Chapter 14
Equilibria in Acid-Base Solutions

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Strategy

- In any problem involving multiple equilibria
  - Identify the key reactions
  - Single out **one** equilibrium and write the reaction and the equilibrium expression
  - Always identify one unknown for which to solve

Outline

1. Buffers
2. Acid-Base Indicators
3. Acid-Base Titrations

Buffers

- Any solution containing appreciable amounts of both a weak acid and its conjugate base
  - Is highly resistant to changes in pH brought about by the addition of a strong acid or base
  - Has a pH close to the pK_a of the weak acid
- Such a solution is called a **buffer**

Equilibria in Solution

- In Chapter 13, we considered single acid or base equilibria in solution
  - The next step is to consider a solution where multiple equilibria are concerned
- Three major concerns
  - Solution of a weak acid and its conjugate base (or *vice-versa*), called a buffer
  - Acid-base indicators
  - Solutions of acids and bases used in titrations

Preparation of a Buffer

- We can prepare a buffer by mixing
  - A weak acid, HB
  - The conjugate base, B^-, as a sodium salt, NaB
    - Recall that Na^+ is a spectator ion so it does not affect pH
- HB reacts with OH^- :
  - $HB (aq) + OH^- (aq) \rightleftharpoons B^- (aq) + H_2O$
- B^- reacts with H^+ :
  - $B^- (aq) + H^+ (aq) \rightleftharpoons HB (aq) + H_2O$

Buffer Reactions

- The (buffer + acid) and (buffer + base) reactions both demonstrate very large equilibrium constants, and go nearly to completion
- Note that
  - The strong base is converted to a weak one by the buffer
  - The strong acid is converted to a weak one by the buffer
  - In this way, a buffer resists large pH changes

Determining [H⁺] in a Buffer System, (Cont'd)

- HB (aq) ⇆ H+ (aq) + B- (aq)

$$K_a = \frac{[H^+][B^-]}{[HB]}$$

$$[H^+] = K_a \frac{[B^-]}{[HB]}$$

$$pH = pK_a + \log\frac{[B^-]}{[HB]}$$

- The last equation is called the Henderson-Hasselbalch equation

Working with Buffers

1. We can determine the pH of a buffer made by mixing a weak acid with its conjugate base
2. We can determine an appropriate **buffer system** (i.e., combination of acid/base) to maintain a desired pH
3. We can determine the small change in pH of a buffer when a strong acid or base is added to it
4. We can determine the **buffer capacity**, i.e., the quantitative ability of the buffer to absorb H⁺ or OH⁻ ions

Notes on the Henderson-Hasselbalch Equation

1. You may always assume that equilibrium is established without appreciably changing the original concentrations of HB or B⁻
2. Because HB and B⁻ are present in the same solution, the ratio of their concentrations is also their mole ratio
   - Can work directly with moles, without converting to concentration for each

Determining [H⁺] in a Buffer System

- The equations that govern a buffer pH are the same as we have seen in Chapter 13: i.e., they are the weak acid or weak base ionization equations
- The equilibrium constants used are the same K_a and K_b constants that we used in Chapter 13 as well

Figure 14.1: Effect of a Buffer

Figure 14.2: Buffer Applications

Buffered aspirin | Blood plasma | Buffer tablets
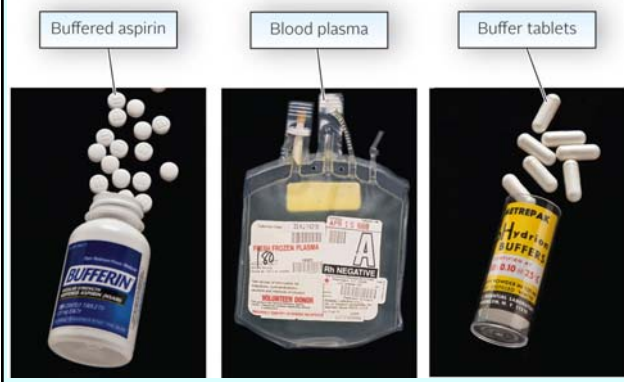
Choosing a Buffer System

- From the Henderson-Hasselbalch equation, we can see:

$$pH = pK_a + \log\frac{[B^-]}{[HB]}$$

- The pH of a buffer depends on two factors:
  - K_a for the acid: if HB and B^- are present in nearly equal amounts, pH = pK_a
  - The ratio of the concentration or amounts of HB and B^-
    - Adding more base than 1:1 will make the buffer more basic

Example 14.1

EXAMPLE 14.1 GRADED

Lactic acid, $C_3H_6O_3$, is a weak organic acid present in both sour milk and buttermilk. It is also a product of carbohydrate metabolism and is found in the blood after vigorous muscular activity. A buffer is prepared by dissolving lactic acid, HLac ($K_a = 1.4 \times 10^{-4}$), and sodium lactate, $NaC_3H_5O_3$, NaLac. Calculate $[H^+]$ and the pH of the buffer if it is made of

(a) 1.00 mol of sodium lactate and 1.00 mol of lactic acid in enough water to form 550.0 mL of solution.

(b) 34.6 g of NaLac dissolved in 550.0 mL of a 1.20 M aqueous solution of HLac. (Assume no volume change after addition of NaLac.)

	ANALYSIS
Information given:	K_a HLac (1.4×10^{-4}); n_{HLac} (1.00 mol); n_{Lac^-} (1.00 mol) volume of solution (550.0 mL)
Asked for:	$[H^+]$ and pH of the buffer

STRATEGY
1. Substitute into Equation 14.2 to obtain $[H^+]$. $$[H^+] = K_a \times \frac{n_{HB}}{n_{B^-}}$$
2. Find pH: $pH = -\log_{10}[H^+]$

continued

Table 14.1: Buffer Systems for Various pH Values

TABLE 14.1 Buffer Systems at Different pH Values

Desired pH	Weak Acid	Weak Base	K_a (Weak Acid)	pK_a
4	Lactic acid (HLac)	Lactate ion (Lac$^-$)	1.4×10^{-4}	3.85
5	Acetic acid ($HC_2H_3O_2$)	Acetate ion ($C_2H_3O_2^-$)	1.8×10^{-5}	4.74
6	Carbonic acid (H_2CO_3)	Hydrogen carbonate ion (HCO_3^-)	4.4×10^{-7}	6.36
7	Dihydrogen phosphate ion ($H_2PO_4^-$)	Hydrogen phosphate ion (HPO_4^{2-})	6.2×10^{-8}	7.21
8	Hypochlorous acid (HClO)	Hypochlorite ion (ClO$^-$)	2.8×10^{-8}	7.55
9	Ammonium ion (NH_4^+)	Ammonia (NH_3)	5.6×10^{-10}	9.25
10	Hydrogen carbonate ion (HCO_3^-)	Carbonate ion (CO_3^{2-})	4.7×10^{-11}	10.32

Example 14.1, (Cont'd)

	SOLUTION
1. $[H^+]$	$[H^+] = 1.4 \times 10^{-4} \times \frac{1.00}{1.00} = 1.4 \times 10^{-4} M$
2. pH	$pH = -\log_{10}(1.4 \times 10^{-4}) = 3.85$

(b)

	ANALYSIS
Information given:	K_a HLac (1.4×10^{-4}); mass of NaLac (34.6 g); M HLac (1.20) volume of solution (550.0 mL)
Information implied:	MM NaLac
Asked for:	$[H^+]$ and pH of the buffer

STRATEGY
1. Find n_{HLac} in solution: $n = V \times M$
2. Find n_{Lac^-} in solution. Recall 1 mol Lac$^-$/1 mol NaLac. Thus $n_{Lac^-} = n_{NaLac} = $ mass NaLac/MM NaLac
3. Substitute into Equation 14.2 to find $[H^+]$.
4. $pH = -\log_{10}[H^+]$

	SOLUTION
1. n_{HLac}	$n = 0.5500 L \times 1.20 \frac{mol}{L} = 0.660$ mol
2. n_{Lac^-}	$n_{Lac^-} = \frac{34.6 \text{ g NaLac}}{112.06 \text{ g/mol}} = 0.309$ mol
3. $[H^+]$	$[H^+] = 1.4 \times 10^{-4} \times \frac{0.660}{0.309} = 3.0 \times 10^{-4} M$
4. pH	$pH = -\log_{10}(3.0 \times 10^{-4}) = 3.52$

END POINT
Looking back at part (a), note that when equal amounts of a weak acid and its conjugate base are present, pH = pK_a.

Example 14.2

EXAMPLE 14.2 GRADED

Suppose you need to prepare a buffer with a pH of 9.00.

(a) Which of the buffer systems in Table 14.1 would you choose?

(b) What should be the ratio of the concentration of weak acid, HB, to its conjugate base, B^-?

(c) What mass in grams of B^- should be added to 245 mL of 0.880 M HB to give a pH of 9.00?

(a)

STRATEGY AND SOLUTION
Check the K_a values in Table 14.1. Find the buffer system with a pK_a value closest to 9.00. The clear choice is the NH_4^+/NH_3 system with a pK_a of 9.25.

(b)

	ANALYSIS
Information given:	pH (9.00); from part (a): buffer system (NH_4^+/NH_3)
Information implied:	K_a of NH_4^+
Asked for:	$[NH_4^+]/[NH_3]$

STRATEGY
1. Find $[H^+]$.
2. Substitute into Equation 14.1 where [HB] is $[NH_4^+]$ and B^- is $[NH_3]$.

	SOLUTION
1. $[H^+]$	$pH = -\log_{10} 9.00 = 1.0 \times 10^{-9} M$
2. $\frac{NH_4^+}{NH_3}$	$[H^+] = K_a \times \frac{NH_4^+}{NH_3} \longrightarrow \frac{NH_4^+}{NH_3} = \frac{[H^+]}{K_a} = \frac{1.0 \times 10^{-9}}{5.6 \times 10^{-10}} = 1.8$

Example 14.2, (Cont'd)

ANALYSIS	
Information given:	from part (a): buffer system (NH_4^+/NH_3) from part (b): [H^+] (1.0×10^{-9} M); NH_4^+/NH_3 (1.8) NH_4^+ solution: V (0.245 L); M (0.880)
Information implied:	molar mass of NH_3
Asked for:	mass of NH_3 required to prepare a buffer with pH 9.0.

continued

Example 14.3

EXAMPLE 14.3 GRADED

The food industry uses the acetic acid/sodium acetate buffer to control the pH of food. Given the following mixtures of acetic acid, $HC_2H_3O_2$ (HAc), and sodium hydroxide, show by calculation which of the following solutions is/are a buffer.

(a) 0.300 mol NaOH and 0.500 mol $HC_2H_3O_2$
(b) 25.00 mL of 0.100 M NaOH and 35.00 mL of 0.125 M $HC_2H_3O_2$
(c) 5.00 g of NaOH and 150.0 mL of 0.500 M $HC_2H_3O_2$

ANALYSIS	
Information given:	mol NaOH = mol OH$^-$ (0.300); mol HAc (0.500)
Information implied:	K_a for HAc (Table 13.2)
Asked for:	Is the solution a buffer?

STRATEGY
1. Write the reaction for a strong base and a weak acid, where HB is HAc. $\quad$ HB(aq) + OH$^-$(aq) $\longrightarrow$ B$^-$(aq) + H_2O 2. Fill in a table like the one shown in the preceding discussion. 3. Recall that for a solution to be a buffer, the solution must have a weak acid and its conjugate base.

SOLUTION			
1. Reaction	HAc(aq) + OH$^-$(aq) $\longrightarrow$ Ac$^-$(aq) + H_2O		
2. Table		n_{OH^-}	n_{HAc}	n_{Ac^-}

	n_{OH^-}	n_{HAc}	n_{Ac^-}
Original	0.300	0.500	0
Change	−0.300	−0.300	+0.300
Final	0	0.200	0.300

3. Buffer?	There are 0.200 mol HAc and 0.300 mol Ac$^-$ after reaction. The solution is a buffer.

Example 14.2, (Cont'd)

STRATEGY
1. Find mol NH_4^+. $\quad n = V \times M$ 2. Since there is only one solution, [NH_4^+]/[NH_3] = mol NH_4^+/mol NH_3 = 1.8. Substitute mol NH_4^+ and find mol NH_3. 3. Find the mass of NH_3 required using its molar mass.

SOLUTION	
1. mol NH_4^+	$n = (0.245$ L)(0.880 mol/L) = 0.216 mol
2. mol NH_3	$\dfrac{0.216}{\text{mol } NH_3} = 1.8 \longrightarrow$ mol NH_3 = 0.12
3. mass NH_3	mass = (0.12 mol)(17.03 g/mol) = 2.0 g

Example 14.3, (Cont'd)

ANALYSIS	
Information given:	from part (a): reaction (HAc(aq) + OH$^-$(aq) $\longrightarrow$ Ac$^-$(aq) + H_2O) NaOH: V (25.00 mL); M (0.100) HAc: V (35.00 mL); M (0.125)
Information implied:	K_a for HAc
Asked for:	Is the solution a buffer?

STRATEGY
1. Find mol OH$^-$. 2. Find mol HAc. 3. Make a table as in part (a). 4. Check for the presence of the weak acid (HAc) and its conjugate base (Ac$^-$) after reaction is complete.

continued

Alternate Route to Buffers

- Partial neutralization of a weak acid by a strong base will produce a buffer
- Partial neutralization of a weak base by a strong acid will also produce a buffer
  - H^+ (aq) + NH_3 (aq) $\rightleftharpoons$ NH_4^+ (aq)
  - Adding 0.18 mol HCl to 0.28 mol NH_3 will produce 0.18 mol NH_4^+ and leave 0.10 mol NH_3 unreacted
  - There must be both species present in order to produce a buffer

Example 14.3, (Cont'd)

SOLUTION	
1. mol OH$^-$	(0.02500 L)(0.100 mol/L) = 2.50×10^{-3} mol
2. mol HAc	(0.03500 L)(0.125 mol/L) = 4.38×10^{-3} mol
3. Table	

	n_{OH^-}	n_{HAc}	n_{Ac^-}
Original	2.50×10^{-3}	4.38×10^{-3}	0
Change	-2.50×10^{-3}	-2.50×10^{-3}	$+2.50 \times 10^{-3}$
Final	0	1.88×10^{-3}	2.50×10^{-3}

4. Buffer?	There are 2.50×10^{-3} mol Ac$^-$ and 1.88×10^{-3} mol HAc after reaction. The solution is a buffer.

Example 14.3, (Cont'd)

ANALYSIS

Information given:	from part (a): reaction (HAc(aq) + OH⁻(aq) ⟶ Ac⁻(aq) + H₂O) NaOH: mass (5.00 g) HAc: V (150.0 mL); M (0.500)
Information implied:	K_a for HAc
Asked for:	Is the solution a buffer?

STRATEGY

1. Find mol OH⁻.
2. Find mol HAc.
3. Make a table as in part (a).
4. Check for the presence of the weak acid (HAc) and its conjugate base (Ac⁻) after reaction is complete.

SOLUTION

1. mol OH⁻	mol NaOH = $\frac{5.00\ g}{40.0\ g/mol}$ = 0.125 = mol OH⁻
2. mol HAc	(0.1500 L)(0.500 mol/L) = 0.0750 mol
3. Table	

	P_{HAc}	$P_{OH⁻}$	$P_{Ac⁻}$
Original	0.125	0.0750	0
Change	−0.0750	−0.0750	+0.0750
Final	0.050	0	0.0750

4. Buffer?	There are 0.0750 mol Ac⁻ and no mol HAc after reaction. The solution is not a buffer.

END POINT

To make a buffer from a strong base and a weak acid (or a strong acid and a weak base), the strong base (or strong acid) must be the limiting reactant (the reactant with the smaller number of moles).

Example 14.4, (Cont'd)

STRATEGY

1. Write the reaction between the strong acid H⁺ and the conjugate base, Lac⁻.
2. Adding H⁺ uses up the conjugate base in a 1:1 stoichiometric ratio.
   mol Lac⁻ after addition = mol Lac⁻ − mol H⁺
3. Adding H⁺ produces more weak acid in a 1:1 stoichiometric ratio.
   mol HLac after addition = mol HLac + mol H⁺
4. Substitute into Equation 14.2 to find [H⁺] and pH.

SOLUTION

1. Reaction	Lac⁻(aq) + H⁺(aq) ⟶ HLac (aq)
2. mol Lac⁻ after H⁺ addition	mol Lac⁻ = 1.00 − 0.08 = 0.92 mol
3. mol HLac after H⁺ addition	mol HLac = 1.00 + 0.08 = 1.08 mol
4. [H⁺]; pH	[H⁺] = $1.4 \times 10^{-4} \times \frac{1.08}{0.92}$ = 1.6×10^{-4}
	pH = −log₁₀(1.6 × 10⁻⁴) = 3.80

Effect of Added H⁺ or OH⁻ on Buffer Systems

- Fundamental equations
  - Acid
    - H^+ (aq) + B^- (aq) ⇌ HB (aq)
  - Base
    - OH^- (aq) + HB (aq) ⇌ B^- (aq) + H_2O

Example 14.4, (Cont'd)

ANALYSIS

Information given:	mol HLac (1.00); mol Lac⁻ (1.00); mol NaOH = mol OH⁻ (0.08) pH of the buffer (3.85) K_a for HLac (1.4 × 10⁻⁴)
Asked for:	pH of the buffer after the addition of strong base

STRATEGY

1. Write the reaction between the strong base OH⁻ and the weak acid, HLac.
2. Adding OH⁻ uses up the weak acid in a 1:1 stoichiometric ratio.
   mol HLac after addition = mol HLac − mol OH⁻
3. Adding OH⁻ produces more conjugate base in a 1:1 stoichiometric ratio.
   mol Lac⁻ after addition = mol Lac⁻ + mol OH⁻
4. Substitute into Equation 14.2 to find [H⁺] and pH.

SOLUTION

1. Reaction	HLac(aq) + OH⁻(aq) ⟶ Lac⁻(aq) + H₂O
2. mol HLac after OH⁻ addition	mol HLac = 1.00 − 0.08 = 0.92 mol
3. mol Lac⁻ after OH⁻ addition	mol Lac⁻ = 1.00 + 0.08 = 1.08 mol
4. [H⁺]; pH	[H⁺] = $1.4 \times 10^{-4} \times \frac{0.92}{1.08}$ = 1.2×10^{-4}
	pH = −log₁₀(1.2 × 10⁻⁴) = 3.92

continued

Example 14.4

EXAMPLE 14.4

Consider the buffer described in Example 14.1, where $n_{HLac} = n_{Lac⁻} = 1.00$ mol (K_a HLac = 1.4 × 10⁻⁴). You will recall that in this buffer the pH is 3.85. Calculate the pH after addition of

(a) 0.08 mol of HCl   (b) 0.08 mol of NaOH

(a)

ANALYSIS

|	
Information given:	mol HLac (1.00); mol Lac⁻ (1.00); mol HCl = mol H⁺ (0.08) pH of the buffer (3.85) K_a for HLac (1.4 × 10⁻⁴)
Asked for:	pH of the buffer after the addition of acid

continued

Example 14.4, (Cont'd)

END POINTS

1. Adding a strong acid to a buffer
   - increases the number of moles of the weak acid.
   - decreases the number of moles of the conjugate base.
   - decreases the pH by a small amount. (In this case: 3.85 ⟶ 3.80)
2. Adding a strong base to a buffer
   - increases the number of moles of the conjugate base.
   - decreases the number of moles of the weak acid.
   - increases the pH by a small amount. (In this case: 3.85 ⟶ 3.92)
3. One cannot add an unlimited amount of strong acid or base. When the weak acid or its conjugate base becomes the limiting reactant, then the buffer is destroyed and only H⁺ and the weak acid are present (if H⁺ is added) or OH⁻ and the weak base are left (if OH⁻ is added).

Buffer Function

- Example 14.4 illustrates how a buffer functions:
  - Strong acid is converted to weak acid
  - Strong base is converted to weak base

Figure 14.3
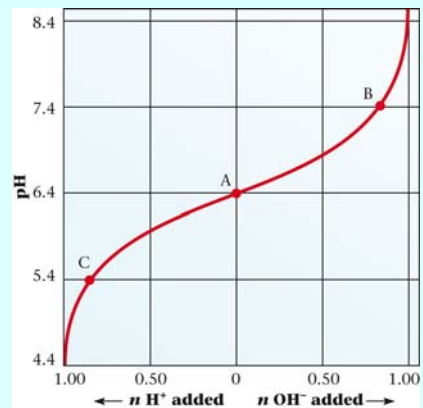
Buffer Illustration with Acid-Base Indicator

These tubes show the effect of adding a few drops of strong acid or strong base to water. The pH changes drastically, giving a pronounced color change with universal indicator.

The experiment is repeated in these tubes using a buffer of pH 7 instead of water. This time the pH changes only very slightly, and there is no change in color of the indicator.

Buffer Range

- The **buffer range** is the pH range over which the buffer is effective
  - Buffer range is related to the ratio of HB/B⁻
  - The further the ratio is from 1:1, the less effective the buffer is and the shorter the buffer range

Buffer Capacity

- The **buffer capacity** to react with acid or base is limited
  - Eventually, all the HB reacts with OH⁻
  - Eventually, all the B⁻ reacts with H⁺
- We can plot the pH on the y-axis and the number of moles of H⁺ and OH⁻ added on the X-axis to prepare a buffer capacity plot
  - Point A is the native buffer pH
  - Point B is the effective limit of base buffering
  - Point C is the effective limit of acid buffering

Example 14.5

6

Acid-Base Indicators

- An acid-base indicator is useful in determining the equivalence point in a titration
  - The indicator changes color to signal the point at which neutralization has occurred (the **equivalence point**)
  - The point at which the indicator changes color is called the **endpoint**

Figure 14.4

Methyl red goes from red at low pH, to orange at about pH 5, to yellow at high pH.

Bromthymol blue is yellow at low pH, blue at high pH, and green at about pH 7.

Phenolphthalein goes from colorless to pink at about pH 9.
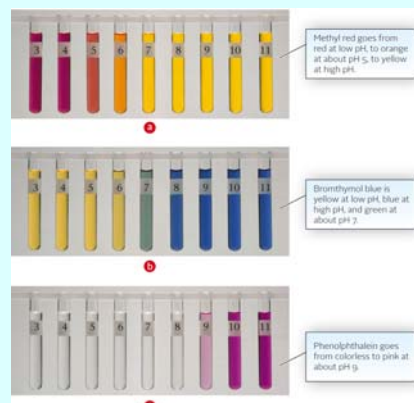
Indicators as Weak Organic Acids

- Indicators are weak organic acids with a special property
  - They are one color in acid and …
  - Another color in base
- We can write the formula for an indicator as HIn
- Equilibrium for HIn is the same as for any other weak acid
  - HIn (aq) $\rightleftharpoons$ H$^+$ (aq) + In$^-$ (aq)

$$K_a = \frac{[H^+][In^-]}{[HIn]}$$

Table 14.2

TABLE 14.2 Colors and End Points of Indicators

	Color [HIn]	Color [In⁻]	K_a	pH at End Point
Methyl red	Red	Yellow	1×10^{-5}	5
Bromthymol blue	Yellow	Blue	1×10^{-7}	7
Phenolphthalein	Colorless	Pink	1×10^{-9}	9

Which Color?

- The color of the indicator is controlled by [H$^+$], which determines [HIn]/[In]

- If $\dfrac{[HIn]}{[In^-]} \geq 10$ the indicator will be the acid color

- If $\dfrac{[HIn]}{[In^-]} \leq 0.10$ the indicator will be the base color

- If $\dfrac{[HIn]}{[In^-]} \approx 1$ the indicator will be an intermediate color

Summary of Properties of an Indicator

- Two factors control the color of the indicator and the pH at which it will change color
  - The ratio of [HIn]/[In$^-$]
  - The K_a of the indicator
  - A color change occurs when [H$^+$] ≈ pK$_a$ (or, expressed in logarithmic terms, pH ≈ pK$_a$)

Bromthymol Blue

- Yellow in acid
- Blue in base
- $K_a = 1 \times 10^{-7}$
- As the pH increases,
  - At pH 6, the indicator is yellow
  - Between pH 6 and 7, the color changes to green
  - At pH 7, we have a green color
  - Between pH 7 and 8, the green changes to blue
  - At pH 8 (and above) the indicator is blue

Acid-Base Titrations

- Recall from Chapter 4 that we can analyze an acid (or base) by reacting it with a known quantity of a known concentration of base (or acid)
  - Strong acid-strong base
  - Weak acid-strong base
  - Weak base-strong acid

Example 14.6

EXAMPLE 14.6

Consider bromthymol blue ($K_a = 1 \times 10^{-7}$). At pH 6.5,
(a) calculate the ratio [In⁻]/[HIn].
(b) what is the color of the indicator at this point?

ANALYSIS	
Information given:	K_a for bromthymol blue (1×10^{-7}) pH (6.5)
Information implied:	color of bromthymol blue at different pH values
Asked for:	(a) [In⁻]/[HIn] (b) color of bromthymol blue at pH 6.5

continued

Strong Acid-Strong Base Titration

- Recall that strong acids ionize 100% to H^+
- Strong bases ionize 100% to OH^-
- H^+ and OH^- combine to produce water
  - The other two ions – the anion of the acid and the cation of the base – are spectators

Example 14.6, (Cont'd)

STRATEGY	

(a) Convert pH to [H⁺] and substitute into Equation 14.1 to find [In⁻]/[HIn].
(b) Find the color of bromthymol blue at pH 6.5 by using the information in the above discussion of the colors for bromthymol blue at different pH values.
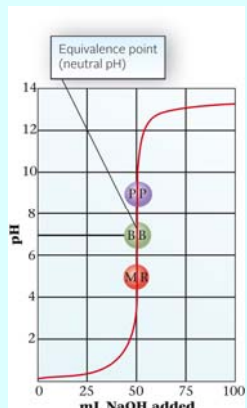
SOLUTION	
(a) [In⁻]/[HIn]	$6.5 = -\log_{10}[H^+] \longrightarrow [H^+] = 3 \times 10^{-7}$ $\dfrac{[In^-]}{[HIn]} = \dfrac{K_a}{[H^+]} = \dfrac{1 \times 10^{-7}}{3 \times 10^{-7}} = \dfrac{1}{3}$
(b) bromthymol blue color	At pH 7, bromthymol blue is green. Below pH 6, bromthymol blue is yellow. Since 6.5 is halfway between 6 and 7, bromthymol blue at pH 6.5 is yellow-green.

Titrating

Figure 14.5

Equivalence point (neutral pH)

PP
BB
MB

pH (y-axis), mL NaOH added (x-axis)

SOLUTION

Reaction	$H^+(aq) + OH^-(aq) \longrightarrow H_2O$
mol HCl	mol HCl $= V \times M = (0.05000 \text{ L})(1.000 \text{ mol/L}) = 0.05000$
mol NaOH	$0.05000 \text{ mol HCl} \times \frac{1 \text{ mol } H^+}{1 \text{ mol HCl}} \times \frac{1 \text{ mol } OH^-}{1 \text{ mol } H^+} \times \frac{1 \text{ mol NaOH}}{1 \text{ mol } OH^-} = 0.05000 \text{ mol NaOH}$
Volume of NaOH	$V = \frac{0.05000 \text{ mol}}{0.7450 \text{ mol/L}} = 0.06711 \text{ L}$

(b)

ANALYSIS

| Information given: | HCl: V (0.05000 L); M (1.000)
from part (a): mol H^+ (0.05000); V NaOH (67.11 mL)
volume NaOH in the titration (67.11 − 0.02 = 67.09 mL) |
| Asked for: | pH of the solution after NaOH is added *continued* |

Features of a Strong Acid-Strong Base Titration

- The pH starts out very low
- There is a gradual rise in pH as base is added
- Near the equivalence point, the pH rises sharply
  - Most of the acid has been neutralized
- After the equivalence point, the pH rises slowly as more base is added to the titration mixture
- The K for this reaction is $1/K_w$ or 1×10^{14}
- The pH at the equivalence point is 7.00
- Any acid-base indicator can be used for a strong acid-strong base titration

STRATEGY

1. Find mol OH^-.
2. Fill in the following stoichiometric table.

	H^+	OH^-
Mol before reaction		
Change		
Mol after reaction		
Volume		

This table looks almost like the equilibrium table in Chapter 12.

3. Find [excess reactant]

$$[\text{excess reactant}] = \frac{\text{mol excess reactant}}{(\text{volume } H^+) + (\text{volume } OH^-)}$$

4. Find pH

SOLUTION

1. mol OH^- $(0.06709 \text{ L})(0.7450 \text{ mol/L}) = 0.04998 \text{ mol}$
2. Table

	H^+	OH^-
Mol before reaction	0.05000	0.04998
Change	−0.04998	−0.04998
Mol after reaction	2×10^{-5}	0
Volume	50.00 mL	67.09 mL

3. $[H^+]$ $[H^+] = \frac{2 \times 10^{-5}}{(0.05000 + 0.06709) \text{ L}} = 2 \times 10^{-4} M$

4. pH $pH = -\log_{10}(2 \times 10^{-4}) = 3.7$

Example 14.7

EXAMPLE 14.7

When 50.00 mL of 1.000 M HCl is titrated with 0.7450 M NaOH, the pH increases.

(a) How many milliliters of NaOH are required to reach the equivalence point and a pH of 7.00?

(b) Find the pH when the volume of NaOH added is 0.02 mL less than the volume required to reach the equivalence point.

(c) Find the pH when the volume of NaOH added is 0.02 mL more than the volume required to reach the equivalence point.

(a)

ANALYSIS

Information given:	HCl: V (50.00 mL); M (1.000) NaOH: M (0.7450)
Information implied:	acid-base reaction
Asked for:	volume of NaOH required to reach the equivalence point

STRATEGY

1. Recall the stoichiometry of acid-base reactions discussed in Chapter 4.
2. Write the reaction.
3. Find mol HCl.
4. Follow the plan:

mol HCl $\xrightarrow{\text{atomic ratio}}$ mol H^+ $\xrightarrow{\text{stoichiometric ratio}}$ mol OH^- $\xrightarrow{\text{atomic ratio}}$ mol NaOH $\xrightarrow{M}$ V NaOH

(c)

ANALYSIS

| Information given: | HCl: V (0.05000 L); M (1.000)
from part (a): mol H^+ (0.05000); V NaOH (67.11 mL)
volume NaOH in the titration (67.11 + 0.02 = 67.13 mL) |
| Asked for: | pH of the solution after NaOH is added |

STRATEGY

1. Find mol OH^-.
2. Fill in a stoichiometric table as in part (b).
3. Find [excess reactant] as in part (b).
4. Find pH. *continued*

Example 14.7, (Cont'd)

SOLUTION

1. mol OH⁻	$(0.06713 \text{ L})(0.7450 \text{ mol/L}) = 0.05001$ mol	
2. Table		

	H⁺	OH⁻
Mol before reaction	0.05000	0.05001
Change	−0.05000	−0.05000
Mol after reaction	0	1×10^{-5}
Volume	50.00 mL	6713 mL

3. [OH⁻]	$[OH^-] = \dfrac{1 \times 10^{-5}}{0.05000 + 0.06713 \text{ L}} = 9 \times 10^{-5}\,M;\ [H^+] = 1 \times 10^{-10}\,M$
4. pH	$pH = -\log_{10}(1 \times 10^{-10}) = \underline{10.0}$

END POINT

Note that half a drop before the end point (pH = 7) is reached, the pH is 3.8. When half a drop is added after the end point is reached, the end point changes from 7 to 10. This is predicted by Figure 14.5.

## Figure 14.7: Molecular View of a Titration

$nHB = nB^- = 3$

$[H^+] = K_a \dfrac{nHB}{nB^-} = K_a \dfrac{3}{3} = K_a$

$pH = pK_a$
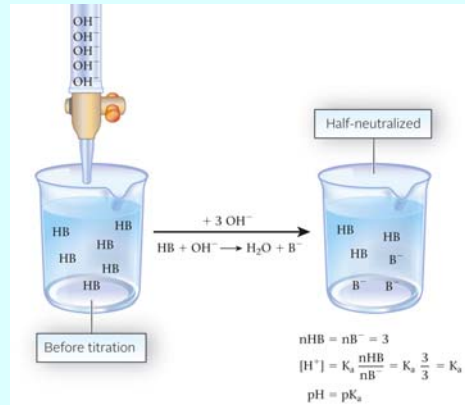
Weak Acid-Strong Base Titration

- Consider the titration of acetic acid with sodium hydroxide
  - $HC_2H_3O_2\ (aq) + OH^-\ (aq) \rightleftharpoons C_2H_3O_2^-\ (aq) + H_2O$
  - K is the inverse of the K_b for $C_2H_3O_2^-$
  - $K = 1/5.6 \times 10^{-10} = 1.8 \times 10^9$
  - K is very large, but not as large as that for a strong acid-strong base titration

---

Notes on Acetic Acid-Sodium Hydroxide Titration

- The pH starts out above 2; the titration begins with a weak acid
- The pH rises slowly until the equivalence point is approached, then rises rapidly
  - The region between the beginning and the equivalence point has $HC_2H_3O_2 \rightleftharpoons C_2H_3O_2^-$, which is a buffer solution
- At the equivalence point, we have a solution of a weak base ($C_2H_3O_2^-$), with a pH greater than 7 as a result
- After the equivalence point, the pH rises slowly, as a strong base is being added to a weak one

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Figure 14.6
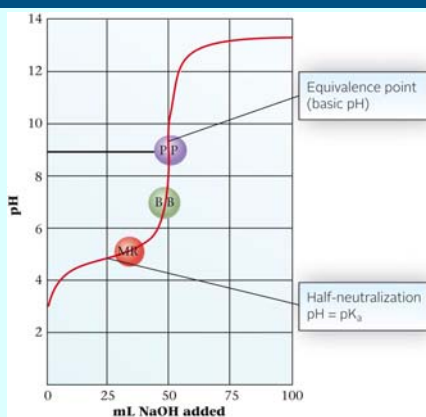
Example 14.8

EXAMPLE 14.8

50.00 mL of 1.000 M acetic acid, $HC_2H_3O_2$, is titrated with 0.8000 M NaOH. Find the pH of the solution at the following points in the titration:

ⓐ before any base is added

ⓑ when half the acetic acid has been neutralized

ⓒ at the equivalence point

ⓐ

ANALYSIS

Information given:	$HC_2H_3O_2$ (HAc): V (0.05000 L), M (1.000) NaOH: M (0.8000)
Information implied:	K_a for HAc
Asked for:	pH before titration starts (no base added)

STRATEGY

1. This is simply determining the pH of a weak acid. Recall Example 13.7.
2. Let $x = [H^+] = [Ac^-]$ at equilibrium. HAc at equilibrium = $[HAc]_o - x$. Make the assumption that $x = [H^+] \ll [HAc]_o$.
3. Substitute into Equation 13.5, solve for x, and check the assumption.
4. Find pH.

Example 14.8, (Cont'd)

SOLUTION

$x = [H^+]$	$1.8 \times 10^{-5} = \dfrac{(x)(x)}{1.000 - x} = \dfrac{x^2}{1.000} \longrightarrow x = 4.2 \times 10^{-3}\ M$
Check assumption	% ionization $= \dfrac{4.2 \times 10^{-3}}{1.00} \times 100\% = 0.42\% < 5\%$
	The assumption is valid.
pH	$pH = -\log_{10}(4.2 \times 10^{-3}) = 2.38$

(b)

ANALYSIS

Information given:	$HC_2H_3O_2$ (HAc): V (0.05000 L), M (1.000)
	NaOH: M (0.8000)
Information implied:	K_a for HAc
Asked for:	pH at half-neutralization.

SOLUTION

1. $[H^+]$	At half-neutralization $[H^+] = K_a$; $[H^+] = 1.8 \times 10^{-5}$
2. pH	$pH = -\log_{10}(1.8 \times 10^{-5}) = 4.74$

continued

Weak Acid- Strong Base Indicator Selection

- In choosing an indicator for the acetic acid-sodium hydroxide titration, we need one that will change color at basic pH
  - Because the product of the titration is a weak base, the equivalence point will be basic
  - Phenolphthalein, with endpoint pH = 9, is a good choice for this titration

---

Example 14.8, (Cont'd)

(c)

ANALYSIS

Information given:	$HC_2H_3O_2$ (HAc): V (0.05000 L), M (1.000); from part (a): n (0.05000 mol)
	NaOH: M (0.8000)
Information implied:	K_a for HAc and K_b for Ac^-
Asked for:	pH at the equivalence point

STRATEGY

1. Write the reaction for the titration.
2. Find the volume of NaOH required to reach the equivalence point.
   For the titration: mol HAc = mol OH^-
3. At the equivalence point, all the acetic acid has been converted to acetate ions and mol Ac^- = mol HAc at the start. Find $[Ac^-]$.
   $[Ac^-] = \dfrac{mol\ Ac^-}{V_{HAc} + V_{OH^-}}$
4. Find $[OH^-]$ by substituting into Equation 13.8.
5. Find $[H^+]$ and pH.

Strong Acid-Weak Base Titration

- Hydrochloric acid with ammonia
  - H_3O^+ (aq) + NH_3 (aq) $\rightleftharpoons$ NH_4^+ (aq) + H_2O
- Simplified reaction:
  - H^+ (aq) + NH_3 (aq) $\rightleftharpoons$ NH_4^+ (aq)
    - Note that K is $1/K_a$ for NH_4^+
    - K = $1/5.6 \times 10^{-10}$ = 1.8×10^9
- K is large; it is of the same magnitude as the K for a weak acid-strong base titration

---

Example 14.8, (Cont'd)

SOLUTION

1. Reaction	$HAc(aq) + OH^-(aq) \longrightarrow Ac^-(aq) + H_2O$
2. Volume NaOH required	mol HAc = 0.05000 mol = mol OH^- = mol NaOH
	volume $= \dfrac{0.05000\ mol}{0.800\ mol/L} = 0.0625\ L$
3. $[Ac^-]$	mol Ac^- = mol HAc = 0.05000 mol
	$[Ac^-] = \dfrac{0.05000\ mol}{(0.05000 + 0.06250)\ L} = 0.4444\ M$
4. $[OH^-]$	$K_b = \dfrac{[OH^-][HAc]}{[Ac^-]} \longrightarrow 5.6 \times 10^{-10} = \dfrac{(x)(x)}{0.4444}$
	$x = [OH^-] = 1.6 \times 10^{-5}\ M$
5. $[H^+]$; pH	$[H^+] = \dfrac{1.0 \times 10^{-14}}{1.6 \times 10^{-5}} = 6.2 \times 10^{-10}$; pH = 9.20

Figure 14.8
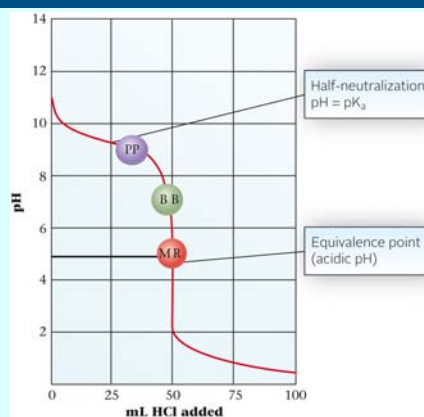
Notes on HCl-NH$_3$ Titration

- The original pH is that of the weak base, which is approximately 12
- The pH falls slowly with the addition of the acid
  - Again, the addition of the acid to the weak base produces a buffer solution
- Near the equivalence point, the buffer is exhausted and the pH falls rapidly
- After the equivalence point, the pH falls slowly, as strong acid is being added to weak acid

Titrating Diprotic Acids

- Diprotic acids can be titrated similarly to monoprotic acids
  - Because there are two ionizable hydrogen ions, there are two equivalence points
  - Both equivalence points appear on the titration curve

Strong Acid-Weak Base Indicator Selection

- The pH at the equivalence point of a strong acid-weak base titration is acidic
- The indicator must change color at an acidic pH
- For this titration, methyl red is a suitable choice
  - Color change takes place at a pH of approximately 5

Figure 14.9
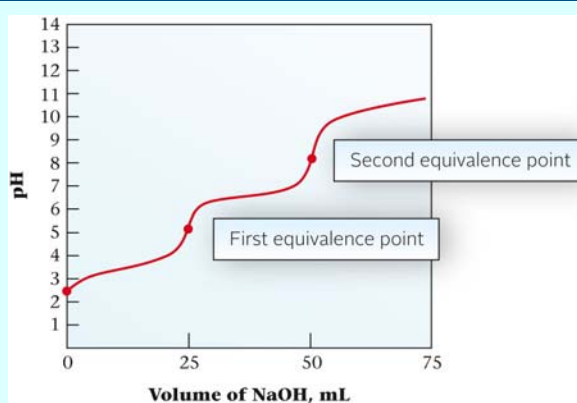
Table 14.3

TABLE 14.3 Characteristics of Acid-Base Titrations

Summary Notes on Acid-Base Titrations

- The equations that describe the reactions differ
  - Strong acids and strong bases are H$^+$ and OH$^-$ in water
- The equilibrium constants (K) for the reactions are very large, indicating that the reactions go essentially to completion
- The pH at the equivalence point is controlled by the species present
  - Strong acid-strong base: pH = 7; neutral salt in water
  - Weak acid-strong base: pH > 7; weak base in water
  - Strong acid-weak base: pH < 7; weak acid in water

Example 14.9

Consider the titration of formic acid, $HCHO_2$, with barium hydroxide.

(a) Write a balanced net ionic equation for the reaction.

(b) Calculate K for the reaction.

(c) Is the solution at the equivalence point acidic, basic, or neutral?

(d) What would be an appropriate indicator for the titration?

SOLUTION

(a) Reaction	$HCH_2O(aq) + OH^-(aq) \longrightarrow CHO_2^-(aq) + H_2O$
(b) K	$CHO_2^-(aq) + H_2O \rightleftharpoons HCH_2O(aq) + OH^-(aq)$ K_b
	$K = 1/K_b = 1/5.3 \times 10^{-11} = 1.9 \times 10^{10}$
(c) Acidic, basic or neutral?	basic, due to the presence of CHO_2^-
(d) Indicator	phenolphthalein

Key Concepts

1. Calculate the pH of a buffer as initially prepared.
2. Choose a buffer for a specified pH.
3. Determine whether a combination of a strong acid/base and its salt is a buffer (or not).
4. Calculate the pH of a buffer after the addition of strong acid or base.
5. Determine the color of an indicator at a specific pH, given its K_a.
6. Calculate the pH during an acid-base titration.
7. Choose the proper indicator for a titration.
8. Calculate K for an acid-base reaction.