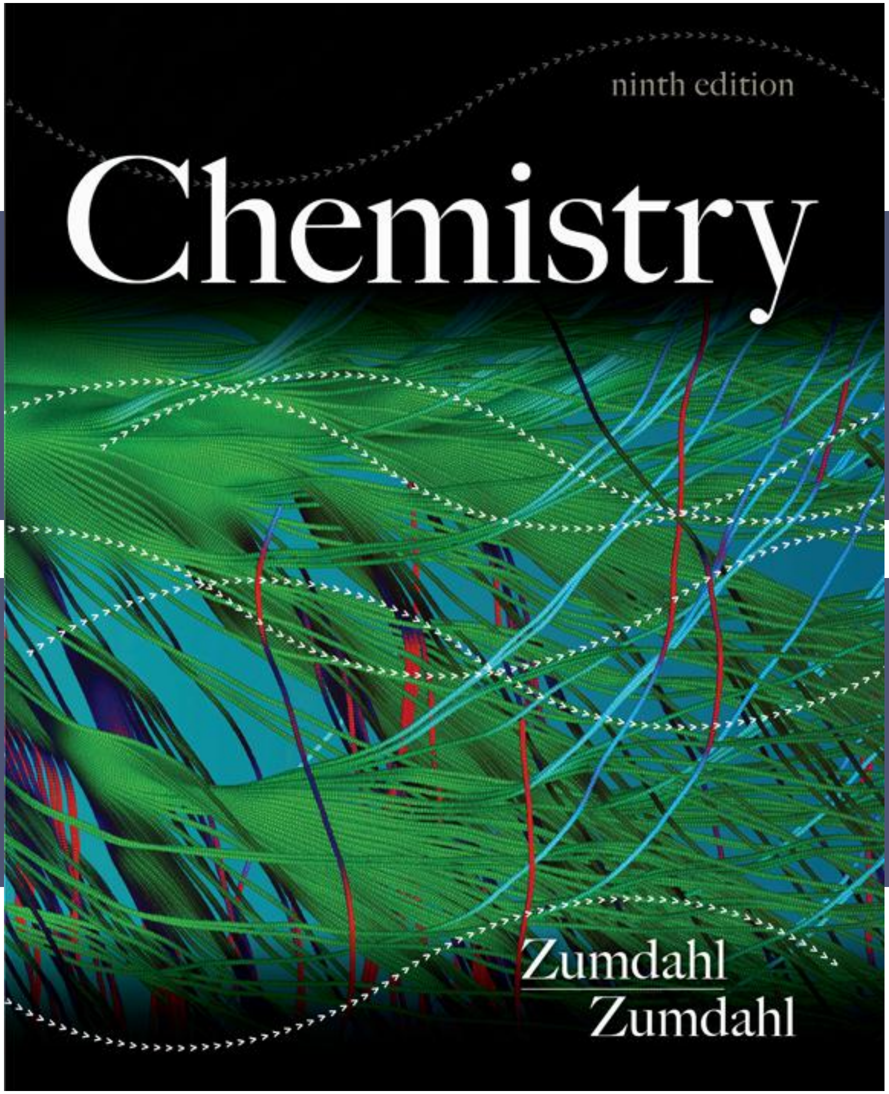
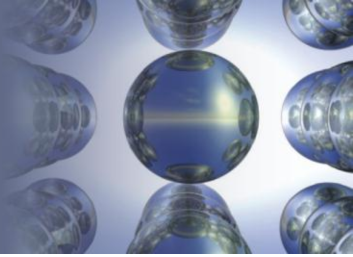


Chapter 15

Acid–Base Equilibria



Chapter 15

Table of Contents

Common Ion Effect

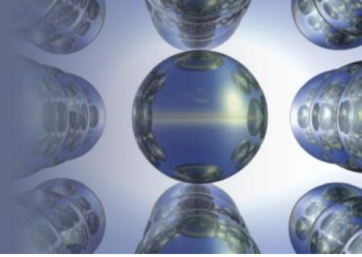
- Shift in equilibrium position that occurs due to the addition of an ion already involved in the equilibrium reaction
  - Consider the addition of NH_4Cl to a 1.0 *M* NH_3 solution

$$NH_4Cl(s) \xrightarrow{H_2O} NH_4^+(aq) + Cl^-(aq)$$

    - Production of extra ammonium ions causes a shift in the position of the ammonia–water equilibrium

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

      - Equilibrium concentration of OH^- ions decreases

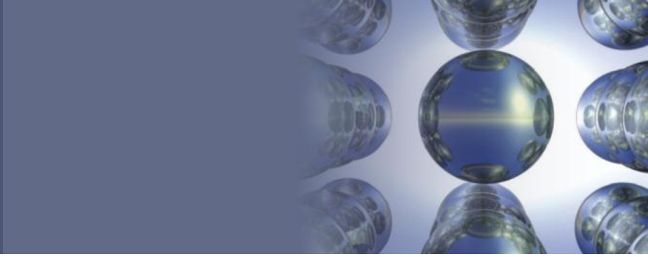


Common Ion Effect (Continued)

- In solutions containing polyprotic acids:
    - Production of protons by the first dissociation significantly inhibits the succeeding dissociation

Interactive Example 15.1 - Acidic Solutions Containing Common Ions

- The equilibrium concentration of H^+ in a 1.0 *M* HF solution is 2.7×10^{-2} *M*
  - The percent dissociation of HF is 2.7%
  - Calculate $[H^+]$ and the percent dissociation of HF in a solution containing 1.0 *M* HF ($K_a = 7.2 \times 10^{-4}$) and 1.0 *M* NaF



Interactive Example 15.1 - Solution

- In a solution containing 1.0 *M* HF and 1.0 *M* NaF, the major species are HF, F^-, Na^+, and H_2O
- The equilibrium equation is

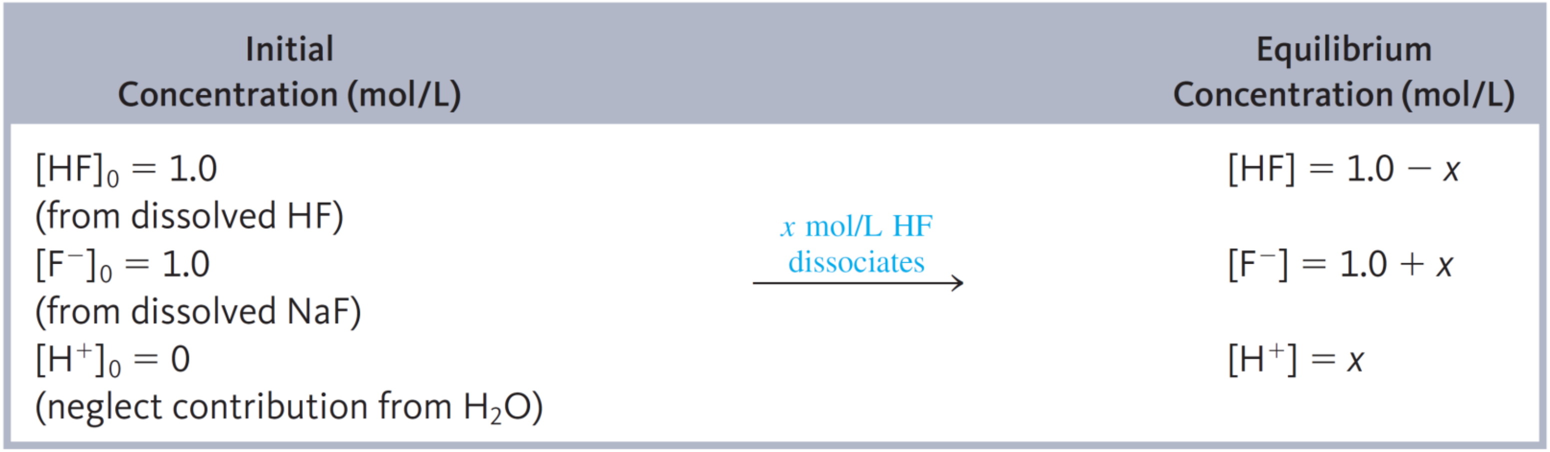
$$\mathrm{HF}(aq) \rightleftharpoons \mathrm{H}^+(aq) + \mathrm{F}^-(aq)$$

- The equilibrium expression is

$$K_\mathrm{a} = \frac{\left[\mathrm{H}^+\right]\left[\mathrm{F}^-\right]}{\left[\mathrm{HF}\right]} = 7.2 \times 10^{-4}$$

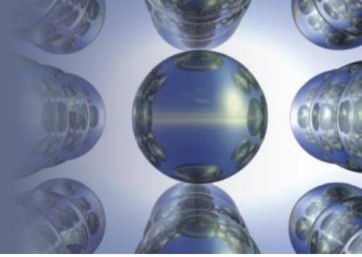
Interactive Example 15.1 - Solution (Continued 1)

- Important concentrations are shown in the following table:



Initial Concentration (mol/L)		Equilibrium Concentration (mol/L)
$[HF]_0 = 1.0$ (from dissolved HF)		$[HF] = 1.0 - x$
$[F^-]_0 = 1.0$ (from dissolved NaF)	$\xrightarrow{x \text{ mol/L HF dissociates}}$	$[F^-] = 1.0 + x$
$[H^+]_0 = 0$ (neglect contribution from H_2O)		$[H^+] = x$

  - $[F^-]_0$ = 1.0 *M* due to the dissolved sodium fluoride



Interactive Example 15.1 - Solution (Continued 2)

- At equilibrium, $[\mathrm{F}^-] > 1.0$ *M* because the acid produces F^- as well as H^+ during dissociation
- Therefore,

$$K_\mathrm{a} = 7.2 \times 10^{-4} = \frac{[\mathrm{H}^+][\mathrm{F}^-]}{[\mathrm{HF}]} = \frac{(x)(1.0 + x)}{1.0 - x} \approx \frac{(x)(1.0)}{1.0}$$

$$x = \frac{1.0}{1.0}\left(7.2 \times 10^{-4}\right) = 7.2 \times 10^{-4}$$

- Since *x* is small compared to 1.0, this result is acceptable

Interactive Example 15.1 - Solution (Continued 3)

- Thus,

$$\left[\mathrm{H}^{+}\right] = x = 7.2 \times 10^{-4}\ M \qquad \left(\mathrm{pH} = 3.14\right)$$

- The percent dissociation of HF in this solution is

$$\frac{\left[\mathrm{H}^{+}\right]}{\left[\mathrm{HF}\right]_0} \times 100 = \frac{7.2 \times 10^{-4}\ M}{1.0\ M} \times 100 = 0.072\ \%$$

Interactive Example 15.1 - Solution (Continued 4)

- Compare these values for $[H^+]$ and the percent dissociation of HF with those for a 1.0 *M* HF solution, where $[H^+] = 2.7 \times 10^{-2}$ *M* and the percent dissociation is 2.7%
  - The presence of the F^- ions from the dissolved NaF greatly inhibits the dissociation of HF
  - The position of the acid dissociation equilibrium has been shifted to the left by the presence of F^- ions from NaF

Buffered Solutions - An Introduction

- Resist changes in pH when either hydroxide ions or protons are added
- Example - Blood
  - Absorbs acids and bases produced in biologic reactions without alterations to pH
- Contain a weak acid and its salt
  - Buffering is possible at any pH
    - Based on choice of appropriate components used

Interactive Example 15.2 - The pH of a Buffered Solution I

- A buffered solution contains 0.50 *M* acetic acid ($HC_2H_3O_2$, $K_a = 1.8 \times 10^{-5}$) and 0.50 *M* sodium acetate ($NaC_2H_3O_2$)
  - Calculate the pH of this solution

Interactive Example 15.2 - Solution

- Major species in the solution include:
  - $HC_2H_3O_2$ - Weak acid
  - Na^+ - Neither acid nor base
  - $C_2H_3O_2^-$ - Base (conjugate base of $HC_2H_3O_2$)
  - H_2O - Very weak acid or base
- The acetic acid dissociation equilibrium will control the pH of the solution

$$HC_2H_3O_2(aq) \rightleftharpoons H^+(aq) + C_2H_3O_2^-(aq)$$

Interactive Example 15.2 - Solution (Continued 1)

$$K_a = 1.8 \times 10^{-5} = \frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]}$$

- The concentrations are as follows:

Initial Concentration (mol/L)		Equilibrium Concentration (mol/L)
$[HC_2H_3O_2]_0 = 0.50$	$\xrightarrow[\text{dissociates to reach equilibrium}]{x \text{ mol/L of } HC_2H_3O_2}$	$[HC_2H_3O_2] = 0.50 - x$
$[C_2H_3O_2^-]_0 = 0.50$		$[C_2H_3O_2^-] = 0.50 + x$
$[H^+]_0 \approx 0$		$[H^+] = x$

Interactive Example 15.2 - Solution (Continued 2)

- The corresponding ICE table is

	$HC_2H_3O_2(aq)$	$\rightleftharpoons$	$H^+(aq)$	$+$	$C_2H_3O_2^-(aq)$
Initial	0.50		≈ 0		0.50
Change	$-x$		$+x$		$+x$
Equilibrium	$0.50 - x$		x		$0.50 + x$

- Therefore,

$$K_a = 1.8 \times 10^{-5} = \frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} = \frac{(x)(0.50 + x)}{0.50 - x} \approx \frac{(x)(0.50)}{0.50}$$

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

Interactive Example 15.2 - Solution (Continued 3)

- The approximations are valid by the 5% rule

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

$$\mathrm{pH} = 4.74$$

Interactive Example 15.3 - pH Changes in Buffered Solutions

- Calculate the change in pH that occurs when a 0.010 mole of solid NaOH is added to 1.0 L of the buffered solution described in example 15.2
  - Compare this pH change with that which occurs when 0.010 mole of solid NaOH is added to 1.0 L of water

Interactive Example 15.3 - Solution

- The major species in the solution are:
    - $HC_2H_3O_2$, Na^+, $C_2H_3O_2^-$, OH^-, and H_2O
- The reaction that will occur is

$$OH^-(aq) + HC_2H_3O_2(aq) \longrightarrow H_2O(l) + C_2H_3O_2^-(aq)$$

- Steps involved
    1. Assume that the reaction goes to completion and carry out the stoichiometric calculations
    2. Carry out the equilibrium calculations

Interactive Example 15.3 - Solution (Continued 1)

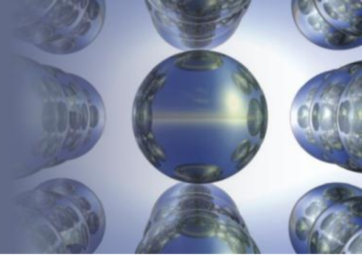
- Determining stoichiometry

	$HC_2H_3O_2(aq)$	+	$OH^-(aq)$	$\longrightarrow$	$C_2H_3O_2^-(aq)$	+	$H_2O(l)$
Before reaction	$1.0\ L \times 0.50\ M = 0.50$ mol		0.010 mol		$1.0\ L \times 0.50\ M = 0.50$ mol		
After reaction	$0.50 - 0.010 = 0.49$ mol		$0.010 - 0.010 = 0$ mol		$0.50 + 0.010 = 0.51$ mol		

  - Note that 0.010 mole of $HC_2H_3O_2$ has been converted to 0.010 mole of $C_2H_3O_2^-$ by the added OH^-

Interactive Example 15.3 - Solution (Continued 2)

- Determining equilibrium
  - Major species in the solution after completion of the reaction between OH^- and $HC_2H_3O_2$ are
    - $HC_2H_3O_2$
    - Na^+
    - $C_2H_3O_2^-$
    - H_2O
  - The dominant equilibrium involves the dissociation of acetic acid



Interactive Example 15.3 - Solution (Continued 3)

- The addition of 0.010 mole of OH^- has consumed $HC_2H_3O_2$ and produced $C_2H_3O_2^-$
  - This yields the following ICE table:

	$HC_2H_3O_2(aq)$	$\rightleftharpoons$	$H^+(aq)$	$+$	$C_2H_3O_2^-(aq)$
Initial	0.49		0		0.51
Change	$-x$		$+x$		$+x$
Equilibrium	$0.49 - x$		x		$0.51 + x$

  - The initial concentrations are defined after the reaction with OH^- is complete but before the system adjusts to equilibrium

Interactive Example 15.3 - Solution (Continued 4)

- Following the usual procedure gives

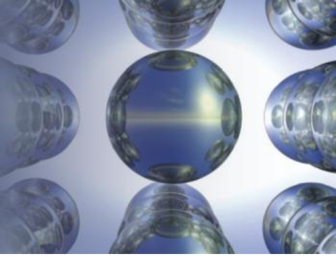
$$K_a = 1.8 \times 10^{-5} = \frac{\left[\mathrm{H}^+\right]\left[\mathrm{C_2H_3O_2}^-\right]}{\left[\mathrm{HC_2H_3O_2}\right]} = \frac{(x)(0.51 + x)}{0.49 - x} \approx \frac{(x)(0.51)}{0.49}$$

$$x \approx 1.7 \times 10^{-5}$$

- The approximations are valid by the 5% rule

$$[\mathrm{H}^+] = x = 1.7 \times 10^{-5}$$

$$\mathrm{pH} = 4.76$$

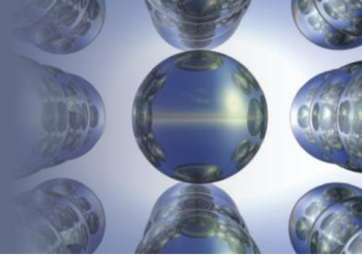


Interactive Example 15.3 - Solution (Continued 5)

- The change in pH produced by the addition of 0.01 mole of OH^- to the buffered solution is

$$\underbrace{4.76}_{\text{New solution}} - \underbrace{4.74}_{\text{Original solution}} = +0.02$$

  - pH is increased by 0.02 pH units
    - Compare the value with the value obtained when 0.01 mole of solid NaOH is added to 1.0 L water to give 0.01 *M* NaOH



Interactive Example 15.3 - Solution (Continued 6)

- In this case, $[OH^-] = 0.01\ M$

$$\left[H^+\right] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-2}} = 1.0 \times 10^{-12}$$

$$\text{pH} = 12.00$$

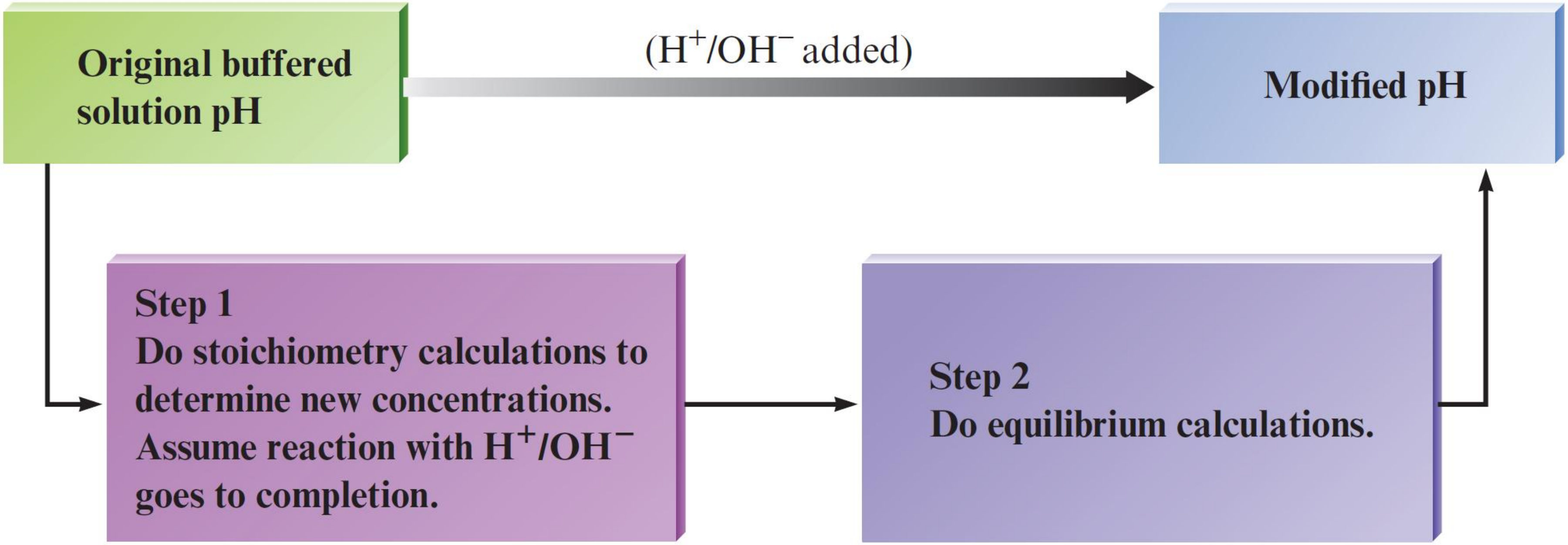
- Thus, the change in pH is

$$\underbrace{12.00}_{\text{New solution}} - \underbrace{7.00}_{\text{Pure water}} = +5.00$$

Solving Buffer Problems - Key Points

- Buffered solutions are solutions of weak acids or bases containing a common ion
- When a strong acid or base is added to a buffered solution, it is best to deal with the stoichiometry of the resulting reaction first

Solving Buffer Problems - A Schematic



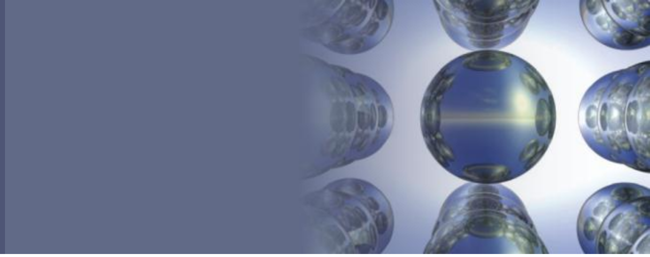
Original buffered solution pH

(H^+/OH^- added)

Modified pH

Step 1
Do stoichiometry calculations to determine new concentrations. Assume reaction with H^+/OH^- goes to completion.

Step 2
Do equilibrium calculations.



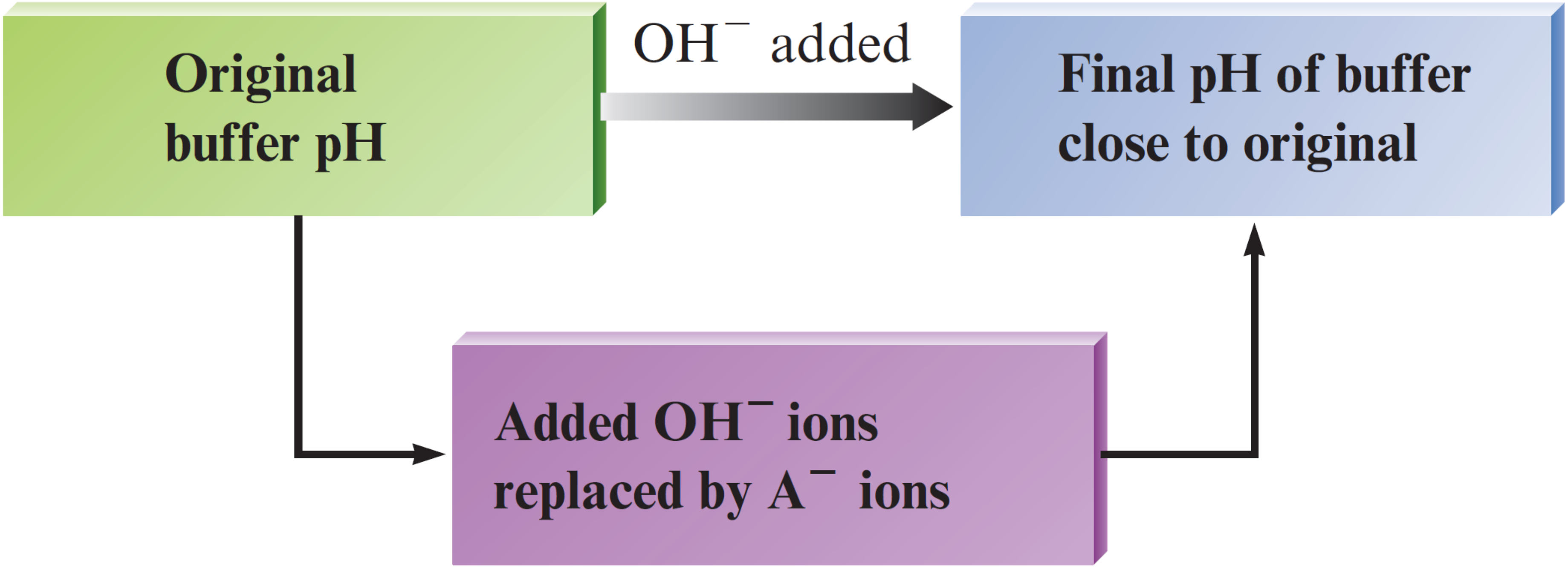
How a Buffered Solution Works

- Consider a buffered solution containing a large quantity of a weak acid HA and its conjugate base A^-
  - When hydroxide ions are added, the following reaction occurs:

$$OH^-(aq) + HA(aq) \longrightarrow A^-(aq) + H_2O(l)$$

  - Net result - OH^- ions are replaced by A^- ions

How a Buffered Solution Works (Continued 1)



Original buffer pH

OH^- added

Final pH of buffer close to original

Added OH^- ions replaced by A^- ions

How a Buffered Solution Works (Continued 2)

- The stability of the pH under these conditions can be understood by the following expressions:

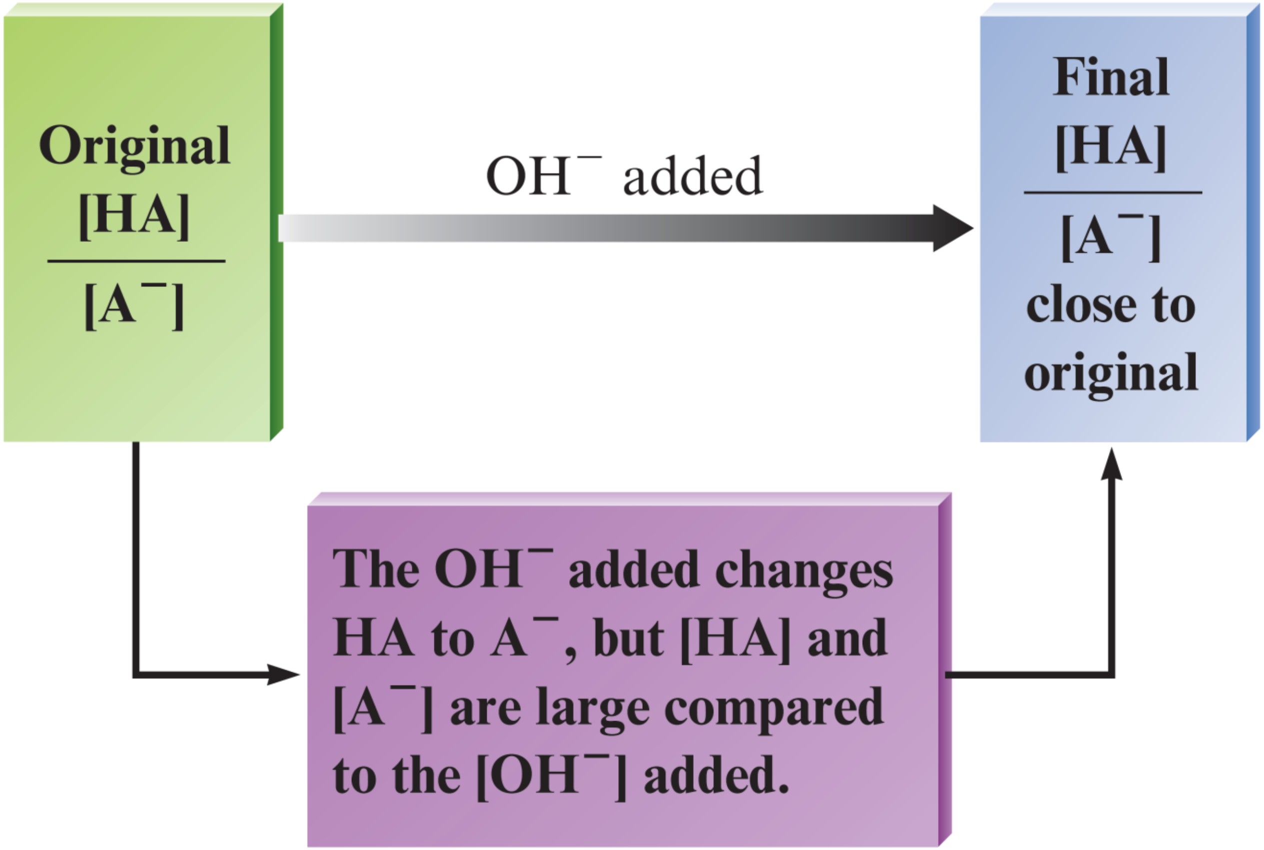
$$K_a = \frac{\left[\mathrm{H}^+\right]\left[\mathrm{A}^-\right]}{\left[\mathrm{HA}\right]} \quad \text{or} \quad [\mathrm{H}^+] = K_a \frac{[\mathrm{HA}]}{[\mathrm{A}^-]}$$

- The equilibrium concentration of H^+, and thus the pH, is determined by the ratio $[HA]/[A^-]$
    - If amounts of HA and A^- originally present are large compared to the amount of OH^- added, the change in the $[HA]/[A^-]$ ratio will be small

How a Buffered Solution Works (Continued 3)

- When a small amount of OH^- is added to much larger amounts of [HA] and [A^-], the concentrations of HA and A^- change by small amounts
    - [H^+] and the pH remain constant

How a Buffered Solution Works (Continued 4)

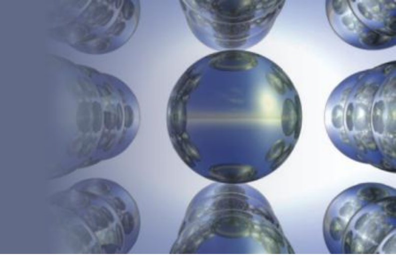


Original
$\frac{[HA]}{[A^-]}$

OH^- added

Final
$\frac{[HA]}{[A^-]}$
close to original

The OH^- added changes HA to A^-, but [HA] and $[A^-]$ are large compared to the $[OH^-]$ added.



How a Buffered Solution Works (Continued 5)

- When protons are added to a buffered solution of a weak acid with its conjugate base
  - High affinity of the A^- ion for H^+ results in a reaction between the two, forming the weak acid

$$H^+(aq) + A^-(aq) \longrightarrow HA(aq)$$

  - If $[A^-]$ and $[HA]$ are large compared with the $[H^+]$ added, the change in pH is small

The Henderson–Hasselbalch Equation

- Used for calculating [H⁺] in a buffered solution when [HA]/[A⁻] ratio is known

$$[\mathrm{H}^+] = K_\mathrm{a}\frac{[\mathrm{HA}]}{[\mathrm{A}^-]} \qquad (15.1)$$

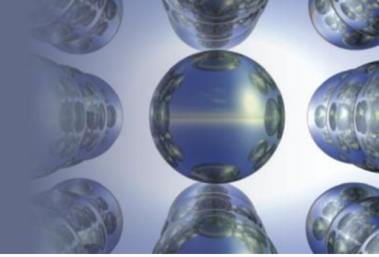
  - Taking the negative log of both sides gives

$$-\log[\mathrm{H}^+] = -\log(K_\mathrm{a}) - \log\left(\frac{[\mathrm{HA}]}{[\mathrm{A}^-]}\right) \quad \text{(or)} \quad \mathrm{pH} = \mathrm{p}K_\mathrm{a} - \log\left(\frac{[\mathrm{HA}]}{[\mathrm{A}^-]}\right)$$

The Henderson–Hasselbalch Equation (Continued)

- Inverting the log term reverses the sign to give the **Henderson–Hasselbalch equation**

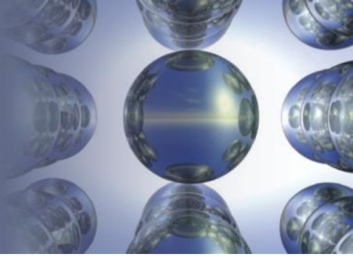
$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\left(\frac{[\mathrm{A}^-]}{[\mathrm{HA}]}\right) = \mathrm{p}K_\mathrm{a} + \log\left(\frac{[\text{base}]}{[\text{acid}]}\right) \qquad (15.2)$$



Conjugate Acid–Base Pair Ratio and pH

- For a particular buffering system, all solutions with the same ratio $[A^-]/[HA]$ will have the same pH
  - Consider the following table:

System	**$[A^-]/[HA]$**
5.0 *M* $HC_2H_3O_2$ and 3.0 *M* $NaC_2H_3O_2$	$\frac{3.0\ M}{5.0\ M} = 0.60$
0.050 *M* $HC_2H_3O_2$ and 0.030 *M* $NaC_2H_3O_2$	$\frac{0.030\ M}{0.050\ M} = 0.60$



Conjugate Acid–Base Pair Ratio and pH (Continued)

- Based on the table,

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\left(\frac{[\mathrm{C_2H_3O_2}^-]}{[\mathrm{HC_2H_3O_2}]}\right) = 4.74 + \log(0.60)$$

$$= 4.74 - 0.22 = 4.52$$

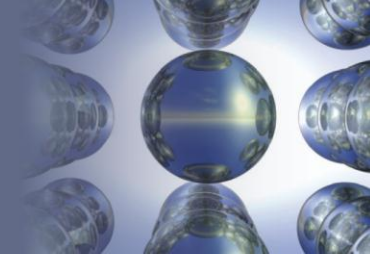
  - Assumption - Equilibrium concentrations of A$^-$ and HA are equal to the initial concentrations

$$[\mathrm{A}^-] = [\mathrm{A}^-]_0 + x \approx [\mathrm{A}^-]_0 \text{ and } [\mathrm{HA}] = [\mathrm{HA}]_0 - x \approx [\mathrm{HA}]_0$$

    - *x* - Amount of acid that dissociates

Interactive Example 15.5 - The pH of a Buffered Solution III

- A buffered solution contains 0.25 M NH_3 (K_b = 1.8×10^{-5}) and 0.40 M NH_4Cl
    - Calculate the pH of the solution



Interactive Example 15.5 - Solution

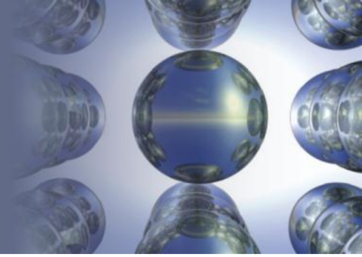
- The major species in solution are

$$NH_3, \quad \underbrace{NH_4^+, Cl^-}_{\text{From the dissolved } NH_4Cl} \quad , \text{ and } H_2O$$

- Cl^- is a weak base and H_2O is a weak acid or base

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

$$K_b = 1.8 \times 10^{-5} = \frac{\left[NH_4^+\right]\left[OH^-\right]}{\left[NH_3\right]}$$



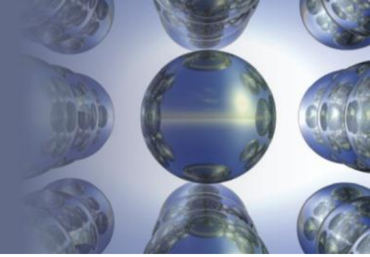
Interactive Example 15.5 - Solution (Continued 1)

- The appropriate ICE table is

	$NH_3(aq)$	$+$	$H_2O(l)$	$\rightleftharpoons$	$NH_4^+(aq)$	$+$	$OH^-(aq)$
Initial	0.25		—		0.40		≈ 0
Change	$-x$		—		$+x$		$+x$
Equilibrium	$0.25 - x$		—		$0.40 + x$		x

$$K_b = 1.8 \times 10^{-5} = \frac{\left[NH_4^+\right]\left[OH^-\right]}{\left[NH_3\right]} = \frac{(0.40 + x)(x)}{0.25 - x} \approx \frac{(0.40)(x)}{0.25}$$

$$x \approx 1.1 \times 10^{-5}$$



Interactive Example 15.5 - Solution (Continued 2)

- The approximations are valid (by the 5% rule)
    - $[OH^-] = x = 1.1 \times 10^{-5}$
    - pOH = 4.95
    - pH = 14.00 – 4.95 = 9.05
- This case is typical of a buffered solution
    - Initial and equilibrium concentrations of buffering materials are essentially the same

Interactive Example 15.5 - Alternative Solution

- The solution contains large quantities of NH_4^+ and NH_3
  - The following equilibrium expression can be used to calculate [$OH^–$], and then [H^+] from K_w:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

  - [H^+] can also be directly determined using the dissociation equilibrium for NH_4^+

$$NH_4^+(aq) \rightleftharpoons NH_3(aq) + H^+(aq)$$

Interactive Example 15.5 - Alternative Solution (Continued 1)

- The K_a value for NH_4^+ can be obtained from the K_b value for NH_3, since $K_a \times K_b = K_w$

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}}$$

$$= 5.6 \times 10^{-10}$$

Interactive Example 15.5 - Alternative Solution (Continued 2)

- Using the Henderson–Hasselbalch equation gives

$$\text{pH} = \text{p}K_\text{a} + \log\left(\frac{[\text{base}]}{[\text{acid}]}\right)$$

$$= 9.25 + \log\left(\frac{0.25\ M}{0.40\ M}\right) = 9.25 - 0.20 = 9.05$$

Buffering Capacity

- Amount of protons or hydroxide ions that a buffer can absorb without a significant change in pH
  - Larger the capacity, more the concentrations of buffering components in the buffer
    - Buffer absorbs relatively large amounts of protons or OH^- ions with minor changes in pH
- Determined by the magnitudes of [HA] and $[A^-]$

Example 15.7 - Adding Strong Acid to a Buffered Solution II

- Calculate the change in pH that occurs when 0.010 mole of gaseous HCl is added to 1.0 L of a solution containing 5.00 *M* $HC_2H_3O_2$ and 5.00 *M* $NaC_2H_3O_2$
  - For acetic acid, $K_a = 1.8 \times 10^{-5}$

Example 15.7 - Solution

- The initial pH can be determined using the Henderson–Hasselbalch equation

$$pH = pK_a + \log\left(\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]}\right)$$

  - Since $[C_2H_3O_2^-] = [HC_2H_3O_2]$, the initial pH is

$$pH = pK_a + \log(1) = pK_a = -\log(1.8 \times 10^{-5}) = 4.74$$

Example 15.7 - Solution (Continued 1)

- After the addition of HCl to each of these solutions, the major species before any reaction occurs are:

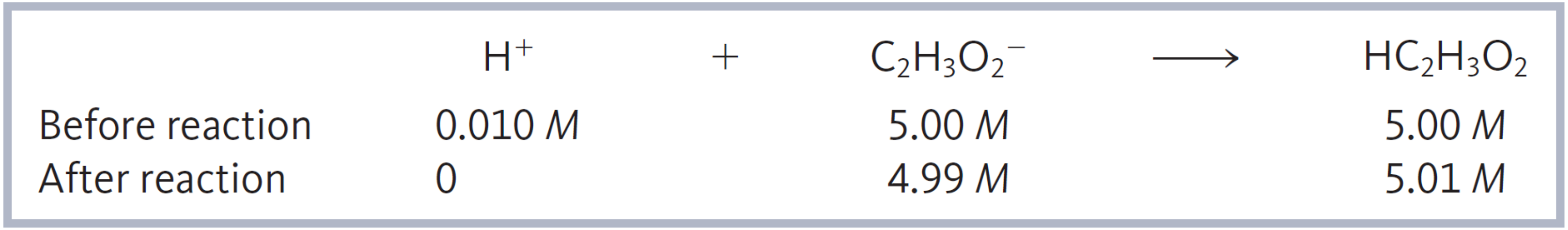
$$HC_2H_3O_2,\ Na^+,\ C_2H_3O_2^-,\ \underbrace{H^+,\ Cl^-}_{\text{From added HCl}},\ \text{and } H_2O$$

- $C_2H_3O_2^-$ will react with H^+ to form the weak acid $HC_2H_3O_2$

$$H^+(aq) + C_2H_3O_2^-(aq) \longrightarrow HC_2H_3O_2(aq)$$

Example 15.7 - Solution (Continued 2)

- $HC_2H_3O_2$ is a weak acid
  - The reaction is assumed to run to completion
    - 0.010 mole of added H^+ will convert 0.010 mole of $C_2H_3O_2^-$ to 0.010 mole of $HC_2H_3O_2$
  - The following calculations apply:



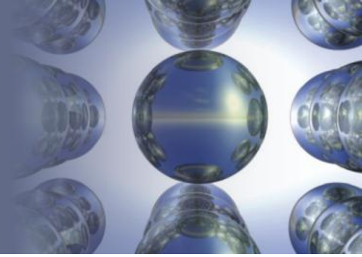
	H^+	+	$C_2H_3O_2^-$	$\longrightarrow$	$HC_2H_3O_2$
Before reaction	0.010 *M*		5.00 *M*		5.00 *M*
After reaction	0		4.99 *M*		5.01 *M*

Example 15.7 - Solution (Continued 3)

- The new pH can be obtained by substituting the new concentrations into the Henderson–Hasselbalch equation

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\left(\frac{[\mathrm{C_2H_3O_2}^-]}{[\mathrm{HC_2H_3O_2}]}\right)$$

$$= 4.74 + \log\left(\frac{4.99}{5.01}\right) = 4.74 - 0.0017 = 4.74$$



Example 15.7 - Solution (Continued 4)

- Thus, there is virtually no change in pH when 0.010 mole of gaseous HCl is added to 1.0 L of a solution containing 5.00 *M* $HC_2H_3O_2$ and 5.00 *M* $NaC_2H_3O_2$

Determining the Ratio for Optimal Buffering

- Optimal buffering occurs when [HA] is equal to $[A^-]$
  - Causes the ratio $[A^-]/[HA]$ to become resistant to change when H^+ or OH^- is added to the buffered solution

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right) = pK_a + \log(1) = pK_a$$

  - pK_a of the weak acid needs to be as close as possible to the desired pH

Critical Thinking

- It is known that the pK_a for a weak acid to be used in the buffer should be as close as possible to the desired pH
    - What is the problem with choosing a weak acid whose pK_a is not close to the desired pH when making a buffer?

Interactive Example 15.8 - Preparing a Buffer

- A chemist needs a solution buffered at pH 4.30 and can choose from the following acids (and their sodium salts):
  - Chloroacetic acid ($K_a = 1.35 \times 10^{-3}$)
  - Propanoic acid ($K_a = 1.3 \times 10^{-5}$)
  - Benzoic acid ($K_a = 6.4 \times 10^{-5}$)
  - Hypochlorous acid ($K_a = 3.5 \times 10^{-8}$)

Interactive Example 15.8 - Preparing a Buffer (Continued)

- Calculate the ratio [HA]/[A$^-$] required for each system to yield a pH of 4.30
- Determine the system that will work best

Interactive Example 15.8 - Solution

- A pH of 4.30 corresponds to

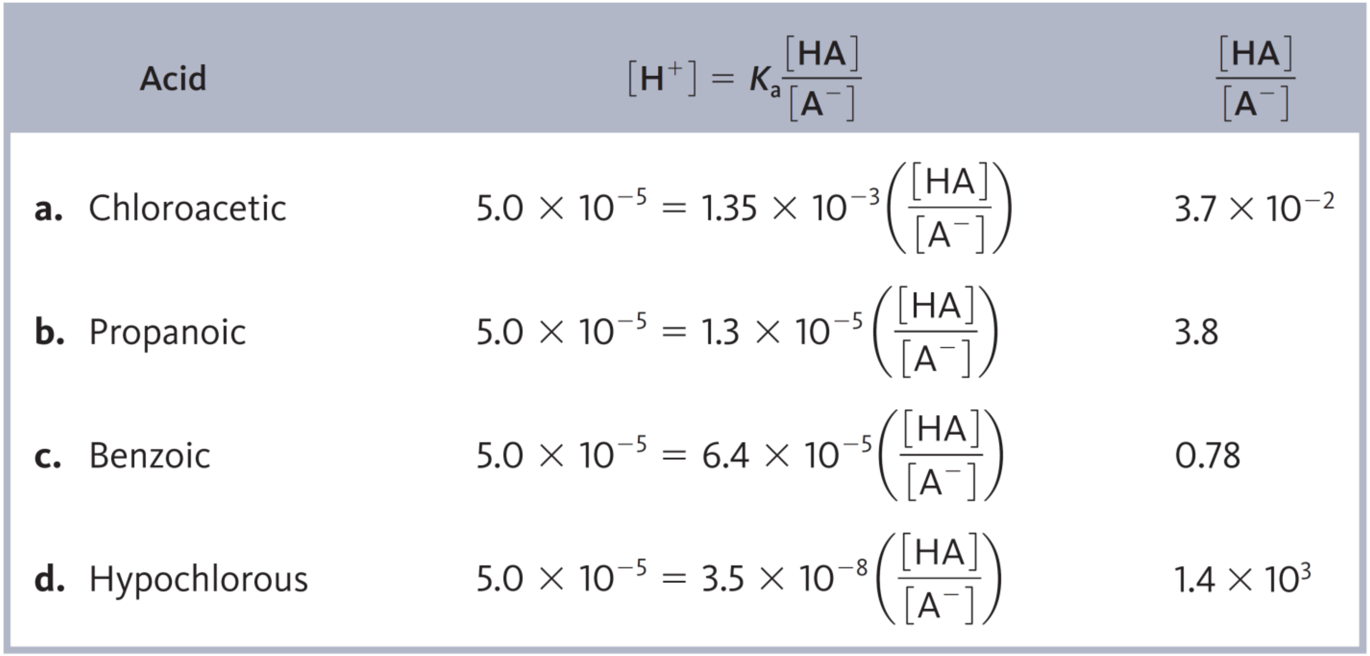
$$\left[\mathrm{H}^+\right] = 10^{-4.30} = \text{antilog}\left(-4.30\right) = 5.0 \times 10^{-5}\ M$$

- Since K_a values rather than pK_a values are given for the various acids, use the following equation:

$$\left[\mathrm{H}^+\right] = K_\mathrm{a}\frac{[\mathrm{HA}]}{\left[\mathrm{A}^-\right]}$$

Interactive Example 15.8 - Solution (Continued 1)

- Substitute the given values into expression (15.1) to calculate the ratio [HA]/[A⁻]



Acid	$[\text{H}^+] = K_a \dfrac{[\text{HA}]}{[\text{A}^-]}$	$\dfrac{[\text{HA}]}{[\text{A}^-]}$
a. Chloroacetic	$5.0 \times 10^{-5} = 1.35 \times 10^{-3}\left(\dfrac{[\text{HA}]}{[\text{A}^-]}\right)$	3.7×10^{-2}
b. Propanoic	$5.0 \times 10^{-5} = 1.3 \times 10^{-5}\left(\dfrac{[\text{HA}]}{[\text{A}^-]}\right)$	3.8
c. Benzoic	$5.0 \times 10^{-5} = 6.4 \times 10^{-5}\left(\dfrac{[\text{HA}]}{[\text{A}^-]}\right)$	0.78
d. Hypochlorous	$5.0 \times 10^{-5} = 3.5 \times 10^{-8}\left(\dfrac{[\text{HA}]}{[\text{A}^-]}\right)$	1.4×10^{3}

Interactive Example 15.8 - Solution (Continued 2)

- Since [HA]/[A$^-$] for benzoic acid is closest to 1, the system of benzoic acid and its sodium salt will be the best choice among those given for buffering a solution at pH 4.30
  - Optimal buffering system has a pK_a value close to the desired pH
    - The pK_a for benzoic acid is 4.19

Titration

- Used to determine the amount of acid or base in a solution
  - Titrant is delivered from a buret into the solution being analyzed
  - Stoichiometric (equivalence) point is determined by change in the color of an indicator
- **Titration (pH) curve**: Plots the pH of the solution being analyzed as a function of the amount of titrant added

Strong Acid–Strong Base Titrations

- Net ionic reaction

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$$

- Determining $[H^+]$ at a given point in the titration involves:
  - Determining the amount of H^+ remaining at the given point
  - Dividing the remaining amount of H^+ by the total volume of the solution

Determining a Measuring Unit for Titration

- **Millimole (mmol)**: One thousandth of a mole

$$1\ \text{mmol} = \frac{1\ \text{mol}}{1000} = 10^{-3}\ \text{mol}$$

- Defining molarity in terms of millimoles per milliliter

$$\text{Molarity} = \frac{\text{mol solute}}{\text{L solution}} = \frac{\frac{\text{mol solute}}{1000}}{\frac{\text{L solution}}{1000}} = \frac{\text{mmol solute}}{\text{mL solution}}$$

Determining a Measuring Unit for Titration (Continued)

- Number of millimoles of solute is obtained from the product of the volume in millilitres and the molarity

$$\text{Number of mmol} = \text{volume (in mL)} \times \text{molarity}$$

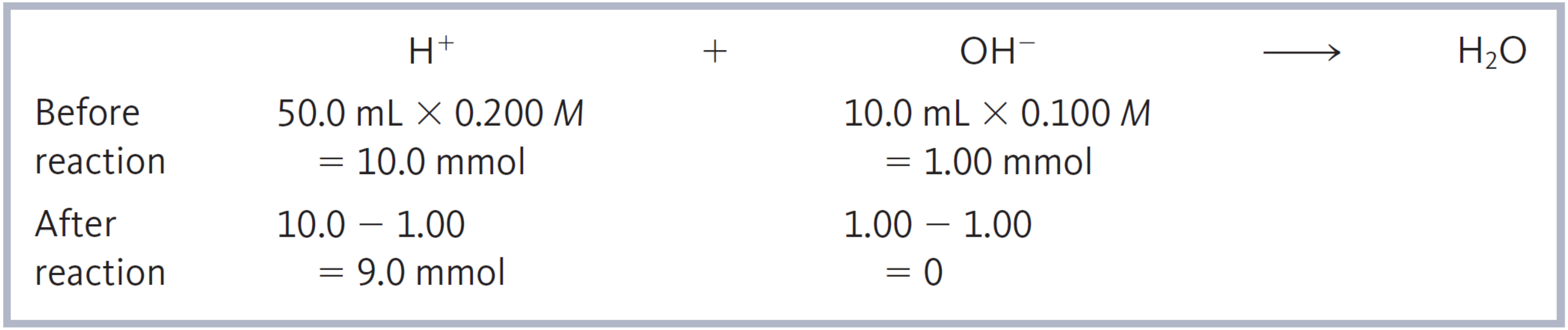
Case Study - Strong Acid–Strong Base Titration

- Consider the titration of 50.0 mL of 0.200 *M* HNO_3 with 0.100 *M* NaOH
- When no NaOH has been added:
  - The major species are H^+, NO_3^-, and H_2O, and pH is determined by the H^+ from the nitric acid
  - 0.200 *M* HNO_3 contains 0.200 *M* H^+

$$[H^+] = 0.200\ M \text{ and pH} = 0.699$$

Case Study - Strong Acid–Strong Base Titration (Continued 1)

- When 10.0 mL of 0.100 *M* NaOH has been added:
  - Major species are H^+, NO_3^-, Na^+, OH^-, and H_2O
  - 1.00 mmol of added OH^- reacts with 1.00 mmol H^+ to form water



	H^+	$+$	OH^-	$\longrightarrow$	H_2O
Before reaction	50.0 mL × 0.200 *M* = 10.0 mmol		10.0 mL × 0.100 *M* = 1.00 mmol		
After reaction	10.0 − 1.00 = 9.0 mmol		1.00 − 1.00 = 0		

Case Study - Strong Acid–Strong Base Titration (Continued 2)

- Major species after the reaction are H^+, NO_3^-, Na^+, and H_2O
- pH is determined by the remaining H^+

$$[H^+] = \frac{\text{mmol } H^+ \text{ left}}{\text{volume of solution (mL)}} = \frac{9.0 \text{ mmol}}{(\underbrace{50.0}_{\substack{\text{Original volume}\\ \text{of } HNO_3 \text{ solution}}} + \underbrace{10.0}_{\substack{\text{Volume of NaOH}\\ \text{added}}})\text{ mL}} = 0.15\ M$$

$$\text{pH} = -\log(0.15) = 0.82$$

Case Study - Strong Acid–Strong Base Titration (Continued 3)

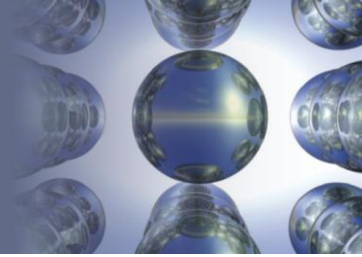
- When 20.0 mL (total) of 0.100 *M* NaOH has been added:

	H^+	$+$	OH^-	$\longrightarrow$	H_2O
Before reaction	50.0 mL × 0.200 *M* = 10.0 mmol		20.0 mL × 0.100 *M* = 2.00 mmol		
After reaction	10.0 − 2.00 = 8.00 mmol		2.00 − 2.00 = 0 mmol		

  - After the reaction

H⁺ remaining

$$[H^+] = \frac{8.00\text{ mmol}}{(50.0 + 20.0)\text{ mL}} = 0.11\ M \text{ and pH} = 0.942$$



Case Study - Strong Acid–Strong Base Titration (Continued 4)

- When 50.0 mL (total) of 0.100 *M* NaOH has been added, the pH is found to be 1.301
- When 100.0 mL (total) of 0.100 *M* NaOH has been added:
  - The amount of NaOH added is 100.0 mL × 0.100 *M* = 10.0 mmol
  - The original amount of HNO_3 was 50.0 mL × 0.200 *M* = 10.0 mmol

Case Study - Strong Acid–Strong Base Titration (Continued 5)

- This provides the **stoichiometric** or **equivalence point** of the equation, the major species being Na^+, NO_3^-, and H_2O
- Na^+ has no acid or base properties, and NO_3^- is the anion of a strong acid and is thus a weak base
  - NO_3^- and Na^+ do not affect the pH
  - pH = 7 (neutral)

Case Study - Strong Acid–Strong Base Titration (Continued 6)

- When 150.0 mL (total) of 1.00 *M* NaOH has been added, the stoichiometric calculations are as follows:

	H^+	$+$	OH^-	$\longrightarrow$	H_2O
Before reaction	50.0 mL $\times$ 0.200 M $=$ 10.0 mmol		150.0 mL $\times$ 0.100 M $=$ 15.0 mmol		
After reaction	10.0 $-$ 10.0 $=$ 0 mmol		15.0 $-$ 10.0 $=$ 5.0 mmol ↑ Excess OH^- added		

Case Study - Strong Acid–Strong Base Titration (Continued 7)

- OH^- is in excess and will determine the pH

$$[\mathrm{OH}^-] = \frac{\text{mmol OH}^- \text{ in excess}}{\text{volume (mL)}}$$

$$= \frac{5.0 \text{ mmol}}{(50.0 + 150.0) \text{ mL}}$$

$$= \frac{5.0 \text{ mmol}}{200.0 \text{ mL}} = 0.025\ M$$

Case Study - Strong Acid–Strong Base Titration (Continued 8)

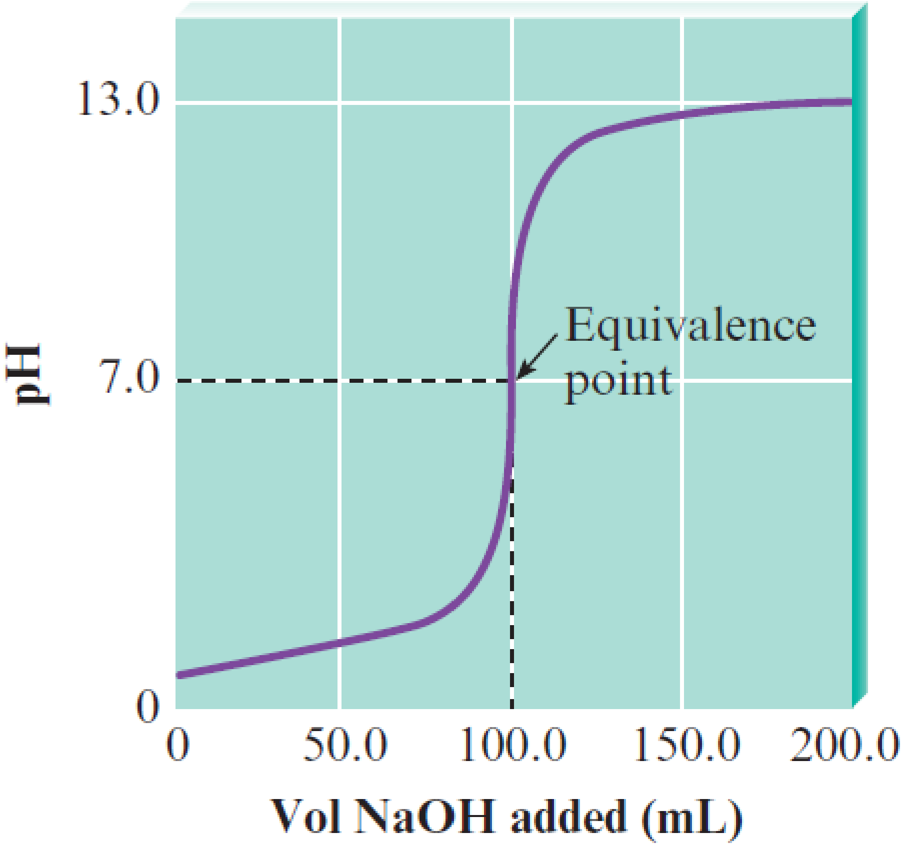
- Since $[H^+][OH^-] = 1.0 \times 10^{-14}$

$$[H^+] = \frac{1.0 \times 10^{-14}}{2.5 \times 10^{-2}} = 4.0 \times 10^{-13}\ M$$

$$\text{pH} = 12.40$$

- 200.0 mL (total) of 0.100 *M* NaOH has been added
  - The pH is found to be 12.60

Figure 15.1 - The pH Curve for the Titration of 50.0 mL of 0.200 *M* Nitric Acid with 0.100 *M* Sodium Hydroxide

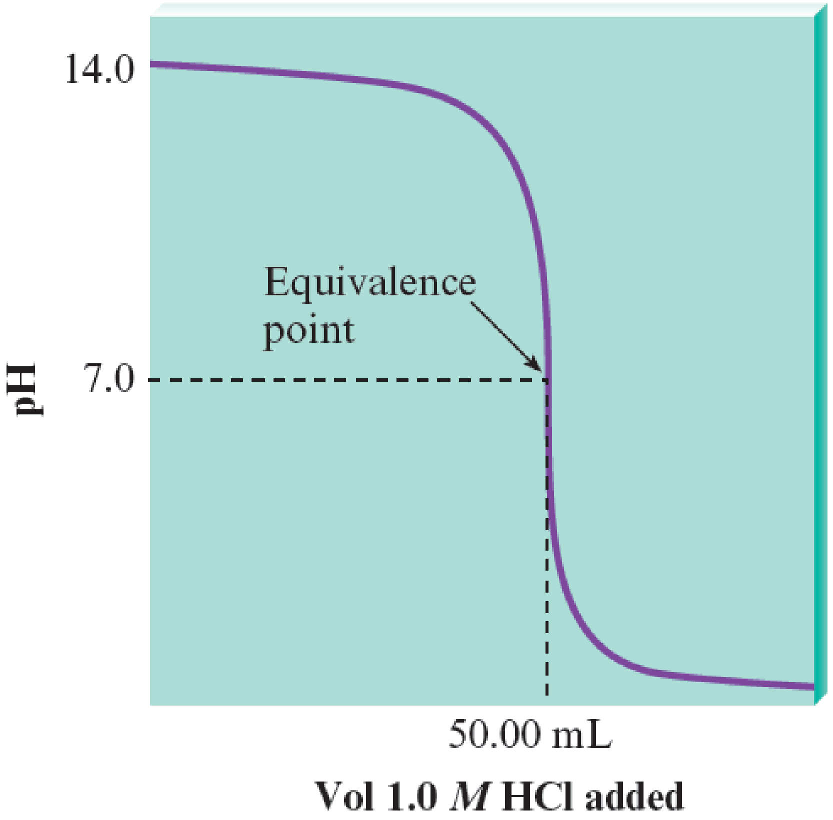


Interpreting the pH Curve for the Titration of Nitric Acid with Sodium Hydroxide

- Calculating $[H^+]$ and pH before equivalence point
  - Divide the number of mmol of H^+ remaining by total volume of solution (in mL)
- pH = 7.00 at equivalence point
- Calculating $[OH^-]$ after equivalence point
  - Divide the number of mmol of excess OH^- by total volume of solution
    - $[H^+]$ is obtained from K_w

Titration of a Strong Base with a Strong Acid

- Consider the pH curve for the titration of 100.0 mL of 0.50 *M* NaOH with 1.0 *M* HCl
  - OH^- is in excess before equivalence point
  - H^+ is in excess after the equivalence point



Titrations of Weak Acids with Strong Bases

- Determining [H^+] after a certain amount of strong base has been added involves considering the dissociation equilibrium of the weak acid
  - Though the acid is weak, it reacts to completion
- pH at the equivalence point of a titration of a weak acid with a strong base is always greater than 7

Problem Solving Strategy - Calculating the pH Curve for a Weak Acid–Strong Base Titration

- Stoichiometry problem
  - Reaction of hydroxide ion with the weak acid is assumed to run to completion
  - Concentrations of the acid that remains and the conjugate base formed are determined
- Equilibrium problem
  - Position of the weak acid equilibrium is determined, and the pH is calculated

Interactive Example 15.9 - Titration of a Weak Acid

- Hydrogen cyanide gas (HCN), a powerful respiratory inhibitor, is highly toxic
  - It is a very weak acid ($K_a = 6.2 \times 10^{-10}$) when dissolved in water
  - If a 50.0 mL sample of 0.100 *M* HCN is titrated with 0.100 *M* NaOH, calculate the pH of the solution:
    a. After 8.00 mL of 0.100 *M* NaOH has been added
    b. At the halfway point of the titration
    c. At the equivalence point of the titration

Interactive Example 15.9 - Solution

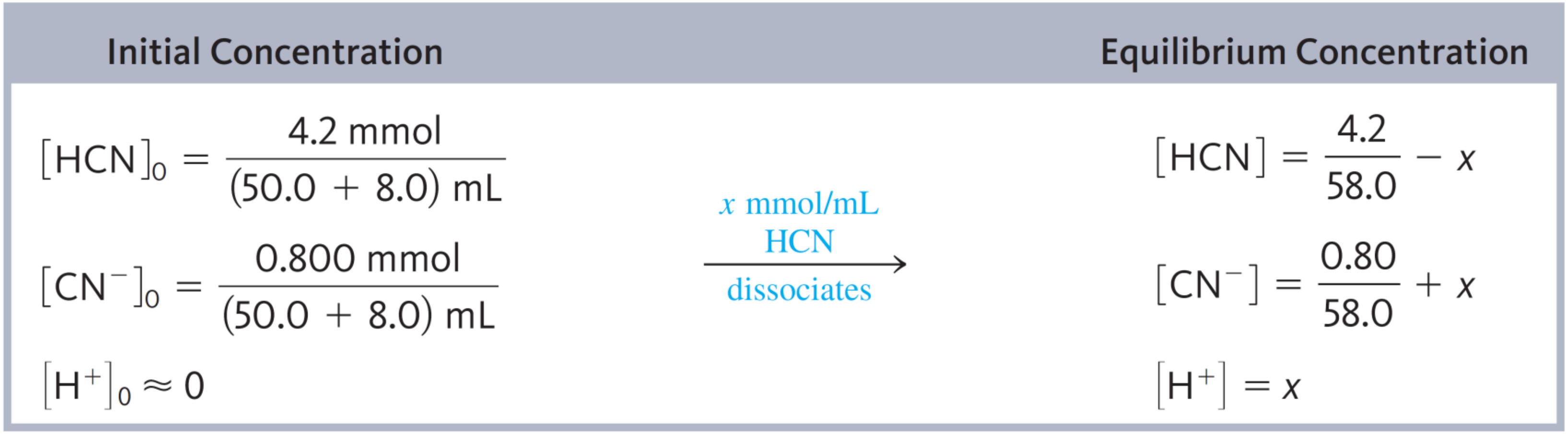
a. After 8.00 mL of 0.100 *M* NaOH has been added, the following calculations apply:

	HCN	+	OH^-	$\longrightarrow$	CN^-	+	H_2O
Before reaction	50.0 mL × 0.100 *M* = 5.00 mmol		8.00 mL × 0.100 *M* = 0.800 mmol		0 mmol		
After reaction	5.00 − 0.800 = 4.20 mmol		0.800 − 0.800 = 0		0.800 mmol		

Interactive Example 15.9 - Solution (Continued 1)

- The major species in the solution are HCN, CN^-, Na^+, and H_2O, and the position of the acid dissociation equilibrium will determine the pH

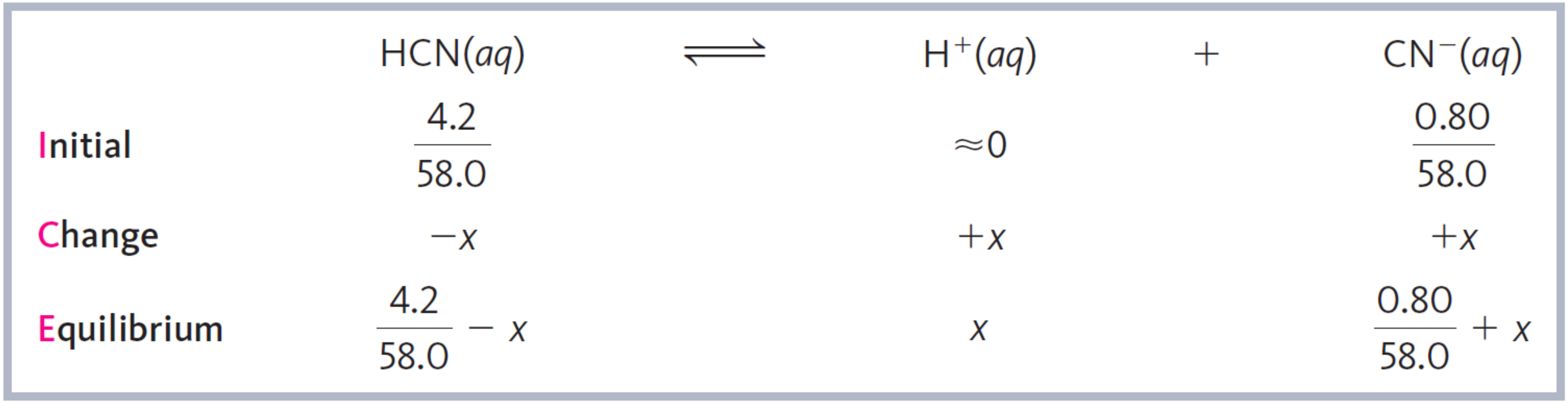
$$\mathrm{HCN}\,(aq) \rightleftharpoons \mathrm{H}^+(aq) + \mathrm{CN}^-(aq)$$



Initial Concentration		Equilibrium Concentration
$[\mathrm{HCN}]_0 = \dfrac{4.2\ \text{mmol}}{(50.0 + 8.0)\ \text{mL}}$		$[\mathrm{HCN}] = \dfrac{4.2}{58.0} - x$
$[\mathrm{CN}^-]_0 = \dfrac{0.800\ \text{mmol}}{(50.0 + 8.0)\ \text{mL}}$	$\xrightarrow[\text{dissociates}]{x\ \text{mmol/mL HCN}}$	$[\mathrm{CN}^-] = \dfrac{0.80}{58.0} + x$
$[\mathrm{H}^+]_0 \approx 0$		$[\mathrm{H}^+] = x$

Interactive Example 15.9 - Solution (Continued 2)

- The corresponding ICE table is



	$HCN(aq)$	$\rightleftharpoons$	$H^+(aq)$	$+$	$CN^-(aq)$
Initial	$\frac{4.2}{58.0}$		≈ 0		$\frac{0.80}{58.0}$
Change	$-x$		$+x$		$+x$
Equilibrium	$\frac{4.2}{58.0} - x$		x		$\frac{0.80}{58.0} + x$

Interactive Example 15.9 - Solution (Continued 3)

- Substituting the equilibrium concentrations into the expression for K_a gives

$$6.2\times10^{-10} = K_{\mathrm{a}} = \frac{[\mathrm{H}^+][\mathrm{CN}^-]}{[\mathrm{HCN}]} = \frac{x\left(\frac{0.80}{58.0} + x\right)}{\frac{4.2}{58.0} - x} \approx \frac{x\left(\frac{0.80}{58.0}\right)}{\left(\frac{4.2}{58.0}\right)} = x\left(\frac{0.80}{4.2}\right)$$

$$x = 3.3 \times 10^{-9}\ M = [\mathrm{H}^+] \text{ and pH} = 8.49$$

Interactive Example 15.9 - Solution (Continued 4)

b. At the halfway point of the titration

- The amount of HCN originally present can be obtained from the original volume and molarity

$$50.0\ \text{mL} \times 0.100\ M = 5.00\ \text{mmol}$$

- Thus, the halfway point will occur when 2.50 mmol OH^- has been added

$$\text{Volume of NaOH (in mL)} \times 0.100\ M = 2.50\ \text{mmol OH}^-$$

or

$$\text{Volume of NaOH} = 25.0\ \text{mL}$$

Interactive Example 15.9 - Solution (Continued 5)

- At the halfway point, [HCN] is equal to [CN^-] and pH is equal to pK_a
  - Thus, after 25.0 mL of 0.100 *M* NaOH has been added

$$\text{pH} = \text{p}K_\text{a} = -\log\left(6.2 \times 10^{-10}\right) = 9.21$$

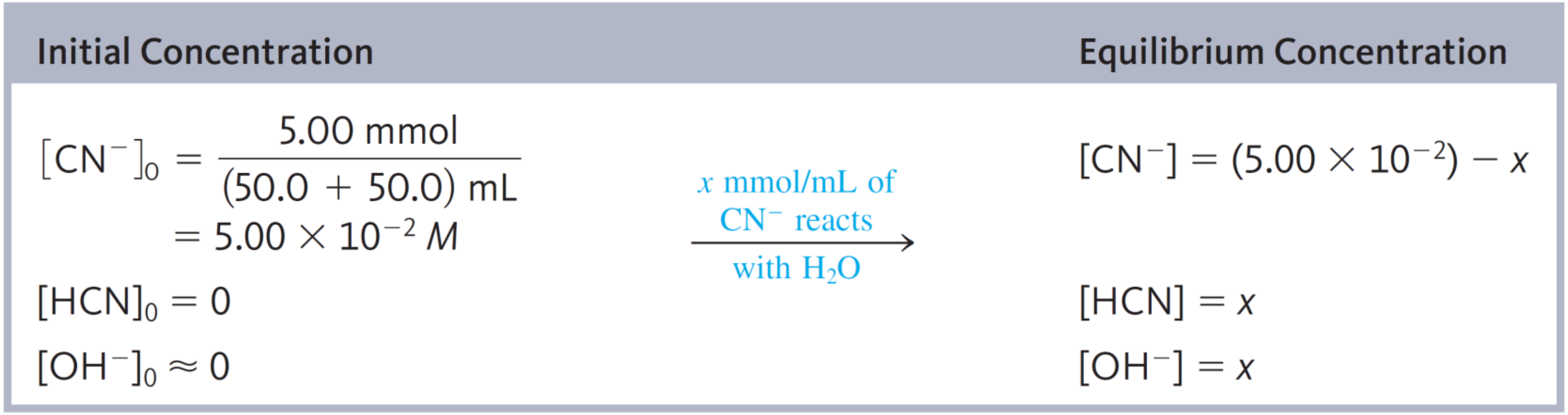
c. At the equivalence point

- The major species in solution at the equivalence point are CN^-, Na^+, and H_2O
  - Thus, the reaction that will control the pH involves the basic cyanide ion extracting a proton from water

Interactive Example 15.9 - Solution (Continued 6)

$$\mathrm{CN^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{HCN}(aq) + \mathrm{OH^-}(aq)$$

$$K_\mathrm{b} = \frac{K_\mathrm{w}}{K_\mathrm{a}} = \frac{1.0 \times 10^{-14}}{6.2 \times 10^{-10}} = 1.6 \times 10^{-5} = \frac{[\mathrm{HCN}]\left[\mathrm{OH^-}\right]}{\left[\mathrm{CN^-}\right]}$$



Initial Concentration		Equilibrium Concentration
$[\mathrm{CN^-}]_0 = \dfrac{5.00\ \mathrm{mmol}}{(50.0 + 50.0)\ \mathrm{mL}}$ $= 5.00 \times 10^{-2}\ M$	$\xrightarrow[\text{with } \mathrm{H_2O}]{x\ \text{mmol/mL of } \mathrm{CN^-}\ \text{reacts}}$	$[\mathrm{CN^-}] = (5.00 \times 10^{-2}) - x$
$[\mathrm{HCN}]_0 = 0$		$[\mathrm{HCN}] = x$
$[\mathrm{OH^-}]_0 \approx 0$		$[\mathrm{OH^-}] = x$

Interactive Example 15.9 - Solution (Continued 7)

- The corresponding ICE table is

	$CN^-(aq)$	+	$H_2O(l)$	$\rightleftharpoons$	$HCN(aq)$	+	$OH^-(aq)$
Initial	0.050		—		0		0
Change	$-x$		—		$+x$		$+x$
Equilibrium	$0.050 - x$		—		x		x

- Substituting the equilibrium concentrations into the expression for K_b and solving in the usual way gives

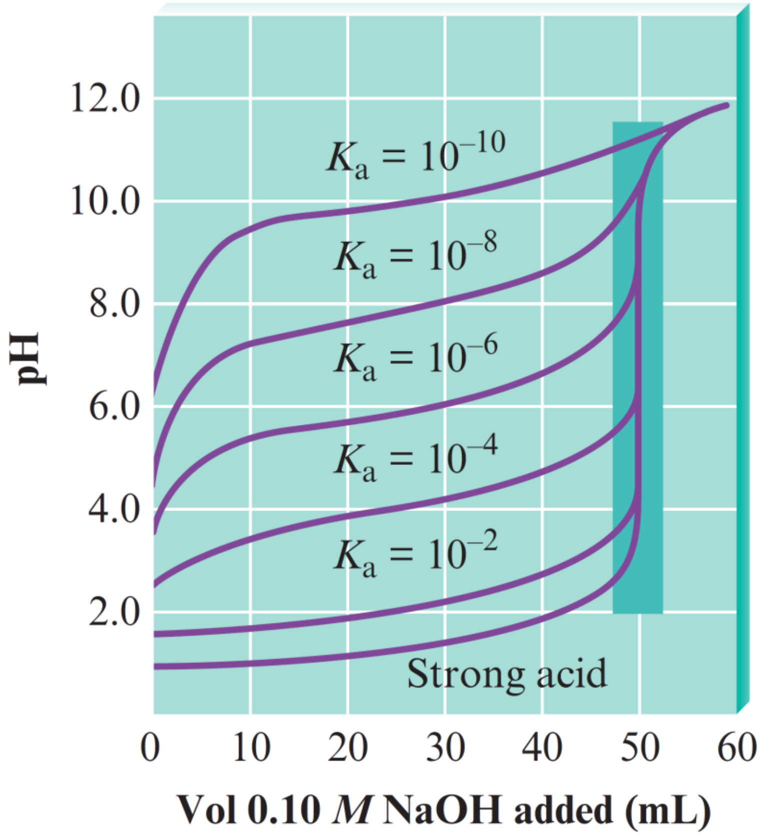
$$\left[OH^-\right] = x = 8.9 \times 10^{-4}$$

$$\text{From } K_w,\ \left[H^+\right] = 1.1 \times 10^{-11}\ M \text{ and pH} = 10.96$$

Titrations of Weak Acids with Strong Bases - Key Points

- Equivalence point of a solution is affected by the amount of acid present in it
- pH value at equivalence point is affected by acid strength
  - Strength of a weak acid significantly affects the shape of its pH curve
    - Weaker the acid, greater the pH value at equivalence point

Figure 15.4 - The pH Curves for the Titrations of 50.0 mL Samples of 0.10 *M* Acids with Various K_a Values



Interactive Example 15.10 - Calculating K_a

- A chemist has synthesized a monoprotic weak acid and wants to determine its K_a value
  - To do so, the chemist dissolves 2.00 mmol of the solid acid in 100.0 mL water and titrates the resulting solution with 0.0500 *M* NaOH
  - After 20.0 mL NaOH has been added, the pH is 6.00
  - What is the K_a value for the acid?

Interactive Example 15.10 - Solution

- Stoichiometry problem
  - The monoprotic acid is represented as HA
    - The stoichiometry for the titration reaction is shown below

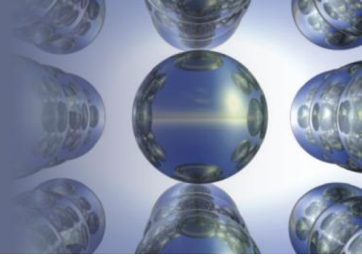
	HA	$+$	OH^-	$\longrightarrow$	A^-	$+$	H_2O
Before reaction	2.00 mmol		20.0 mL $\times$ 0.0500 M $= 1.00$ mmol		0 mmol		
After reaction	$2.00 - 1.00 = 1.00$ mmol		$1.00 - 1.00 = 0$		1.00 mmol		

Interactive Example 15.10 - Solution (Continued 1)

- Equilibrium problem
  - After the reaction, the major species present in the solution are HA, A^-, Na^+, and H_2O
  - The pH will be determined by the following equilibrium:

$$\text{HA}\,(aq) \rightleftharpoons \text{H}^+(aq) + \text{A}^-(aq)$$

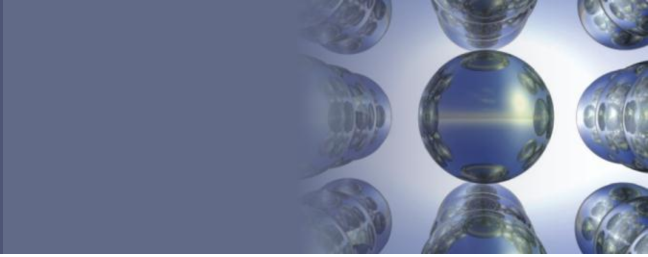
$$K_\text{a} = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$



Interactive Example 15.10 - Solution (Continued 2)

Initial Concentration		**Equilibrium Concentration**
$[\mathrm{HA}]_0 = \dfrac{1.00\text{ mmol}}{(100.0 + 20.0)\text{ mL}} = 8.33 \times 10^{-3}\,M$		$[\mathrm{HA}] = 8.33 \times 10^{-3} - x$
	$\xrightarrow[\text{dissociates}]{x\text{ mmol/mL HA}}$	
$[\mathrm{A}^-]_0 = \dfrac{1.00\text{ mmol}}{(100.0 + 20.0)\text{ mL}} = 8.33 \times 10^{-3}\,M$		$[\mathrm{A}^-] = 8.33 \times 10^{-3} + x$
$[\mathrm{H}^+]_0 \approx 0$		$[\mathrm{H}^+] = x$

	$\mathrm{HA}(aq)$	$\rightleftharpoons$	$\mathrm{H}^+(aq)$	$+$	$\mathrm{A}^-(aq)$
Initial	8.33×10^{-3}		≈ 0		8.33×10^{-3}
Change	$-x$		$+x$		$+x$
Equilibrium	$8.33 \times 10^{-3} - x$		x		$8.33 \times 10^{-3} + x$



Interactive Example 15.10 - Solution (Continued 3)

$$x = \left[\mathrm{H^+}\right] = \text{antilog}\left(-\mathrm{pH}\right) = 1.0 \times 10^{-6}\ M$$

- *x* is known here because the pH at this point is known to be 6.00
- Substituting values into the expression for K_a

$$K_a = \frac{\left[\mathrm{H^+}\right]\left[\mathrm{A^-}\right]}{[\mathrm{HA}]} = \frac{x\left(8.33 \times 10^{-3} + x\right)}{\left(8.33 \times 10^{-3}\right) - x} = \frac{\left(1.0 \times 10^{-6}\right)\left(8.33 \times 10^{-3} + 1.0 \times 10^{-6}\right)}{\left(8.33 \times 10^{-3}\right) - \left(1.0 \times 10^{-6}\right)}$$

$$\approx \frac{\left(1.0 \times 10^{-6}\right)\left(8.33 \times 10^{-3}\right)}{8.33 \times 10^{-3}} = 1.0 \times 10^{-6}$$

Interactive Example 15.10 - Solution (Continued 4)

- An easier way to think about this problem:
  - The original solution contained 2.00 mmol of HA
    - Since 20.0 mL of added 0.0500 *M* NaOH contains 1.0 mmol OH^-, this is the halfway point in the titration (where [HA] = $[A^-]$)
    - Thus,

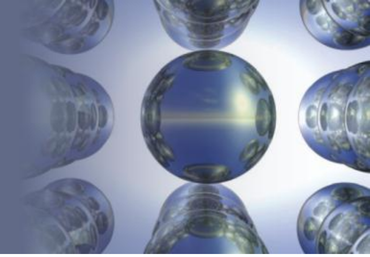
$$\left[H^+\right] = K_a = 1.0 \times 10^{-6}$$

Titrations of Weak Bases with Weak Acids

- Steps involved
  - Determine the major species in solution
  - Decide whether a reaction occurs that runs into completion
    - Let it run to completion and perform stoichiometric calculations
  - Choose the dominant equilibrium and calculate the pH

Case Study - Weak Base–Strong Acid Titration

- Consider the titration of 100.0 mL of 0.050 *M* NH_3 with 0.10 *M* HCl
- Before the addition of any HCl
  - Major species are NH_3 and H_2O
    - H_2O is the only available source of protons as NH_3 is a base
  - No reactions go to completion
    - NH_3 cannot readily take a proton from H_2O (small K_a value of NH_3)

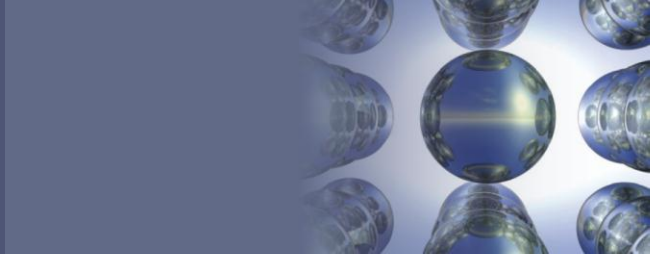


Case Study - Weak Base–Strong Acid Titration (Continued 1)

- The equilibrium controlling the pH involves the reaction of ammonia with water

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

- K_b is used to calculate $[OH^-]$
- Before the equivalence point
  - The major species, prior to any reaction, are NH_3, H^+, Cl^-, and H_2O
    - Source of H^+ and Cl^- is the added HCl



Case Study - Weak Base–Strong Acid Titration (Continued 2)

- NH_3 will react with H^+ from the added HCl

$$NH_3(aq) + H^+(aq) \rightarrow NH_4^+(aq)$$

    - The reaction readily runs to completion as NH_3 readily reacts with a proton
- Major species present after the reaction of NH_3 with H^+ are NH_3, NH_4^+, Cl^-, and H_2O
    - NH_4^+ is formed in the titration reaction

Case Study - Weak Base–Strong Acid Titration (Continued 3)

- Note that the solution contains NH_3 and NH_4^+
  - The equilibria involving these species will determine $[H^+]$
  - The following dissociation reactions can be used:

$$\mathrm{NH_4^+}\,(aq) \rightleftharpoons \mathrm{NH_3}(aq) + \mathrm{H^+}(aq)$$

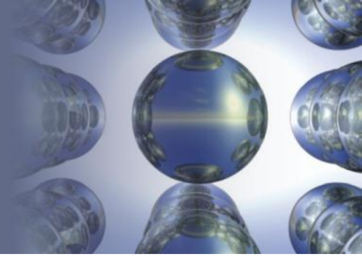
(or)

$$\mathrm{NH_3}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{NH_4^+}(aq) + \mathrm{OH^-}(aq)$$

Case Study - Weak Base–Strong Acid Titration (Continued 4)

- At the equivalence point
    - All the original NH_3 is converted to NH_4^+
        - Major species are NH_4^+, Cl^-, and H_2O
    - No reactions occur that go to completion
    - Dominant equilibrium will be the dissociation of the weak acid NH_4^+ for which,

$$K_a = \frac{K_w}{K_b(\text{for } NH_3)}$$

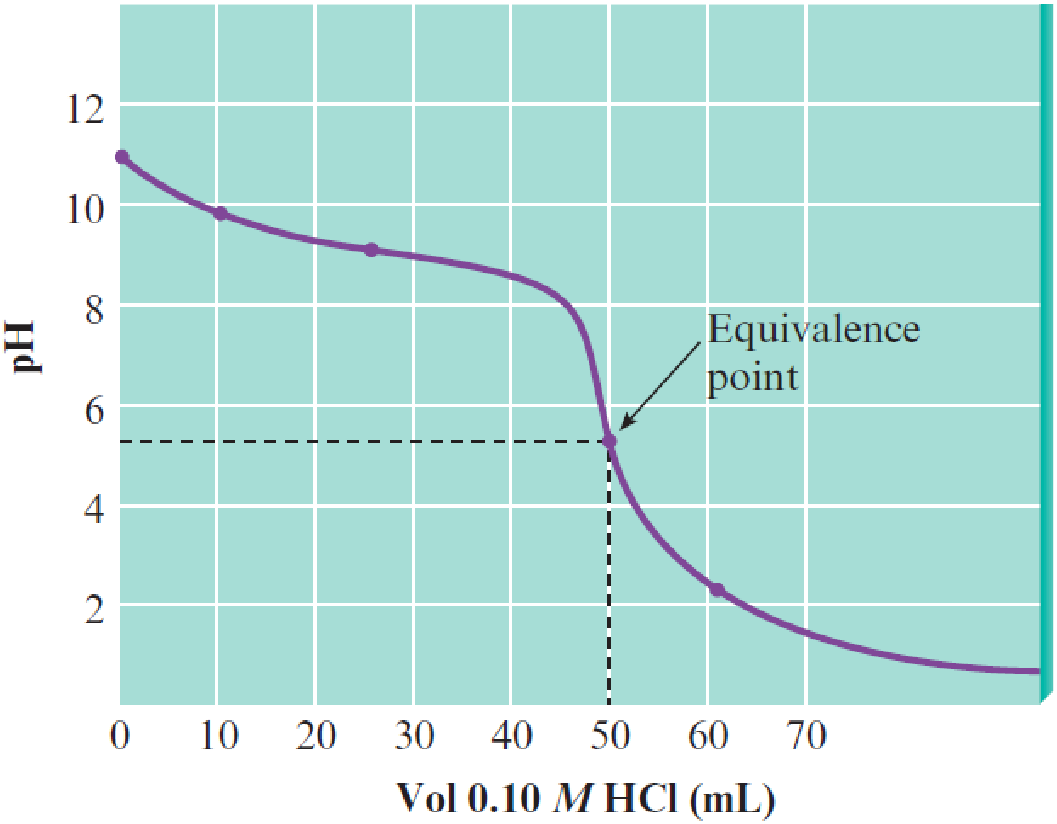


Case Study - Weak Base–Strong Acid Titration (Continued 5)

- Beyond the equivalence point
  - Excess HCl has been added
    - Major species are H^+, NH_4^+, Cl^-, and H_2O
  - No reactions occur that go to completion
  - Although NH_4^+ will dissociate, it is such a weak acid that $[H^+]$ will be determined by the excess H^+

$$[\mathrm{H}^+] = \frac{\text{mmol H}^+ \text{ in excess}}{\text{mL solution}}$$

Figure 15.5 - The pH Curve for the Titration of 100.0 mL 0.050 *M* Ammonia with 0.10 *M* Hydrochloric Acid



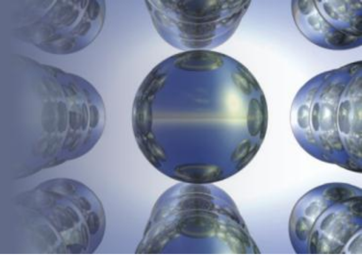
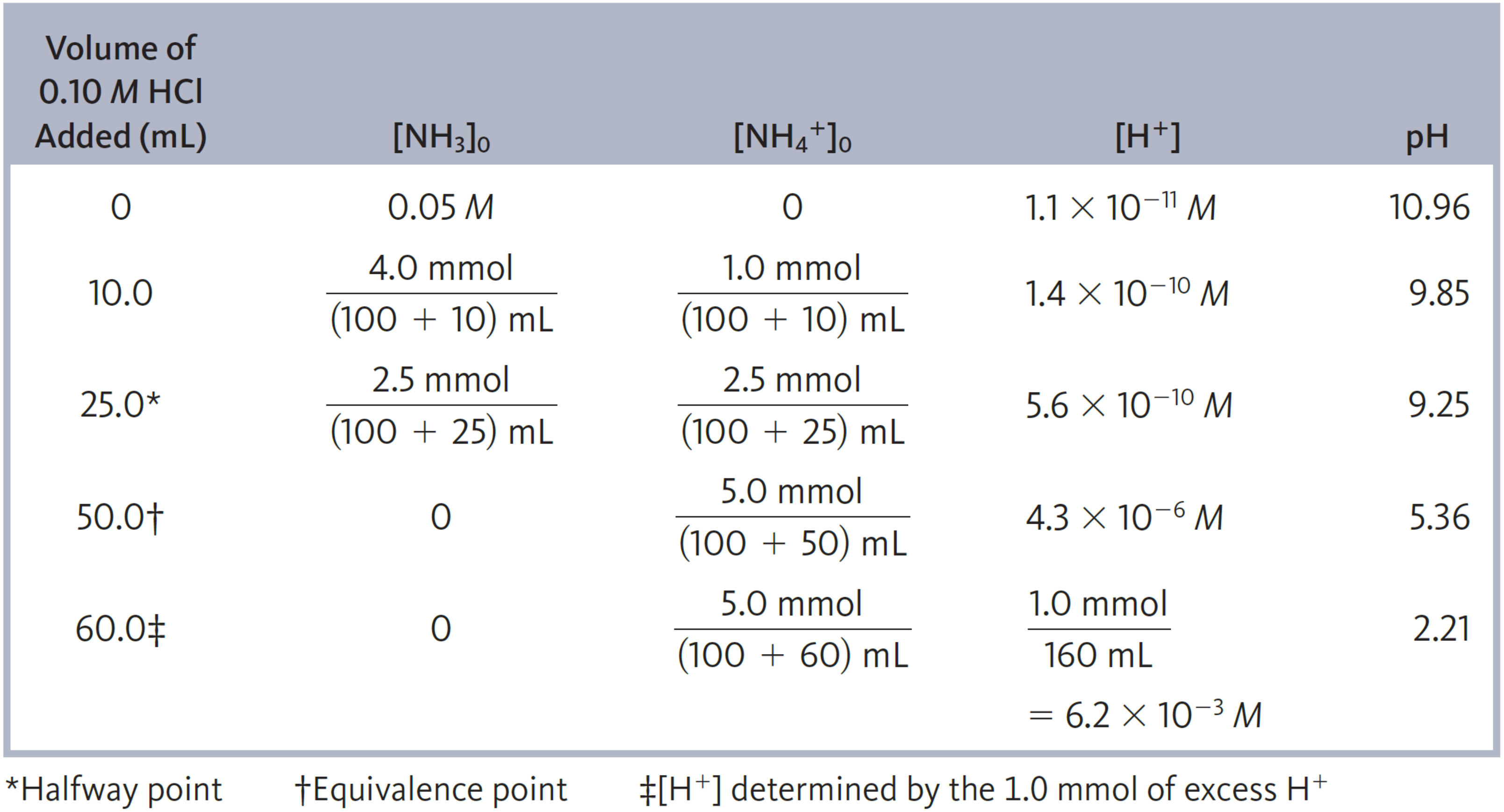


Table 15.2 - Summary of Results for the Titration of 100.0 mL 0.050 *M* Ammonia with 0.10 *M* Hydrochloric Acid



Volume of 0.10 *M* HCl Added (mL)	$[NH_3]_0$	$[NH_4^+]_0$	$[H^+]$	pH
0	0.05 *M*	0	$1.1 \times 10^{-11}\ M$	10.96
10.0	$\frac{4.0\text{ mmol}}{(100 + 10)\text{ mL}}$	$\frac{1.0\text{ mmol}}{(100 + 10)\text{ mL}}$	$1.4 \times 10^{-10}\ M$	9.85
25.0*	$\frac{2.5\text{ mmol}}{(100 + 25)\text{ mL}}$	$\frac{2.5\text{ mmol}}{(100 + 25)\text{ mL}}$	$5.6 \times 10^{-10}\ M$	9.25
50.0†	0	$\frac{5.0\text{ mmol}}{(100 + 50)\text{ mL}}$	$4.3 \times 10^{-6}\ M$	5.36
60.0‡	0	$\frac{5.0\text{ mmol}}{(100 + 60)\text{ mL}}$	$\frac{1.0\text{ mmol}}{160\text{ mL}} = 6.2 \times 10^{-3}\ M$	2.21

*Halfway point †Equivalence point ‡$[H^+]$ determined by the 1.0 mmol of excess H^+

Critical Thinking

- You have read about titrations of strong acids with strong bases, weak acids with strong bases, and weak bases with strong acids
  - What if you titrated a weak acid with a weak base?
    - Sketch a pH curve and defend its shape
      - Label the equivalence point and discuss the possibilities for the pH value at the equivalence point

Methods Used to Determine the Equivalence Point

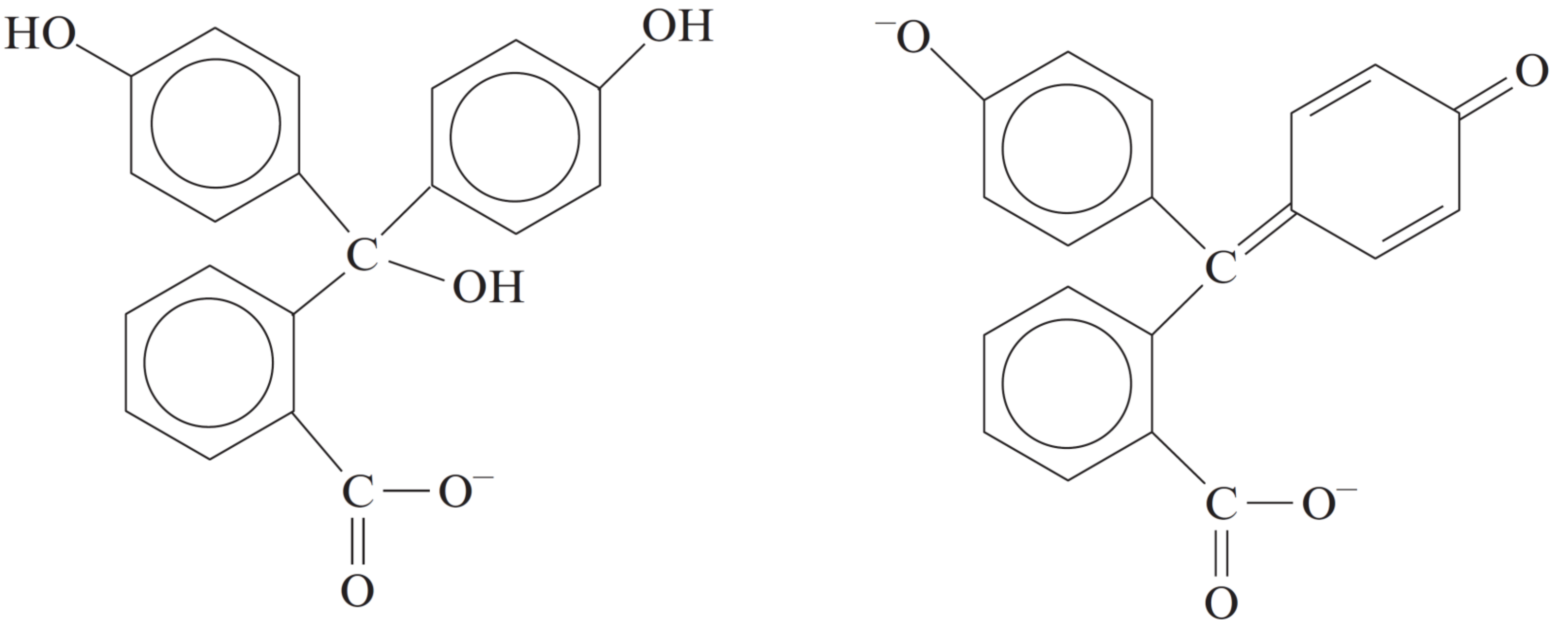
- pH meter
  - Used to monitor the pH and then plot the titration curve
- **Acid–base indicator**: Marks the end point of a titration by changing color
  - Equivalence point is not necessarily the same as the end point
    - Careful selection of the indicator ensures that the margin of error is minimal

Phenolphthalein

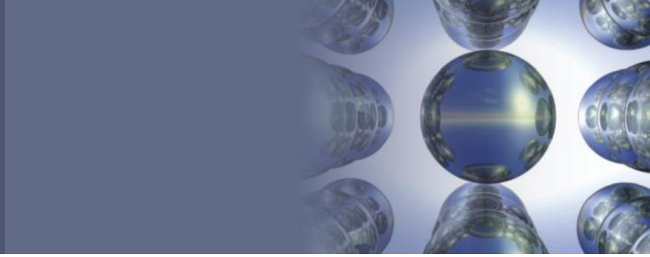
- A commonly used indicator
- Colorless in HIn form and pink in In⁻ form
  - HIn - Weak acid form
  - In⁻ - Basic form

Photo © Cengage Learning. All rights reserved

Figure 15.6 - The Acid and Base Forms of the Indicator Phenolphthalein



Colorless acid form, HIn **Pink base form, In^-**



Example 15.11 - Indicator Color Change

- Bromthymol blue, an indicator with a K_a value of 1.0×10^{-7}, is yellow in its HIn form and blue in its In^- form
  - Assume that a few drops of this indicator is placed in a strongly acidic solution
    - If the solution is then titrated with NaOH, at what pH will the indicator color change first be visible?

Example 15.11 - Solution

- For bromthymol blue

$$K_a = 1.0 \times 10^{-7} = \frac{[H^+][In^-]}{[HIn]}$$

- We assume that the color change is visible when

$$\frac{[In^-]}{[HIn]} = \frac{1}{10}$$

Example 15.11 - Solution (Continued 1)

- We assume that we can see the first hint of a greenish tint (yellow plus a little blue) when the solution contains 1 part blue and 10 parts yellow

Charles D. Winters
Charles D. Winters
Charles D. Winters

Example 15.11 - Solution (Continued 2)

- Therefore,

$$K_a = 1.0 \times 10^{-7} = \frac{\left[\mathrm{H}^+\right](1)}{10}$$

$$\left[\mathrm{H}^+\right] = 1.0 \times 10^{-6} \quad \text{or} \quad \mathrm{pH} = 6.00$$

  - The color change is first visible at pH 6.00

Determining the pH at Which an Indicator Changes Color Using the Henderson–Hasselbalch Equation

- Application of equation (15.2) to the K_a expression for the general indicator HIn yields

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\left(\frac{[\mathrm{In}^-]}{[\mathrm{HIn}]}\right)$$

  - K_a - Dissociation constant for the acid form of the indicator (HIn)

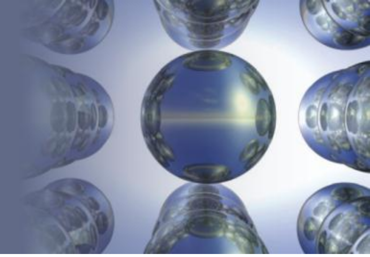
Determining the pH at Which an Indicator Changes Color Using the Henderson–Hasselbalch Equation (Continued 1)

- Assume that the color change is visible when

$$\frac{[\mathrm{In}^-]}{[\mathrm{HIn}]} = \frac{1}{10}$$

  - The following equation can be used to determine the pH at which the color change occurs:

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\left(\frac{1}{10}\right) = \mathrm{p}K_\mathrm{a} - 1$$



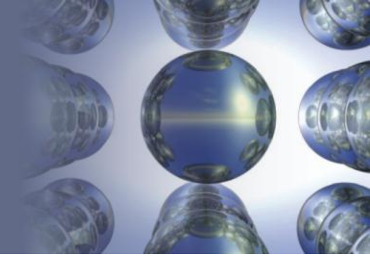
Determining the pH at Which an Indicator Changes Color Using the Henderson–Hasselbalch Equation (Continued 2)

- For bromthymol blue ($K_a = 1 \times 10^{-7}$, or pK_a = 7), the pH at which color change occurs is

$$\text{pH} = 7 - 1 = 6$$

- When a basic solution is titrated, the indicator HIn will initially exist as In^- in solution
  - The color change will be visible when

$$\frac{\left[\text{In}^-\right]}{\left[\text{HIn}\right]} = \frac{10}{1}$$



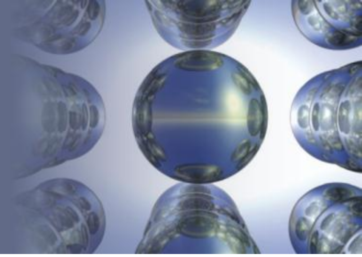
Determining the pH at Which an Indicator Changes Color Using the Henderson–Hasselbalch Equation (Continued 3)

- Substituting the ratio into the Henderson–Hasselbalch equation gives

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\left(\frac{10}{1}\right) = \mathrm{p}K_\mathrm{a} + 1$$

- For bromthymol blue, the color change occurs at

$$\mathrm{pH} = 7 + 1 = 8$$

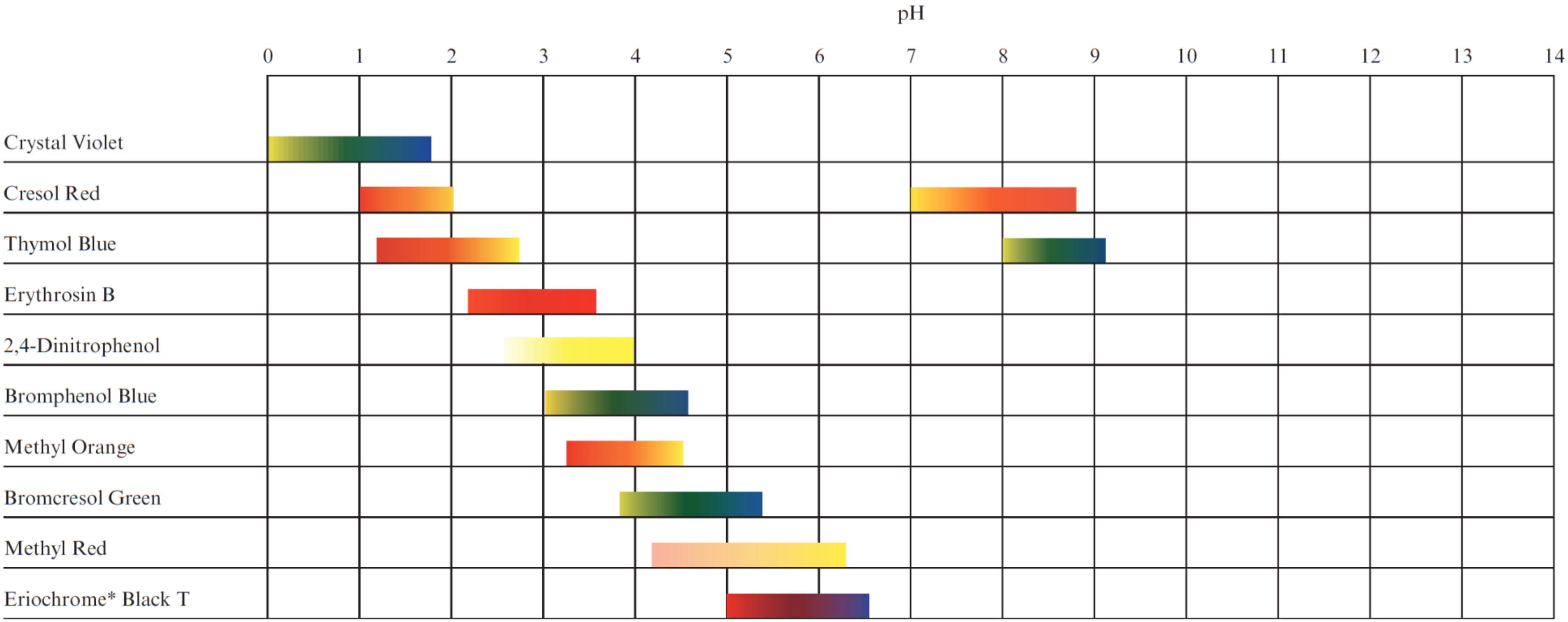


Determining the pH at Which an Indicator Changes Color Using the Henderson–Hasselbalch Equation (Continued 4)

- Summary
  - When bromthymol blue is used for titration of an acid:
    - Starting form will be HIn (yellow), and color change occurs when pH = 6
  - When bromthymol blue is used for titration of a base:
    - Starting form is In^- (blue), and color change occurs when pH = 8
    - The useful pH range for bromthymol blue is

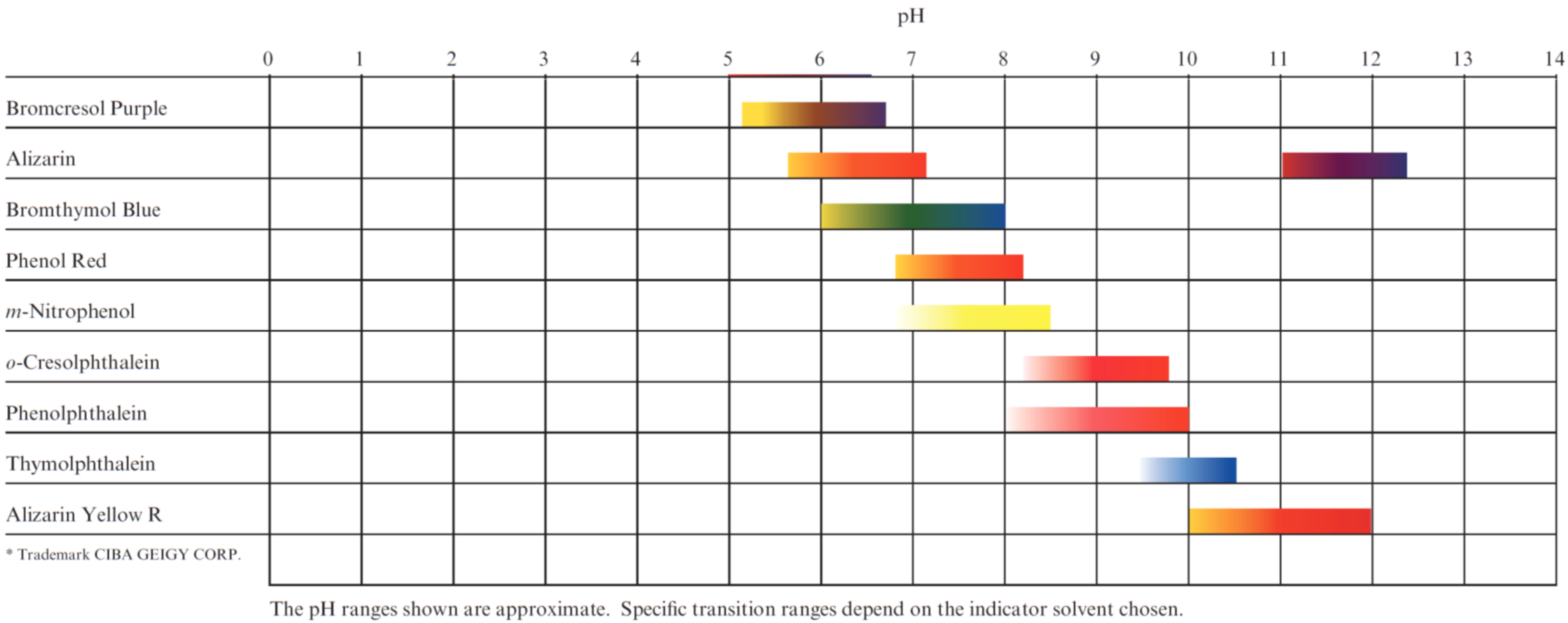
$$\mathrm{p}K_\mathrm{a}\,(\text{bromthymol blue}) \pm 1 = 7 \pm 1$$

Figure 15.8 - The Useful pH Ranges for Several Common Indicators



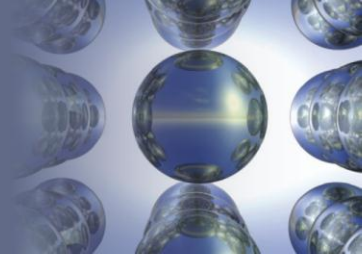
The pH ranges shown are approximate. Specific transition ranges depend on the indicator solvent chosen.

Figure 15.8 - The Useful pH Ranges for Several Common Indicators (Continued)



* Trademark CIBA GEIGY CORP.

The pH ranges shown are approximate. Specific transition ranges depend on the indicator solvent chosen.



Essentials While Choosing an Indicator

- Indicator end point and the titration equivalence point need to be as close as possible
- Good indicators produce a sharp end point during titration
  - Complete color change occurs over one drop of the titrant

Choosing an Indicator - Example

- Consider the titration of 100.0 mL of 0.100 *M* HCl with 0.100 *M* NaOH
  - In the initially acidic solution, the indicator will be in HIn form
  - As OH^- ions are added, pH initially increases slowly and then rises rapidly at the equivalence point
    - Causes the dissociation equilibrium to shift to the right

$$\mathrm{HIn} \rightleftharpoons \mathrm{H}^{+} + \mathrm{In}^{-}$$

Choosing an Indicator - Example (Continued 1)

- In^- ions are produced, and color change can be observed
    - The first observable color change will occur at a pH where

$$\frac{[\mathrm{In}^-]}{[\mathrm{HIn}]} = \frac{1}{10}$$

    - Thus,

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\left(\frac{1}{10}\right) = \mathrm{p}K_\mathrm{a} - 1$$

Choosing an Indicator - Example (Continued 2)

- The following relationship can be used to find the pK_a value of an indicator that changes color at pH 7:

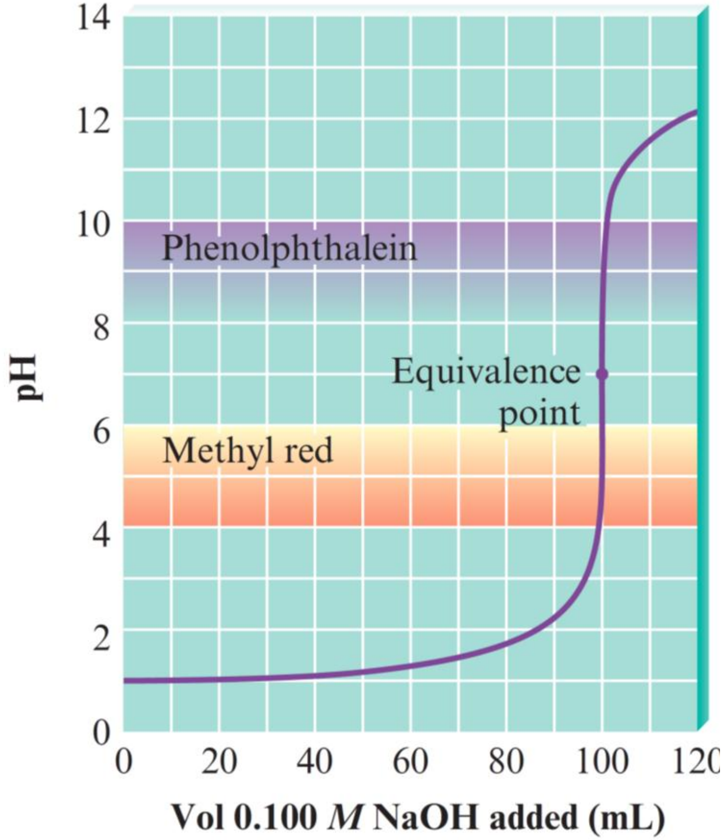
$$\text{pH} = 7 = \text{p}K_a - 1 \quad \text{(or)} \quad \text{p}K_a = 7 + 1 = 8$$

  - Thus, an indicator with a pK_a = 8 ($K_a = 1 \times 10^{-8}$) changes color at about pH = 7
    - Ideal for marking the end point for a strong acid–strong base titration

Indicators for Strong Acid–Strong Base Titration: General Conclusions

- Indicator color changes will be sharp, occurring with the addition of a single drop of titrant
- There is a wide choice of suitable indicators
  - Results will agree within one drop of titrant when indicators with end points that are as far apart as pH 5 and pH 9 are used

Figure 15.9 - The pH Curve for the Titration of 100.0 mL of 0.10 *M* HCl with 0.10 *M* NaOH



Titration of Weak Acids

- The weaker the acid being titrated, the smaller the vertical area around the equivalence point
- Chosen indicator must possess a pH range with a midpoint as close as possible to the pH at the equivalence point

Figure 15.10 - The pH Curve for the Titration of 50 mL of 0.1 *M* $HC_2H_3O_2$ with 0.10 *M* NaOH