

# Lecture 4

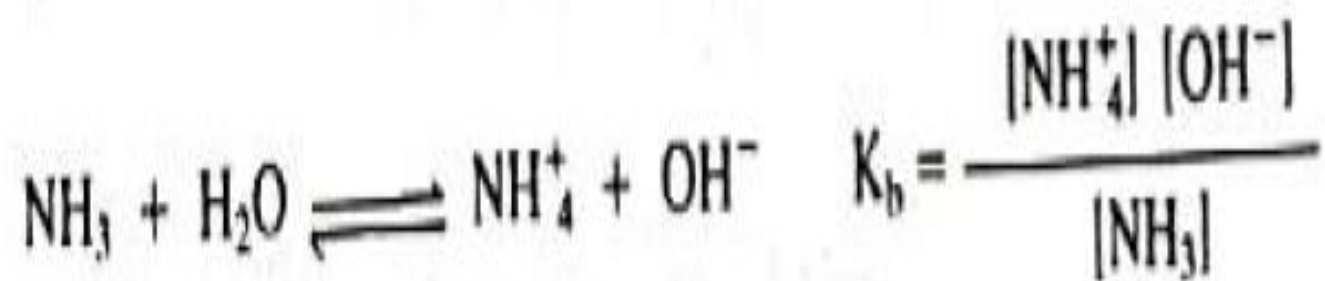
Acid- base titration

Buffer

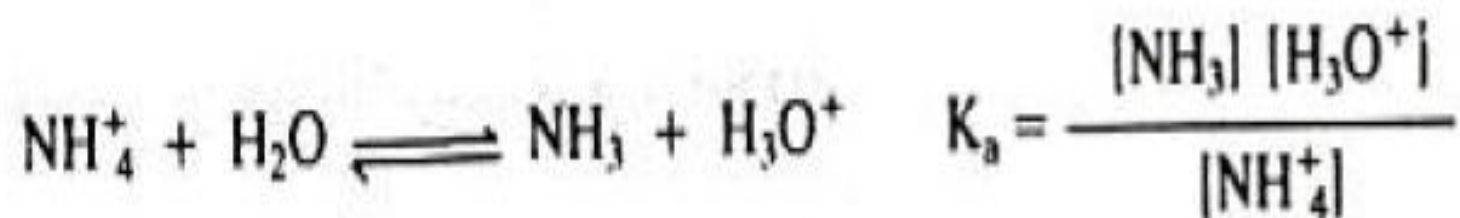
Indicator

**By Dr.Mohammed.J.Hamzah**

# **1-Hydrolysis for weak base**



Hydrolysis for conjugated acid :



$$K_a K_b = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]} \times \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = [\text{H}_3\text{O}^+][\text{OH}^-]$$

$$\boxed{K_a K_b = K_w}$$

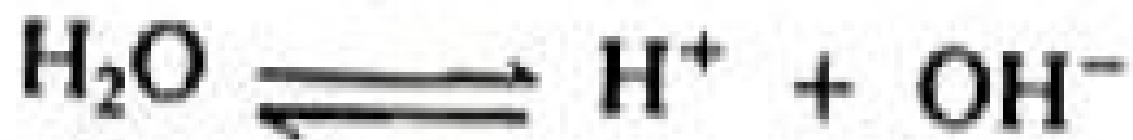
## **2-Hydrolysis of weak acid:**



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

# Hydrolysis of water





$$[\text{H}^+] \cong [\text{A}^-]$$

$$[\text{HA}] = F_{\text{HA}} - [\text{H}^+]$$

$$K_a = \frac{[\text{H}^+]^2}{F_{\text{HA}} - [\text{H}^+]}$$

**By rearrangement of**

$$[H^+]^2 + K_a[H^+] - K_aF_{HA} = 0$$

**By solving above**

$$[H^+] = \frac{-K_a + \sqrt{(K_a)^2 + 4K_a F_{HA}}}{2}$$

**[H<sup>+</sup>] is small as compared with [HA]**

$$F_{HA} = [HA]$$

$$[H^+] = \sqrt{K_a [HA]}$$

By simplified the above relation

$$\text{pH} = \frac{1}{2} \text{pK}_a - \frac{1}{2} \log [\text{HA}]$$

**3- For the weak base we used the same methods:**

$$[\text{OH}^-] = \frac{-K_b + \sqrt{(K_b)^2 + 4K_b F_{\text{BOH}}}}{2}$$

$$F_{\text{BOH}} = [\text{BOH}]$$

$$[\text{OH}^-] = \sqrt{K_b [\text{BOH}]}$$

$$pOH = \frac{1}{2} pK_b - \frac{1}{2} \log [BOH]$$



## **buffer solution:**

**Buffer solution:** is a solution that resists change in pH when a small amount of an acid or base is added or when solution is diluted.

Calculate of pH of buffer solution; consider an acetic acid-acetate buffer.

## 1- Weak Acid + It is Salt



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

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

$$[\text{CH}_3\text{COO}^-] = [\text{salt}]$$

$$[\text{CH}_3\text{COOH}] = [\text{acid}]$$

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

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

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



$$\text{pOH} = \text{p}K_b + \log \frac{[\text{salt}]}{[\text{base}]}$$



These equations is called the Hederson-Hasselbalch equation.

**Buffer capacity of the solution**: is the amount of acid or base that can be added without causing a large change in pH, the buffering capacity increases with the concentration of the buffering species'

The buffer capacity is maximum at  
 $\text{pH}=\text{pka}$ .

$$\beta = dC_{\text{BOH}}/d\text{pH} = -dC_{\text{HA}}/d\text{pH} \quad (7.49)$$

Where  $dC_{\text{BOH}}$  and  $dC_{\text{HA}}$  represent the number of moles per liter of strong base or acid needed to bring about a pH change of  $dpH$ . The buffer capacity is a positive number. The larger it is, the more resistant the solution is to pH change. For weak acid/conjugate base buffer solutions of greater than 0.001M the buffer capacity is

Where  $C_{\text{HA}}$  and  $C_{\text{A}^-}$  represent the analytical; concentrations of the acid and its salt.

$$\beta = 2.303 \frac{C_{\text{HA}} C_{\text{A}^-}}{C_{\text{HA}} + C_{\text{A}^-}} \quad (7.50)$$



# Titration Curve

A titration curve is a plot of pH vs. the amount of titrant added. Typically the titrant is a strong (completely) dissociated acid or base. Such curves are useful for determining endpoints and dissociation constants of weak acids or bases.

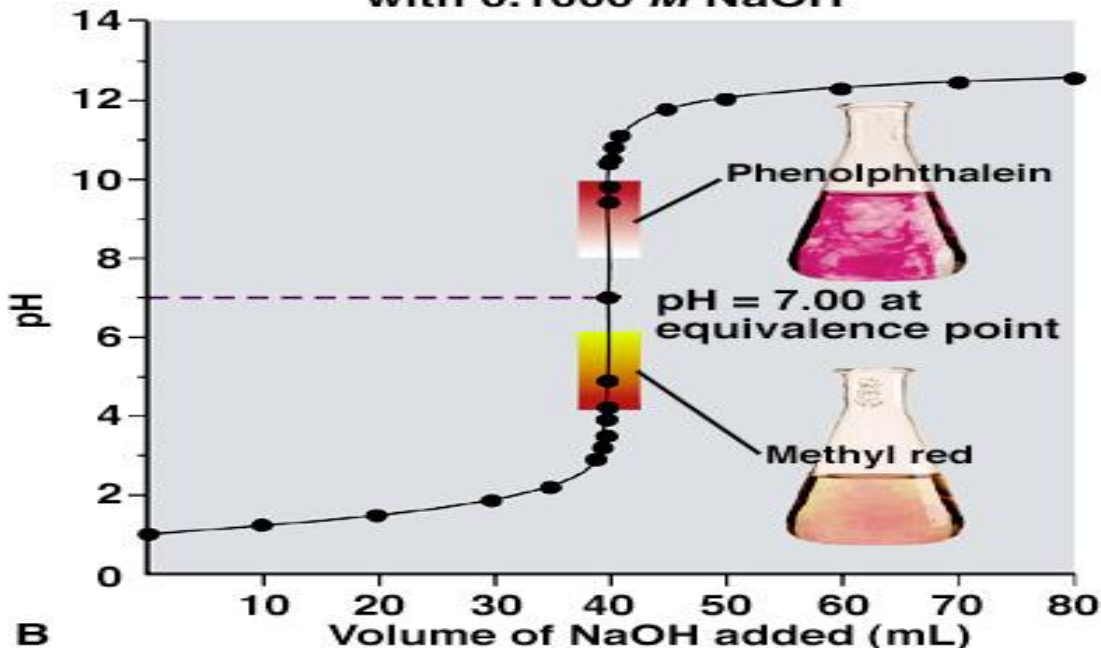
Martin S. Silberberg, *Chemistry: The Molecular Nature of Matter and Change*, 2<sup>nd</sup> Edition. Copyright © The McGraw-Hill Companies, Inc. All rights reserved.

## Strong Acid-Base Titration Curve

Volume of NaOH added (mL)	pH
00.00	1.00
10.00	1.22
20.00	1.48
30.00	1.85
35.00	2.18
39.00	2.89
39.50	3.20
39.75	3.50
39.90	3.90
39.95	4.20
39.99	4.90
40.00	7.00
40.01	9.40
40.05	9.80
40.10	10.40
40.25	10.50
40.50	10.79
41.00	11.09
45.00	11.76
50.00	12.05
60.00	12.30
70.00	12.43
80.00	12.52

A

Titration of 40.00 mL of 0.1000 M HCl with 0.1000 M NaOH



B

# **TITRATION OF STRONG ACIDS AND STRONG BASES**

## **EXAMPLE 14-1 :**

Generate the hypothetical titration curve for the titration of 50.00 mL of 0.0500 M HCl with 0.1000 M NaOH.

## Initial Point

Before any base is added, the solution is 0.0500 M in  $\text{H}_3\text{O}^+$ , and

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log 0.0500 = 1.30$$

### After Addition of 10.00 mL of Reagent

The hydronium ion concentration is decreased as a result of both reaction with the base and dilution. So the analytical concentration of HCl is

$$\begin{aligned}c_{\text{HCl}} &= \frac{\text{no. mmol HCl remaining after addition of NaOH}}{\text{total volume soln}} \\ &= \frac{\text{original no. mmol HCl} - \text{no. mmol NaOH added}}{\text{total volume soln}} \\ &= \frac{(50.00 \text{ mL} \times 0.0500 \text{ M}) - (10.00 \text{ mL} \times 0.1000 \text{ M})}{50.00 \text{ mL} + 10.00 \text{ mL}} \\ &= \frac{(2.500 \text{ mmol} - 1.000 \text{ mmol})}{60.00 \text{ mL}} = 2.500 \times 10^{-2} \text{ M}\end{aligned}$$

$$[\text{H}_3\text{O}^+] = 2.500 \times 10^{-2} \text{ M}$$

$$\text{and pH} = -\log[\text{H}_3\text{O}^+] = -\log(2.500 \times 10^{-2}) = 1.60$$

## After Addition of 25.00 mL of Reagent: The Equivalence Point

At the equivalence point, neither HCl nor NaOH is in excess, and so the concentrations of hydronium and hydroxide ions must be equal. Substituting this equality into the ion-product constant for water yields

$$[\text{H}_3\text{O}^+] = \sqrt{K_w} = \sqrt{1.00 \times 10^{-14}} = 1.00 \times 10^{-7} \text{ M}$$

$$\text{pH} = -\log(1.00 \times 10^{-7}) = 7.00$$

► At the equivalence point, the solution is neutral, and  $\text{pH} = 7.00$ .

#### After Addition of 25.10 mL of Reagent

The solution now contains an excess of NaOH, and we can write

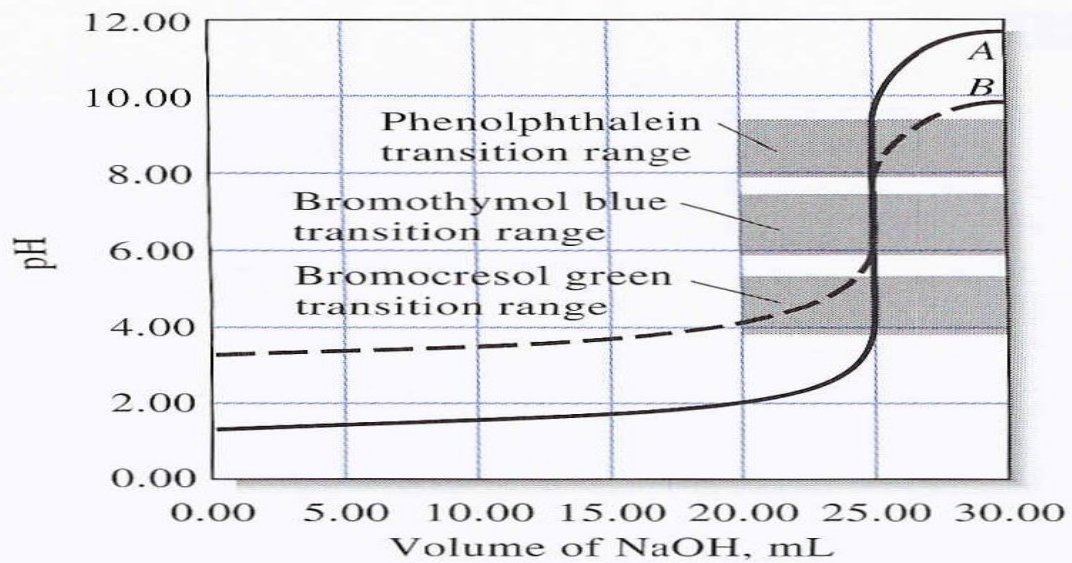
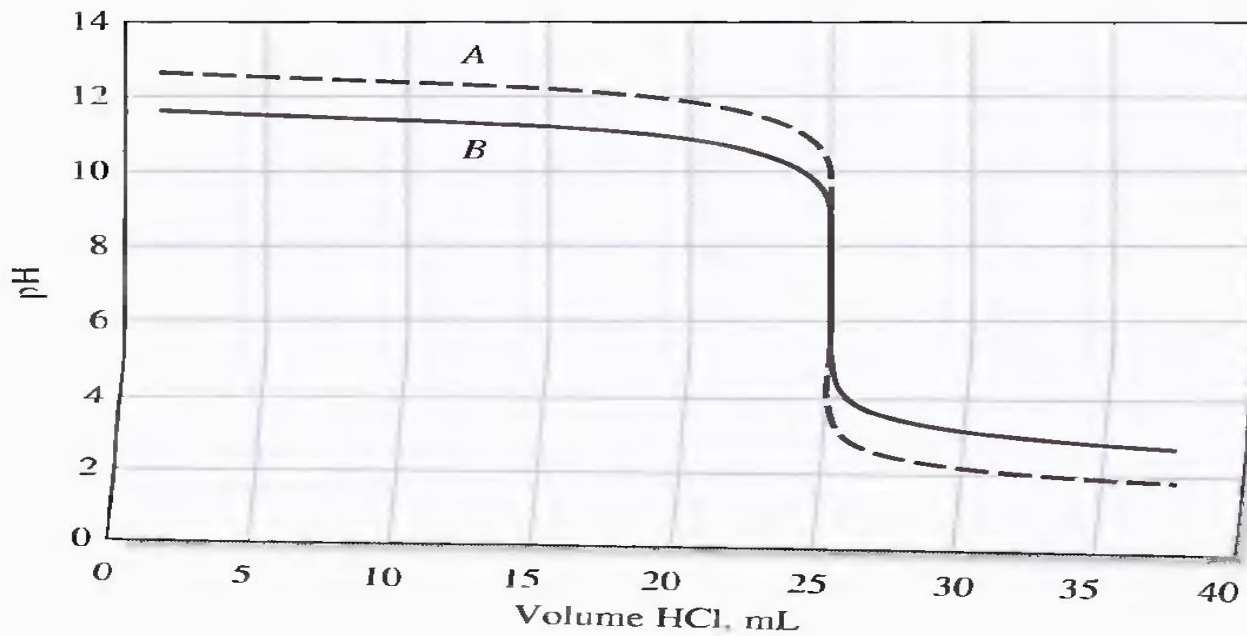
$$\begin{aligned}c_{\text{NaOH}} &= \frac{\text{no. mmol NaOH added} - \text{original no. mmol HCl}}{\text{total volume soln}} \\ &= \frac{25.10 \times 0.100 - 50.00 \times 0.0500}{75.10} = 1.33 \times 10^{-4} \text{ M}\end{aligned}$$

and the equilibrium concentration of hydroxide ion is

$$\begin{aligned}[\text{OH}^-] &= c_{\text{NaOH}} = 1.33 \times 10^{-4} \text{ M} \\ \text{pOH} &= -\log(1.33 \times 10^{-4}) = 3.88\end{aligned}$$

and

$$\text{pH} = 14.00 - 3.88 = 10.12$$



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## EXAMPLE 14-3

Generate a curve for the titration of 50.00 mL of 0.1000 M acetic acid with 0.1000 M sodium hydroxide.



## Initial pH

First, we must calculate the pH of a 0.1000 M solution of HOAc using Equation 9-22.

$$[\text{H}_3\text{O}^+] = \sqrt{K_a c_{\text{HOAc}}} = \sqrt{1.75 \times 10^{-5} \times 0.100} = 1.32 \times 10^{-3} \text{ M}$$

$$\text{pH} = -\log(1.32 \times 10^{-3}) = 2.88$$

### pH after Addition of 5.00 mL of Reagent

A buffer solution consisting of NaOAc and HOAc has now been produced. The analytical concentrations of the two constituents are

$$c_{\text{HOAc}} = \frac{50.00 \text{ mL} \times 0.100 \text{ M} - 5.00 \text{ mL} \times 0.100 \text{ M}}{60.00 \text{ mL}} = \frac{4.500}{60.00} \text{ M}$$

$$c_{\text{NaOAc}} = \frac{5.00 \text{ mL} \times 0.100 \text{ M}}{60.00 \text{ mL}} = \frac{0.500}{60.00} \text{ M}$$

Now for the 5.00-mL volume, we substitute the concentrations of HOAc and OAc<sup>-</sup> into the dissociation-constant expression for acetic acid and obtain

$$K_a = \frac{[\text{H}_3\text{O}^+](0.500/60.00)}{4.500/60.00} = 1.75 \times 10^{-5}$$

$$[\text{H}_3\text{O}^+] = 1.58 \times 10^{-4} \text{ M}$$

$$\text{pH} = 3.80$$

### pH after Addition of 25.00 mL of Reagent

As in the previous calculation, the analytical concentrations of the two constituents are

$$c_{\text{HOAc}} = \frac{50.00 \text{ mL} \times 0.100 \text{ M} - 25.00 \text{ mL} \times 0.100 \text{ M}}{60.00 \text{ mL}} = \frac{2.500}{60.00} \text{ M}$$

$$c_{\text{NaOAc}} = \frac{25.00 \text{ mL} \times 0.100 \text{ M}}{60.00 \text{ mL}} = \frac{2.500}{60.00} \text{ M}$$

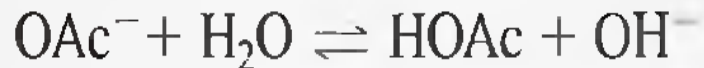
Now for the 25.00-mL volume, we substitute the concentrations of HOAc and OAc<sup>-</sup> into the dissociation-constant expression for acetic acid and obtain

$$K_a = \frac{[\text{H}_3\text{O}^+](2.500/60.00)}{2.500/60.00} = [\text{H}_3\text{O}^+] = 1.75 \times 10^{-5}$$

$$\text{pH} = \text{p}K_a = 4.76$$

## Equivalence Point pH

At the equivalence point, all the acetic acid has been converted to sodium acetate. The solution is therefore similar to one formed by dissolving that salt in water, and the pH calculation is identical to that shown in Example 9-10 (page 250) for a weak base. In the present example, the NaOAc concentration is 0.0500 M. Thus,



$$[\text{OH}^-] = [\text{HOAc}]$$

$$[\text{OAc}^-] = 0.0500 - [\text{OH}^-] \approx 0.0500$$

Substituting in the base dissociation-constant expression for  $\text{OAc}^-$  gives

$$\frac{[\text{OH}^-]^2}{0.0500} = \frac{K_w}{K_a} = \frac{1.00 \times 10^{-14}}{1.75 \times 10^{-5}} = 5.71 \times 10^{-10}$$

$$[\text{OH}^-] = \sqrt{0.0500 \times 5.71 \times 10^{-10}} = 5.34 \times 10^{-6} \text{ M}$$

$$\text{pH} = 14.00 - (-\log 5.34 \times 10^{-6}) = 8.73$$

**Or used  $\text{pH} = 0.5\text{pK}_w + 0.5\text{pK}_a + 0.5\log C$  (salt)**

# pH after Addition of 50.01 mL of Base

$$[\text{OH}^-] \approx c_{\text{NaOH}} = \frac{50.01 \text{ mL} \times 0.1000 \text{ M} - 50.00 \text{ mL} \times 0.1000 \text{ M}}{100.01 \text{ mL}}$$

$$= 1.00 \times 10^{-5} \text{ M}$$

$$\text{pH} = 14.00 - [-\log(1.00 \times 10^{-5})] = 9.00$$



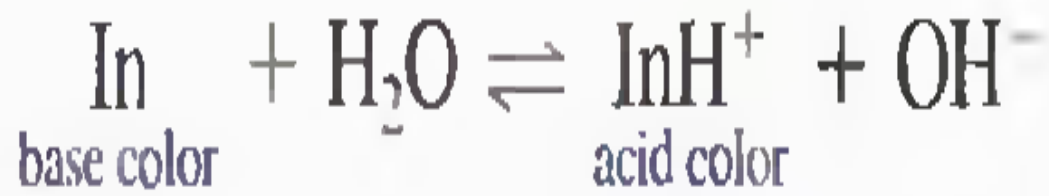
# **SOLUTIONS AND INDICATORS FOR ACID/BASE TITRATIONS:**

## Acid/Base Indicators

An acid/base indicator is a weak organic acid or a weak organic base whose undissociated form differs in color from its conjugate base or its conjugate acid form. For example, the behavior of **an acid-type** indicator,  $\text{HIn}$ , is described by the equilibrium.



The behavior of a **base-type**  
indicator. In, is



The equilibrium-constant expression for the dissociation of an acid-type indicator takes the form.

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{In}^-]}{[\text{HIn}]} \quad (14-1)$$

Rearranging leads to

$$[\text{H}_3\text{O}^+] = K_a \frac{[\text{HIn}]}{[\text{In}^-]} \quad (14-2)$$

The human eye is not very sensitive to color differences in a solution containing a mixture of HIn and In<sup>-</sup>. particularly when the ratio  $[HIn]/[In^-]$  is greater than about 10 or smaller than about 0.1. Consequently, the color change detected by an average observer occurs within a limited range of concentration ratios from about 10 to about 0.1. At greater or smaller ratios, the color appears essentially constant to the eye and is independent of the ratio. As a result, we can write that the average indicator, HIn, exhibits its pure acid color when.



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

and its base color when

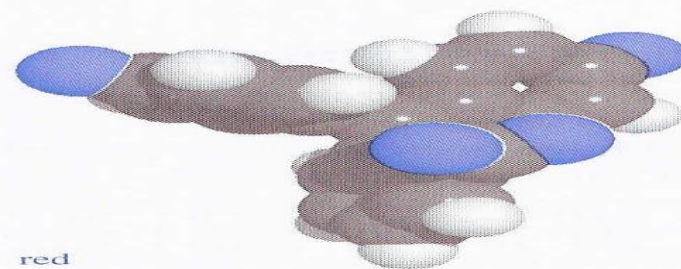
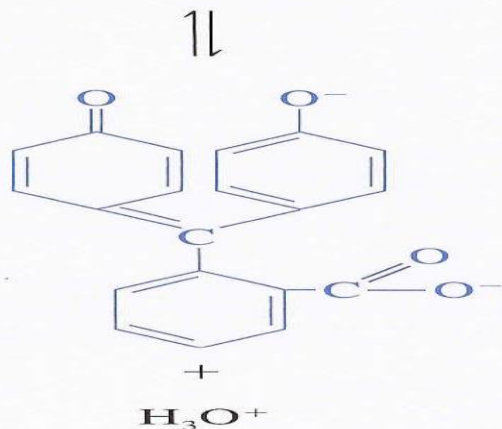
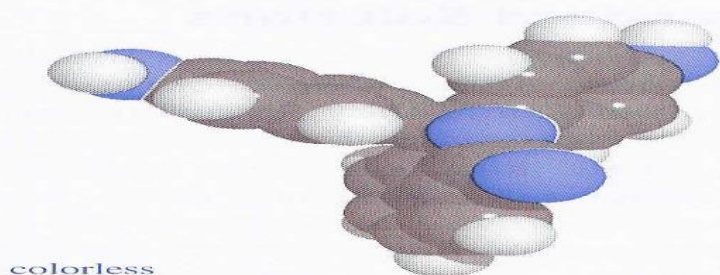
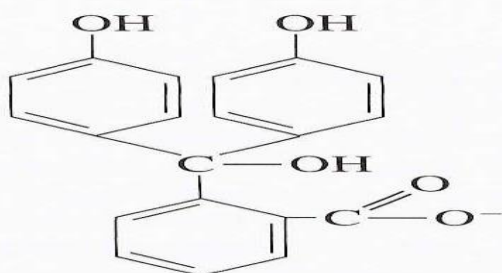
$$\frac{[\text{HIn}]}{[\text{In}^-]} \approx \frac{1}{10}$$

To obtain the indicator pH range,  
we take the negative logarithms of  
the two expressions

$$\text{pH}(\text{acid color}) = -\log(10K_a) = \text{p}K_a + 1$$

$$\text{pH}(\text{basic color}) = -\log(0.1K_a) = \text{p}K_a - 1$$

$$\text{indicator pH range} = \text{p}K_a \pm 1$$



# **Titration Errors with Acid/Base Indicators:**

## Two types of titration errors in acid/base titrations.

The first is a determinate error that occurs when the pH at which the indicator changes color differs from the pH at the equivalence point. This type of error can usually be minimized by choosing the indicator carefully or by making a blank correction.

The second type is an indeterminate error that originates from the limited ability of the eye to distinguish reproducibly the intermediate color of the indicator. The magnitude of this error depends on the change in pH per milliliter of reagent at the equivalence point, on the concentration of the indicator, and on the sensitivity of the eye to the two indicator colors

## Variables That Influence the Behavior of Indicators

The pH interval over which a given indicator exhibits a color change is influenced by **temperature**, by the **ionic strength of the medium**, and by the **presence of organic solvents and colloidal particles**. Some of these effects, particularly the last two, can cause the transition range to shift by one or more pH units.

***Thank You***