pH values of the following solution. The solution was colorless with phenolphthalein, yellow with methyl orange, and yellow with methyl red.

42. A series of acid–base indicators can be used to estimate the pH of an unknown solution. Use the values given in Table 19-4 to determine the possible range of pH values of the following solution. The solution was colorless in phenolphthalein, blue in bromthymol blue, and yellow in methyl orange.

43. Use Table 19-4 to choose one or more indicators that could be used to "signal" reaching a pH of (a) 3.5; (b) 7.0; (c) 10.3; (d) 8.0.

44. A solution of 0.020 M acetic acid is to be titrated with a 0.015 M NaOH solution. What is the pH at the equivalence point? Choose an appropriate indicator for the titration.

45. Demonstrate mathematically that neutral red is red in solutions of pH 3.00, whereas it is yellow in solutions of pH 10.00. HIn is red, and In⁻ is yellow. K_a is 2.0×10^{-7}.

Strong Acid/Strong Base Titration Curves

46. Make a rough sketch of the titration curve expected for the titration of a strong acid with a strong base. What determines the pH of the solution at the following points? (a) No base added; (b) half-equivalence point; (c) equivalence point; (d) excess base added. Compare your curve with Figure 19-3.

For Exercises 47, 52, 57, and 58, calculate and tabulate $[H_3O^+]$, $[OH^-]$, pH, and pOH at the indicated points as we did in Table 19-4. In each case assume that pure acid (or base) is added to exactly 1 L of a 0.0100 molar solution of the indicated base (or acid). This simplifies the arithmetic because we may assume that the volume of each solution is constant throughout the titration. Plot each titration curve with pH on the vertical axis and moles of base (or acid) added on the horizontal axis.

47. Solid NaOH is added to 1 L of 0.0500 M HCl solution. Number of moles of NaOH added: (a) none; (b) 0.00500;

(c) 0.01500; (d) 0.02500 (50% titrated); (e) 0.03500; (f) 0.04500; (g) 0.04750; (h) 0.0500 (100% titrated); (i) 0.0525; (j) 0.0600; (k) 0.0750 (50% excess NaOH). Consult Table 19-4, and list the indicators that could be used in this titration.

48. A 25.0-mL sample of 0.125 M HNO₃ is titrated with 0.100 M NaOH. Calculate the pH of the solution (a) before the addition of NaOH and after the addition of (b) 5.0 mL; (c) 12.5 mL; (d) 25.0 mL; (e) 31.2 mL; (f) 37.5 mL of NaOH.

49. A 33.0-mL sample of 0.245 M HNO₃ solution is titrated with 0.213 M KOH. Calculate the pH of the solution (a) before the addition of KOH and after the addition of (b) 5.55 mL, (c) 12.0 mL, (d) 24.5 mL, (e) 35.2 mL, (f) 38.8 mL of KOH solution.

50. A 44.0-mL sample of 0.145 M HCl solution is titrated with 0.213 M NaOH. Calculate the pH of the solution (a) before the addition of NaOH and after the addition of (b) 5.55 mL, (c) 12.0 mL, (d) 20.5 mL, (e) 27.2 mL, (f) 31.8 mL of NaOH solution.

Weak Acid/Strong Base Titration Curves

51. Make a rough sketch of the titration curve expected for the titration of a weak monoprotic acid with a strong base. What determines the pH of the solution at the following points? (a) No base added; (b) half-equivalence point; (c) equivalence point; (d) excess base added. Compare your curve to Figure 19-4.

52. Solid NaOH is added to exactly 1 L of 0.0200 M CH₃COOH solution. Number of moles NaOH added: (a) none; (b) 0.00400; (c) 0.00800; (d) 0.01000 (50% titrated); (e) 0.01400; (f) 0.01800; (g) 0.01900; (h) 0.0200 (100% titrated); (i) 0.0210; (j) 0.0240; (k) 0.0300 (50% excess NaOH). Consult Table 19-4, and list the indicators that could be used in this titration.

53. A 44.0-mL sample of 0.202 M CH₃COOH solution is titrated with 0.185 M NaOH. Calculate the pH of the solution (a) before the addition of any NaOH solution and after the addition of (b) 15.5 mL, (c) 20.0 mL, (d) 24.0 mL, (e) 27.2 mL, (f) 48.0 mL, (g) 50.2 mL of NaOH solution.

54. A 32.44-mL sample of 0.182 M CH₃COOH solution is titrated with 0.185 M NaOH. Calculate the pH of the solution (a) before the addition of any NaOH solution and after the addition of (b) 15.55 mL, (c) 20.0 mL, (d) 24.02 mL, (e) 27.2 mL, (f) 31.91 mL, (g) 33.12 mL of NaOH solution.

55. A solution contains an unknown weak monoprotic acid, HA. It takes 46.24 mL of NaOH solution to titrate 50.00 mL of the HA solution to the equivalence point. To another 50.00-mL sample of the same HA solution, 23.12 mL of the same NaOH solution is added. The pH of the resulting solution in the second experiment is 5.14. What are K_a and pK_a of HA?

56. Calculate the pH at the equivalence point of the titration of 100.0 mL of each of the following with 0.150 M KOH:

(a) 1.000 M acetic acid; (b) 0.100 M acetic acid; (c) 0.0100 M acetic acid.

Mixed Exercises

*57. Gaseous HCl is added to 1 L of 0.0100 M aqueous ammonia solution. Number of moles HCl added: (a) none; (b) 0.00100; (c) 0.00300; (d) 0.00500 (50% titrated); (e) 0.00700; (f) 0.00900; (g) 0.00950; (h) 0.0100 (100% titrated); (i) 0.0105; (j) 0.0120; (k) 0.0150 (50% excess HCl). Consult Table 19-4, and list the indicators that could be used in this titration.

*58. Gaseous NH_3 is added to exactly 1 L of 0.0100 M HNO_3 solution. Number of moles NH_3 added: (a) none; (b) 0.00100; (c) 0.00400; (d) 0.00500 (50% titrated); (e) 0.00900; (f) 0.00950; (g) 0.0100 (100% titrated); (h) 0.0105; (i) 0.0130. What is the major difference between the titration curve for the reaction of HNO_3 and NH_3 and the other curves you have plotted? Consult Table 19-4. Can you suggest a satisfactory indicator for this titration?

59. Compare the pH of 0.33 M NaCl with the pH of 0.33 M NaCN.

60. Compare the pH of 0.33 M NaCl with the pH of 0.33 M NH_4Cl.

CONCEPTUAL EXERCISES

61. The pH of an equal molar acetic acid/sodium acetate buffer is 4.74. Draw a molecular representation of a small portion of this buffer solution. (You may omit the water molecules.) Draw another molecular representation of the solution after a very small amount of NaOH has been added.

62. Suppose you were asked on a laboratory test to outline a procedure to prepare a buffered solution of pH 8.0 using hydrocyanic acid, HCN. You realize that a pH of 8.0 is basic, and you find that the K_a of hydrocyanic acid is 4.0×10^{-10}. What is your response?

63. The odor of cooked fish is due to the presence of amines. This odor is lessened by adding lemon juice, which contains citric acid. Why does this work?

64. The *end point* of a titration is not the same as the *equivalence point* of a titration. Differentiate between these two concepts.

BUILDING YOUR KNOWLEDGE

65. Acetylsalicylic acid, the active ingredient in aspirin, has a K_a value of 3.0×10^{-4}. We dissolve 0.0100 mole of acetylsalicylic acid in sufficient water to make 1.00 L of solution and then titrate it with 0.500 M NaOH solution. What is the pH at each of these points in the titration? (a) before any of the NaOH solution is added; (b) at the equivalence point; (c) when a volume of NaOH solution has been added that is equal to half the amount required to reach the equivalence point.

*66. What is the pH of a solution that is a mixture of HOCl and HOI, each at 0.15 M concentration?

67. An unknown amount of water is mixed with 350. mL of a 6.0 M NaOH solution. A 75.0-mL sample of the resulting solution is titrated to neutrality with 52.5 mL of 6.00 M HCl. (a) Calculate the concentration of the diluted NaOH solution. (b) What was the concentration of the NaOH solution before it was diluted? (c) What volume of water was added? Assume that the volumes were additive.

68. A 3.5-L container of HCl had no concentration noted on its label. A 20.00-mL sample of this unknown HCl solution is titrated to a pH of 7.0 by 34.0 mL of 3.00 M NaOH solution. Determine the volume of this HCl solution required to prepare 1.5 L of 0.75 M HCl solution.

69. Calculate the pH at the equivalence point for the titration of a solution containing 150.0 mg of ethylamine, $C_2H_5NH_2$, with 0.1000 M HCl solution. The volume of the solution at the equivalence point is 250. mL. Select a suitable indicator. K_b for ethylamine appears in Exercise 28.