

Chapter Six

Neutralisation Reactions

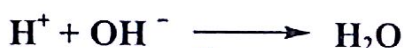
6 Neutralisation Reactions.

These
They are reactions between acid [§] and base or ^{their} its salt [§] and the reactions between base [§] and acid [§] or its salt ^{their}, accompanied with a change in pH.

Examples :



As shown above, one of the products is water (H_2O) and the reactions can be expressed as ^{reaction} reaction between H^+ from acid and OH^- from base : K

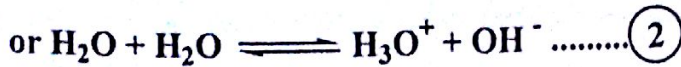
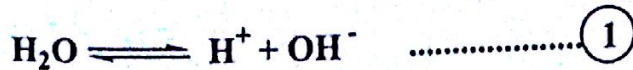


when single
One arrow is used which ^{means} means that the reaction is complete and replaced completely ^{by} to the products. K

Acid ^s may be strong such as HCl , HNO_3 and H_2SO_4 , or weak such as CH_3COOH , $\text{C}_6\text{H}_5\text{COOH}$ and $\text{C}_6\text{H}_5\text{OH}$ which are respectively acetic acid, benzoic acid and phenol. Bases ^{are} also ^{are} either strong such as NaOH and KOH or weak such as NH_3 and amines. Solutions of some salts are basic such as Na_2CO_3 and borax solutions ^{are} or acidic such as NH_4Cl and NH_4NO_3 solutions. The medium of the neutralization reaction is ^{generally} water (aqueous solution), therefore, it is necessary to study the ionisation of water and derive its ionic product constant. K

6.1 Ionic product constant of water:

Pure water is very slightly ionised and has little ability for electrical conductivity according to conductivity experiments done by Kolrawsh in 1894. Thus, water is slightly ionised into:



The first equation is used for simplicity.

Law of mass action is applied ^{on} for this reversible reaction:

$$K_{\text{eq}} = \frac{f_{\text{H}^+} [\text{H}^+] f_{\text{OH}^-} [\text{OH}^-]}{f_{\text{H}_2\text{O}} [\text{H}_2\text{O}]} \dots\dots\dots (3)$$

$f = 1$ in very dilute solutions, therefore:

$$K_{\text{eq}} = \frac{[\text{H}^+] [\text{OH}^-]}{[\text{H}_2\text{O}]} \dots\dots\dots (4)$$

A very small quantity of water is ionised, therefore, $[\text{H}_2\text{O}]$ is constant and equation (4) becomes:

$$K_w = [\text{H}^+] [\text{OH}^-] \dots\dots\dots (5)$$

Where K_w is the ionic product constant of water which equals 1.01×10^{-14} at 25°C . Ionic product constant of water (K_w), is temperature dependent which increased with increasing temperature as a result of increasing of ionisation with increasing temperature as shown in table (6-1).

Table (6-1): The effect of temperature on ionisation product constant of water

Temp. °C	$\times 10^{-14}$	Temp. °C	$\times 10^{-14}$
0	0.12	35	2.09
5	0.19	40	2.92
10	0.29	45	4.02
15	0.45	50	5.47
20	0.68	55	7.30
25	1.01	60	9.61
30	1.47	100	10.01

From equation (5):

$$[\text{H}^+] = [\text{OH}^-] = \sqrt{10^{-14}} = 10^{-7} \text{ M.}$$

When $[H^+] > 10^{-7}$, the solution is acidic. When $[H^+] = 10^{-7}$, the solution is neutral. When $[H^+] < 10^{-7}$, the solution is basic.

Also, from equation (5):

$$[H^+] = \frac{K_w}{[OH^-]} \text{ and } [OH^-] = \frac{K_w}{[H^+]}$$

6.2 Hydrogen-Ion Exponent (pH):

It is preferred to express hydrogen ion concentration as hydrogen-ion exponent or function of hydrogen ion (pH) instead of using negative exponents.

$$\therefore \text{pH} = -\log[H^+] = \log \frac{1}{[H^+]} \text{ or } [H^+] = 10^{-\text{pH}}$$

and

$$\text{pOH} = -\log[OH^-] = \log \frac{1}{[OH^-]} \text{ or } [OH^-] = 10^{-\text{pOH}}$$

Therefore from equation (5): $[H^+][OH^-] = K_w$

$$\mp \log[H^+] \mp \log[OH^-] = \mp \log K_w \therefore \text{pH} + \text{pOH} = \text{p}K_w = 14$$

$$\text{pH} = 14 - \text{pOH} \text{ and } \text{pOH} = 14 - \text{pH} \text{ and } \text{pH} = \text{pOH} = 7$$

Thus, when $\text{pH} = 7$, the solution is neutral.

When $\text{pH} < 7$, the solution is acidic. When $\text{pH} > 7$, the solution is basic.

Therefore, the pH range is from zero to 14

0 1 2 3 4 5 6 7 8 9 10 11 12 13 14

acidic ←———— neutral —————→ basic

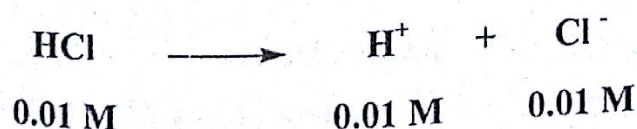
6.3 Calculations of pH of acidic and basic solutions.

6.3.1 The strong acids.

They are completely ionised such as HCl, HNO₃ and H₂SO₄etc .

Ex: Calculate the pH of 0.01 M HCl and calculate its pOH.

The solution:



$$\therefore [\text{H}^+] = 0.01 \text{ M} = 10^{-2} \text{ M} \longrightarrow \text{pH} = -\log [\text{H}^+] = -\log 10^{-2} = 2$$

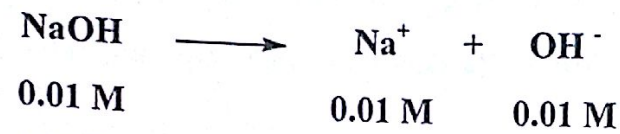
$\text{pOH} = 14 - 2 = 12$. The solution is acidic.

6.3.2 The strong bases.

They are also completely ionised such as NaOH and KOH.

Ex: Calculate the pH and pOH of 0.01 M NaOH?

The solution:



$$\therefore [\text{OH}^-] = 0.01 \text{ M} = 10^{-2} \text{ M} \longrightarrow \text{pOH} = -\log [\text{OH}^-] = -\log 10^{-2} = 2$$

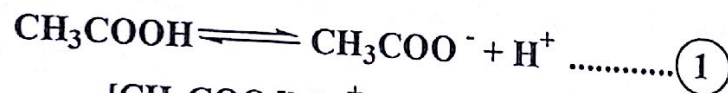
$\text{pH} = 14 - 2 = 12$. The solution is basic.

6.3.3 The weak acids.

They are partially ionised such as CH_3COOH , HCOOH and $\text{H}_2\text{C}_2\text{O}_4$ (oxalic acid).

Ex: Calculate the pH of 0.01 M CH_3COOH , where its ionisation constant is 1.85×10^{-5} at 25°C .

The solution:



$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} \dots\dots\dots (2)$$

From relation (1), $[\text{H}^+] = [\text{CH}_3\text{COO}^-]$

$$\therefore K_a = \frac{[\text{H}^+]^2}{[\text{CH}_3\text{COOH}]} \dots\dots\dots (3)$$

The concentration of unionised CH_3COOH is approximately equal to the concentration of original CH_3COOH in solution, i.e. $= 0.01 = C_a$ and $a =$ acid.

$$\therefore K_a = \frac{[\text{H}^+]^2}{C_a} \dots\dots\dots (4) \quad \text{p}K_a = -\log K_a = -\log 1.85 \times 10^{-5}$$

$$[H^+]^2 = K_a \cdot C_a$$

$$[H^+] = (K_a \cdot C_a)^{1/2}$$

.....(5)

$$= -(-5 + 0.026)$$

$$= -(-4.74) \longrightarrow = 4.74$$

Taking log of both sides:

$$\mp \log[H^+] = \mp \frac{1}{2} \log K_a \mp \frac{1}{2} \log C_a$$

$$pH = 1/2 pK_a - 1/2 \log C_a$$

.....(6)

$$= 1/2 \times 4.74 - 1/2 \log 10^{-2}$$

$$= 2.37 + 1 = 3.73$$

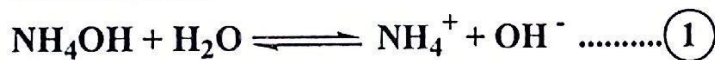
The solution is acidic also, but it is less acidic than 0.01M HCl ^{whose} which its pH = 2

6.3.4 The weak bases.

They are also partially ionised such as NH₃ in solution:

Ex: Calculate the pH of 0.01 M NH₄OH, K_b = 1.85 × 10⁻⁵ at 25°C.

The solution:



$$K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]} \text{(2)}$$

$$K_b = \frac{[OH^-]^2}{C_b}$$

C_b concentration of NH₃ in solution.

$$[OH^-]^2 = K_b \cdot C_b$$

$$[OH^-] = (K_b \cdot C_b)^{1/2} \text{(3)}$$

$$\mp \log[OH^-] = \mp \frac{1}{2} \log K_b \mp \frac{1}{2} \log C_b$$

$$pK_b = -\log K_b$$

$$= -\log 1.85 \times 10^{-5}$$

$$= -(-5 + 0.026)$$

$$= -(-4.74) \longrightarrow = 4.74$$

$$pOH = 1/2 pK_b - 1/2 \log C_b$$

$$= 1/2 \times 4.74 - 1/2 \log 10^{-2} \longrightarrow 2.37 + 1 = 3.37 \quad pH = 14 - 3.37 = 10.63$$

The medium is basic, but it is less basic than 0.01 M KOH or NaOH

where pH = 12 .

6.4 Calculation of pHs of salts solutions.

6.4.1 pH of salts solutions derived from strong acids and strong bases such as NaCl, NaNO₃, KCl, KNO₃, K₂SO₄, Na₂SO₄,etc.

Ex: Calculate the pH of 0.1 M NaCl solution

The solution:

NaCl is a salt derived from strong HCl and Strong NaOH and completely ionised:



Neither of Na⁺ nor of Cl⁻ reacts with water which means that there is no effect of water on these ions and its action is to isolate Na⁺ ions from Cl⁻ ions. The equilibrium attains between water and its ions (no hydrolysis).

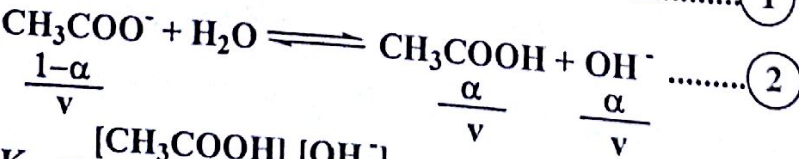
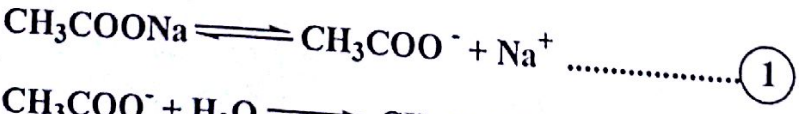


[H⁺] = [OH⁻] = 10⁻⁷ M pH = pOH = 7. Then the solution is neutral.

6.4.2 pH of salts solutions derived from weak acids and strong bases such as CH₃COONa and HCOOK.

Ex: Calculate the pH, pK_h and degree of hydrolysis of 0.01 M CH₃COONa, K_a_{CH₃COOH} = 1.85 × 10⁻⁵ at 25°C.

The solution:



$$K_{eq} = \frac{[CH_3COOH][OH^-]}{[H_2O][CH_3COO^-]}$$
 (3)

[H₂O] is constant.

$$K_h = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$$
 (4)

- K_{eq} = equilibrium constant.
- α = degree of hydrolysis.
- v = volume of solution.
- K_h = hydrolysis constant.

Hydrolysis: It is the combination of salt with water to form weak acid or weak base or both ~~weak acid and weak base~~. The above example gives an instance for ^{the} formation of ^a weak acid (CH_3COOH).

Multiply the denominator and numerator of equation (4) by $\frac{[\text{H}^+]}{[\text{H}^]}$

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

$$\therefore K_h = \frac{K_w}{K_a} = \frac{10^{-14}}{1.85 \times 10^{-5}} = 5.40 \times 10^{-10} \dots\dots\dots (5)$$

$$\mp \log pK_h = \mp \log K_w \pm \log K_a$$

$$\therefore pK_h = pK_w - pK_a \dots\dots\dots (6)$$

$$pK_h = 14 - 4.74 = 9.26$$

Return to equation (4) and substitute $\frac{\alpha}{v}$ and $\frac{1-\alpha}{v}$

$$K_h = \frac{\frac{\alpha}{v} \cdot \frac{\alpha}{v}}{\frac{1-\alpha}{v}} = \frac{\alpha^2}{(1-\alpha)v} \dots\dots\dots (7)$$

$$\text{But } C = \frac{1}{v}$$

$$\therefore K_h = \frac{C \cdot \alpha^2}{1-\alpha}$$

α is small compared with one unit, thus it can be rejected from ~~the~~

denominator to get:

$$K_h = C_s \cdot \alpha^2 \text{ and } \alpha = \left(\frac{K_h}{C_s} \right)^{\frac{1}{2}} \dots\dots\dots (8)$$

$$\therefore \alpha = \left(\frac{K_h}{C_s} \right)^{\frac{1}{2}} = \left(\frac{5.4 \times 10^{-10}}{10^{-2}} \right)^{\frac{1}{2}} = \frac{2.32 \times 10^{-5}}{10^{-1}} = 2.32 \times 10^{-4} = 0.0232 \%$$

From equation (2): $[\text{CH}_3\text{COOH}] = [\text{OH}^-]$, Also $[\text{CH}_3\text{COO}^-] \approx$ salt concentration = C_s .

$$\therefore K_h = \frac{[\text{OH}^-]^2}{C_s} \quad \text{But } K_h = \frac{K_w}{K_a}$$

$$\begin{aligned} \therefore \frac{K_w}{K_a} &= \frac{[\text{OH}^-]^2}{C_s} & \text{But } [\text{OH}^-] &= \frac{K_w}{[\text{H}^+]} \\ \therefore \frac{K_w}{K_a} &= \frac{(\frac{K_w}{[\text{H}^+]})^2}{C_s} & \therefore \frac{K_w}{K_a} &= \frac{K_w}{[\text{H}^+]^2 \cdot C_s} \\ \therefore [\text{H}^+]^2 &= \frac{K_w \cdot K_a}{C_s} & \longrightarrow & [\text{H}^+] = \left(\frac{K_w \cdot K_a}{C_s}\right)^{\frac{1}{2}} \end{aligned}$$

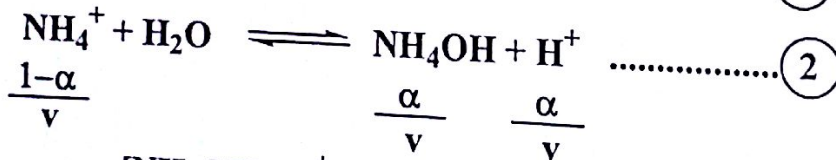
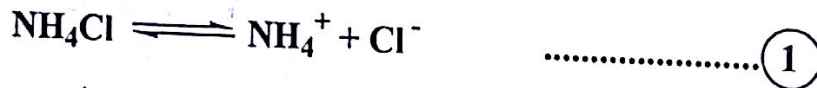
$$\begin{aligned} \therefore \log[\text{H}^+] &= \frac{1}{2} \log K_w - \frac{1}{2} \log K_a - \frac{1}{2} \log C_s \quad \therefore \text{pH} = \frac{1}{2} \text{p}K_w + \frac{1}{2} \text{p}K_a + \frac{1}{2} \log C_s \\ &= \frac{1}{2} \times 14 + \frac{1}{2} \times 4.74 + \frac{1}{2} \log 10^{-2} \\ &= 7 + 2.37 - 1 = 8.37. \end{aligned}$$

Therefore, the solution is basic since pH = 8.37.

6.4.3 pH of salts derived from weak base and strong acid such as NH_4Cl , NH_4NO_3 and $(\text{NH})_2\text{SO}_4$.

Ex: Calculate pH, $\text{p}K_h$ and degree of hydrolysis of 0.01 M NH_4Cl and $K_b_{\text{NH}_4\text{OH}} = 1.85 \times 10^{-5}$ at 25°C .

The solution:



$$K_{eq} = \frac{[\text{NH}_4\text{OH}][\text{H}^+]}{[\text{H}_2\text{O}][\text{NH}_4^+]}$$

$$\therefore K_h = \frac{[\text{NH}_4\text{OH}][\text{H}^+]}{[\text{NH}_4^+]} \quad \text{..... (3)}$$

Multiply denominator and numerator by $\frac{[\text{OH}^-]}{[\text{OH}^-]}$

$$K_h = \frac{[\text{NH}_4\text{OH}][\text{H}^+]}{[\text{NH}_4^+]} \times \frac{[\text{OH}^-]}{[\text{OH}^-]}$$

$$\therefore K_h = \frac{K_w}{K_b} = \frac{10^{-14}}{1.85 \times 10^{-5}} = 5.40 \times 10^{-10} \quad \text{..... (4)}$$

$$K_h = \frac{\frac{\alpha}{v} \cdot \frac{\alpha}{v}}{\frac{1-\alpha}{v}} = \frac{\alpha^2}{(1-\alpha)v} = \alpha^2 C_s$$

$$\therefore \alpha = \left(\frac{K_h}{C_s} \right)^{\frac{1}{2}} = \left(\frac{5.4 \times 10^{-10}}{10^{-2}} \right)^{\frac{1}{2}} = \frac{2.32 \times 10^{-5}}{10^{-1}} = 2.32 \times 10^{-4} = 0.0232 \%$$

According to equation (2): $[H^+] = [NH_4OH]$ and $[NH_4^+] = C_s$,

Apply equation (3):

$$K_h = \frac{[H^+]^2}{C_s} \quad \text{And } K_h = \frac{K_w}{K_a}$$

$$\therefore [H^+]^2 = \frac{K_w \cdot C_s}{K_b}$$

$$\therefore [H^+] = \left(\frac{K_w \cdot C_s}{K_b} \right)^{\frac{1}{2}} \quad \dots\dots\dots (5)$$

$$\mp \log[H^+] = \frac{1}{2} \log K_w + \frac{1}{2} \log C_s - \frac{1}{2} \log K_b$$

$$\text{pH} = 1/2 \text{p}K_w - 1/2 \text{p}K_b - 1/2 \log C_s \quad \dots\dots\dots (6)$$

$$= 1/2 \times 14 - 1/2 \times 4.74 - 1/2 \log 10^{-2}$$

$$= 7 - 2.37 + 1 = 8 - 2.37 = 5.63$$

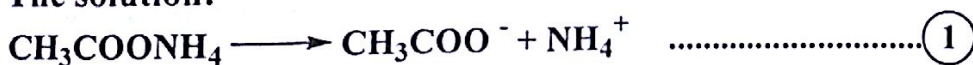
Therefore, the pH is less than 7 and the solution is acidic.

6.4.4 pH of salts derived from weak acids and weak bases such as CH_3COONH_4 and $HCOONH_4$.

Ex: Calculate pH, pK_h and degree of hydrolysis of 0.01 M CH_3COONH_4

$$K_a_{CH_3COOH} = 1.85 \times 10^{-5}, \quad K_b_{NH_4OH} = 1.85 \times 10^{-5}$$

The solution:



$$\frac{1-\alpha}{v} \quad \frac{1-\alpha}{v} \quad \frac{\alpha}{v} \quad \frac{\alpha}{v}$$

$$K_{eq} = \frac{[CH_3COOH][NH_4OH]}{[CH_3COO^-][NH_4^+][H_2O]}$$

$$K_h = \frac{[CH_3COOH][NH_4OH]}{[CH_3COO^-][NH_4^+]} = \frac{\frac{\alpha}{v} \cdot \frac{\alpha}{v}}{\frac{1-\alpha}{v} \cdot \frac{1-\alpha}{v}} = \frac{\alpha^2}{1-\alpha^2} = \alpha^2$$

$$\therefore \alpha = (K_h)^{\frac{1}{2}} \quad \dots\dots\dots (3)$$

$$K_h = \frac{[\text{CH}_3\text{COOH}][\text{NH}_4\text{OH}] \times [\text{H}^+][\text{OH}^-]}{[\text{CH}_3\text{COO}^-][\text{NH}_4^+] \times [\text{H}^+][\text{OH}^-]} = \frac{K_w}{K_a \cdot K_b} \dots\dots (4)$$

$$\therefore K_h = \frac{10^{-14}}{(1.85 \times 10^{-5}) \times (1.85 \times 10^{-5})} = 2.92 \times 10^{-5}$$

$$\therefore \alpha = (K_h)^{\frac{1}{2}} = (2.92 \times 10^{-5})^{\frac{1}{2}} = 5.4 \times 10^{-3} = 0.54\%$$

According to equation (2):

$$K_h = \frac{[\text{CH}_3\text{COOH}]^2}{[\text{CH}_3\text{COO}^-]^2} = \frac{K_w}{K_a \cdot K_b}$$

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

$$\therefore \frac{K_w}{K_a \cdot K_b} = \frac{[\text{CH}_3\text{COO}^-]^2 [\text{H}^+]^2}{K_a^2} = \frac{[\text{H}^+]^2}{K_a^2}$$

$$\therefore \frac{K_w}{K_b} = \frac{[\text{H}^+]^2}{K_a} \quad [\text{H}^+] = \left(\frac{K_w \cdot K_a}{K_b} \right)^{\frac{1}{2}}$$

$$\text{pH} = \frac{1}{2} \text{p}K_w + \frac{1}{2} \text{p}K_a - \frac{1}{2} \text{p}K_b$$

$$\text{pH} = 1/2 \text{p}K_w + 1/2 \text{p}K_a - 1/2 \text{p}K_b \dots\dots\dots (5)$$

$1/2 \times 14 + 1/2 \times 4.74 - 1/2 \times 4.74 = 7$ Therefore the solution is neutral.

Another example: Calculate pH, $\text{p}K_h$ and degree of hydrolysis of 0.01 M

of NH_4CN where $K_{a_{\text{HCN}}} = 7.2 \times 10^{-10}$, $K_{b_{\text{NH}_4\text{OH}}} = 1.85 \times 10^{-5}$

The solution:

$$K_h = \frac{K_w}{K_a \cdot K_b} = \frac{10^{-14}}{(7.2 \times 10^{-10}) \times (1.85 \times 10^{-5})} = 0.8$$

$$\alpha = (K_h)^{1/2} = (0.8)^{1/2} = 0.8944. \quad K_a = 7.2 \times 10^{-10} \therefore \text{p}K_a = 9.16.$$

$$\text{pH} = 1/2 \text{p}K_w + 1/2 \text{p}K_a - 1/2 \text{p}K_b = 1/2 \times 14 + 1/2 \times 9.16 - 1/2 \times 4.74 = 9.21$$

The medium is basic because $K_b > K_a$ by 10^5 times.

6.5 Acid-base indicators.

They are weak organic acids or weak organic bases which exhibit change in their colours in a certain range of pH. This range of pH depends

on the properties of the indicator. These indicators are also called neutralisation indicators since their colours are changed in the neutralisation point of acid with base or base with acid.

Examples; Methyl red and methyl orange which are weak organic bases and their colours are changed in acidic medium (pH 4.4 – 6.4).

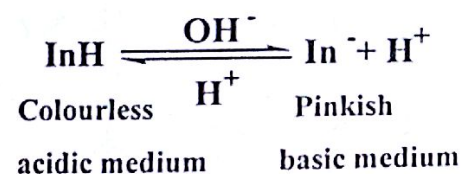
Phenolphthalein, thymolphthalein and para nitrophenol are weak organic acids and their colours are changed in basic medium (pH 8.3 – 10.0).

6.5.1 Theories which explain the action of acid-base indicators.

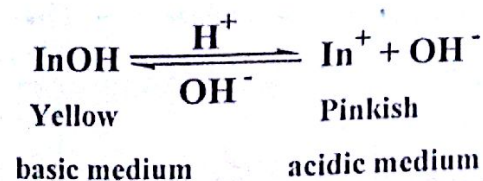
6.5.1.1 Ionic theory.

Since these indicators are weak organic acids or weak organic bases, therefore, there are two different formula of the indicator; one ^{is} of its ionised form with special colour and ^{the} other form ^{is} of unionised ^{and} which has another colour. /

Examples: Phenolphthalein indicator is a weak organic acid which may be expressed as InH where In means indicator:



Another example is methyl orange which is a weak organic base and may be expressed as InOH:



6.5.1.2 Chromophoric theory.

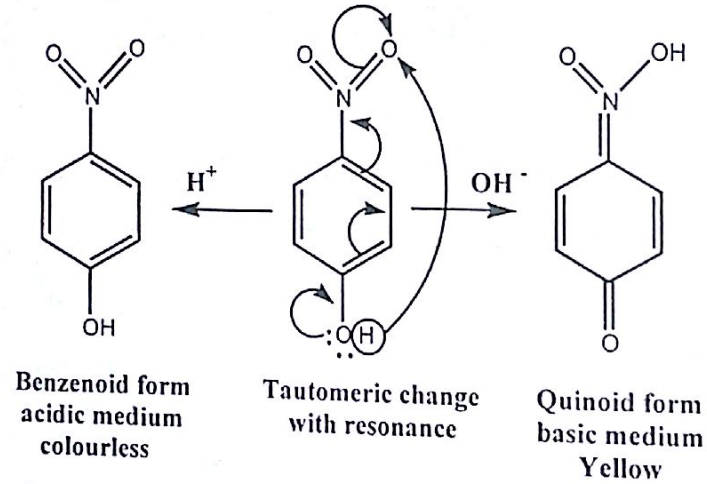
This theory is based on the spectrophotometric studies on a number of organic compounds. This theory stated that the indicator is present in more than one of the tautomeric forms which is followed by resonance arrangement.

Tautomerism: It is a process of transferring atoms within the molecules.

Resonance: Transferring of electrons within the molecule. Therefore, the colour of organic compounds is due to the presence of groups which exhibit colours called Chromophores such as NO₂, NO, -N=N- etc.

These colours become sharper in the presence of electron-donating groups such as NH₂, OH, CH₃ etc. which are called auxochromes.

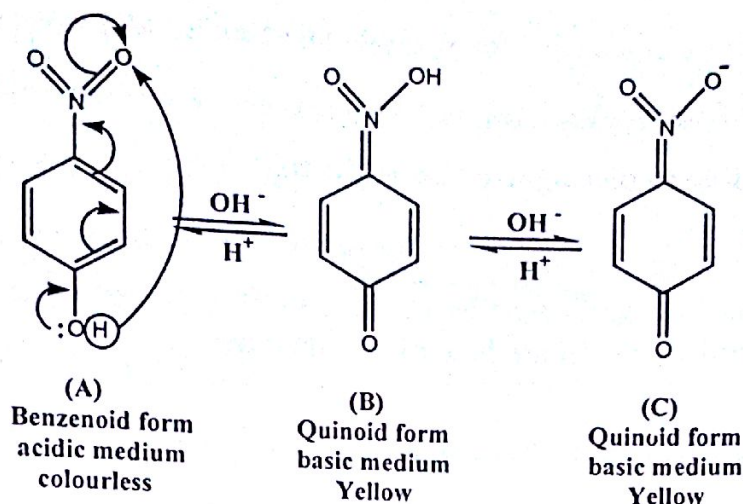
Example: Para nitro phenol.



6.5.1.3 Ionic chromophoric theory.

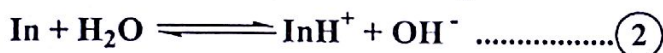
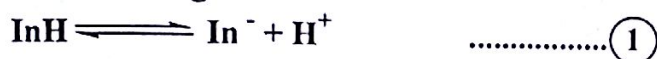
It is clear from the chromophoric theory that the change in colour is related to the change of indicator molecule composition of its molecule. The composition change of indicator molecules is attained by addition of base or acid to its solution.

Therefore, the chromophoric theory is combined to the ionic theory to offer clear explanation to the action of acid-base indicators as shown in the following diagram of change in colour of para nitro phenol in basic and acidic media:



6.5.2 pH range of acid-base indicator behaviour.

The dissociation reactions of indicators are accompanied by internal structural rearrangement of the molecules which are responsible for the colour change:



where InH and In are weak organic acids and bases respectively.

Law of mass action is applied to ionisations (1) and (2)

$$K_a = \frac{[\text{In}^-][\text{H}^+]}{[\text{InH}]} \quad \text{..... (3)}$$

K_a = ionisation constant of the acidic indicator

$$K_b = \frac{[\text{InH}^+][\text{OH}^-]}{[\text{In}]} \quad \text{..... (4)}$$

K_b = ionisation constant of the basic indicator

Equations (3) and (4) can be rearranged to get:

$$\frac{[\text{In}^-]}{[\text{InH}]} = \frac{K_a}{[\text{H}^+]} \quad \text{..... (5)}$$

$$\frac{[\text{InH}^+]}{[\text{In}]} = \frac{K_b}{[\text{OH}^-]} \quad \text{..... (6)}$$

The colour of the indicator is changed at equivalence point. Therefore, in order to distinguish the change in colour, the human eye could not sense

this change unless the basic form concentration is at least ten times the concentration of the acidic form and vice versa.

Thus, it is possible to distinguish the acidic indicator colour when :

$$\frac{[\text{In}^-]}{[\text{InH}]} \geq \frac{1}{10} \quad \dots\dots\dots(7)$$

And the basic indicator colour is distinguished as:

$$\frac{[\text{In}^-]}{[\text{InH}]} \geq \frac{10}{1} \quad \dots\dots\dots(8)$$

Substitution in equation (3) instead of acidic and basic forms we get:

$$\frac{[\text{H}_3\text{O}^+][\text{In}^-]}{[\text{InH}]} = [\text{H}_3\text{O}^+] \times \frac{1}{10} = K_a$$

$$\therefore [\text{H}_3\text{O}^+] = 10K_a \quad \dots\dots\dots(9)$$

$$\frac{[\text{H}_3\text{O}^+][\text{In}^-]}{[\text{InH}]} = [\text{H}_3\text{O}^+] \times \frac{10}{1} = K_a$$

$$\therefore [\text{H}_3\text{O}^+] = \frac{K_a}{10} \quad \dots\dots\dots(10)$$

Take logarithms of equations (9) and (10) :

$$\mp \log[H^+] = \mp \log 10 \mp \log K_a$$

$$\therefore \text{pH} = \text{p}K_a - 1 \quad \dots\dots\dots(11)$$

$$\mp \log[H^+] = \mp \log K_a \mp \log 10$$

$$\therefore \text{pH} = \text{p}K_a + 1 \quad \dots\dots\dots(12)$$

Therefore, the indicator pH change extent should be at least two units of pH to get sudden colour change.

\therefore pH range that ~~that~~ ^{within} which the colour of the indicator is changed will be:

$$\text{pH} = \text{p}K_a \pm 1 \quad \dots\dots\dots(13)$$

If K_a of the indicator is 10^{-5} ($\text{p}K_a = 5$):

$$\therefore \text{pH} = \text{pK}_a \pm 1 = 5 \pm 1$$

\therefore pH range = 4-6 such as ~~methyl orange~~ and methyl red which subjects colour change in acidic medium.

If K_a of indicator is equal 10^{-9} ($\text{pK}_a = 9$):

\therefore undergoes $\text{pH} = \text{pK}_a \pm 1 = 9 \pm 1 = 8-10$ such as phenolphthalein indicator which subjects colour change in basic medium. The following table (6-2) contains a number of acid-base indicators with their pH change extent: A

Table (6-2): Some acid base indicators.

<u>Indicator</u>	<u>Its colour in acid medium</u>	<u>Its colour in basic medium</u>	<u>Extent of pH change</u>
Cresol red	red	yellow	0.2 – 1.8
Cresol red	yellow	red	7.2 – 8.8
Methyl orange	red	yellow	2.9 – 4.0
Methyl red	red	yellow	4.2 – 6.2
Chlorophenol red	yellow	red	4.8 – 6.4
Bromothymol blue	yellow	blue	6.0 – 7.6
Phenol red	yellow	red	6.8 – 8.4
Phenolphthalein	colourless	red	8.3 – 10.0
Thymolphthalein	colourless	blue	9.4 – 10.5
Alizarin yellow	yellow	purple	10.1 – 12.1

6.6 Calculations of pH of buffer solutions.

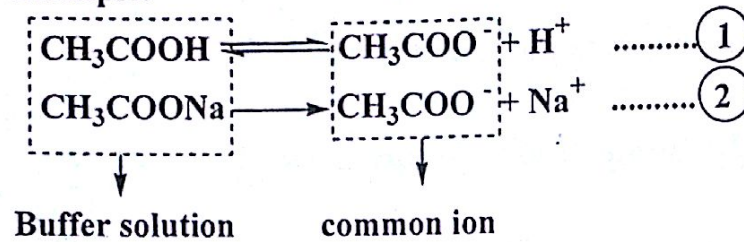
Buffer solution: It is a solution of weak acid with its salt or weak base with its salt which has the ability to resist the change in pH when little amounts of strong acid or base are added or by dilution.

Buffer solution^s are very important since there are many reactions ~~that~~ X occur inside the living cells at certain pH values. Also, many chemical

reactions such as precipitation, oxidation-reduction reactions and complex formations reactions ~~are not occurred~~ unless the pH is stabilised at certain values. These pH values are determined experimentally.

Common ion: It is the ion which is liberated from weak and strong electrolytes and its role is to reduce the ionisation of the weak electrolyte.

Example:



$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} \quad \dots\dots\dots (3)$$

Rearrangement of equation (3), ^{gives} we get:

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

$[\text{CH}_3\text{COOH}]$ is approximately equal ^{to} the concentration of original acid because the ionised species is very little because of the effect of ^{the} common ion (CH_3COO^-).

Also, $[\text{CH}_3\text{COO}^-]$ is equal to the concentration of the salt (CH_3COONa).

Therefore, $[\text{CH}_3\text{COOH}] = C_a \approx$ the concentration of acid and

$[\text{CH}_3\text{COO}^-] = C_s \approx$ the concentration of salt.

$$\therefore [\text{H}^+] = K_a \times \frac{C_a}{C_s} \quad \dots\dots\dots (4)$$

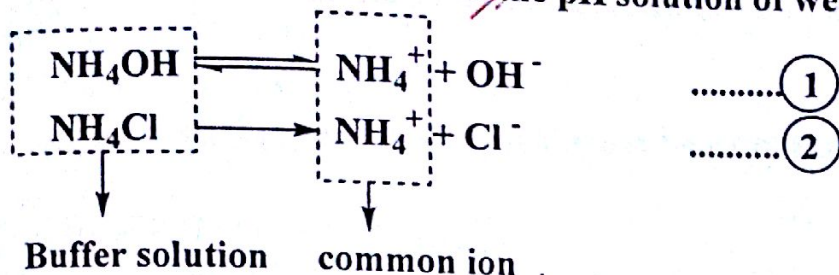
$$\mp \log[\text{H}^+] = \mp \log K_a \mp \log \frac{C_a}{C_s}$$

$$pH = pK_a - \log \frac{C_a}{C_s} \quad \text{or} \quad pH = pK_a + \log \frac{C_s}{C_a}$$

$$\text{or } pH = pK_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} \quad \text{..... (5)}$$

Equation (5) is used to calculate pH solutions of weak acid and its salt.

Another example : Derivation ^{of} the pH solution of weak base and its salt.



$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]} \quad \text{..... (3)}$$

Rearrangement ^{ing} of equation (3), we get:

$$[\text{OH}^-] = K_b \frac{[\text{NH}_4\text{OH}]}{[\text{NH}_4^+]}$$

$[\text{NH}_4\text{OH}] \approx$ the concentration of ^{the} original base = C_b .

$[\text{NH}_4^+] \approx$ the concentration of the salt = C_s .

$$\therefore [\text{OH}^-] = K_b \times \frac{C_b}{C_s} \quad \text{..... (4)}$$

$$\mp \log[\text{OH}^-] = \mp \log K_b \mp \log \frac{C_b}{C_s}$$

$$pOH = pK_b - \log \frac{C_b}{C_s} \quad \text{or} \quad pOH = pK_b + \log \frac{C_s}{C_b}$$

$$\therefore pOH = pK_b + \log \frac{[\text{salt}]}{[\text{Base}]} \quad \text{..... (5)}$$

$$pH = 14 - pK_b - \log \frac{[\text{Salt}]}{[\text{Base}]} \quad \text{..... (6)}$$

Equation (5) and (6) are used to calculate the pH of buffer solutions formed from ^{the} weak base and its salt.

Note: The high concentrated solutions of acids and bases are considered buffer solutions.

Therefore, 1 M NaOH is ^a buffer solution because it resists the pH change when little amounts of strong acid or strong base are added. But their pH is changed by dilution by ^{the} addition of water which changes pH value. Table (6-3) contains some standard buffer solutions.

Table (6-3): A group of standard buffer solutions.

	<u>Buffer solution</u>	<u>pH value</u>
1	0.01 M potassium tetra oxalate	1.48
2	0.01 M potassium dihydrogen citrate	3.72
3	0.01 M CH ₃ COOH + 0.01 M CH ₃ COONa	4.64
4	0.01 M K ₂ HPO ₄ + 0.01 M Na ₂ HPO ₄	6.85
5	0.05 M Na ₂ B ₄ O ₇ ·10H ₂ O	9.18
6	0.1 M NH ₄ OH + 0.1 M NH ₄ Cl	9.26
7	0.025 M NaHCO ₃ + 0.025 M Na ₂ CO ₃	10.00
8	0.01 M Na ₃ PO ₄	11.72

Example: Calculate pH of ^a buffer solution formed by addition ^{10 ml} of 0.1M CH₃COOH to 10ml of 0.1 M CH₃COONa. Also, calculate the change in pH when 1ml of 0.1 M HCl and 1ml of 0.1 M NaOH ^{is} added separately to this mixture of buffer solution. $K_a_{\text{CH}_3\text{COOH}} = 1.85 \times 10^{-5}$ at 25°C

The solution:

Concentrations of the acid and its salt are reduced to 0.05 M as a result of dilution effect.

∴ [CH₃COOH] = 0.05 M and [CH₃COONa] = 0.05 M .

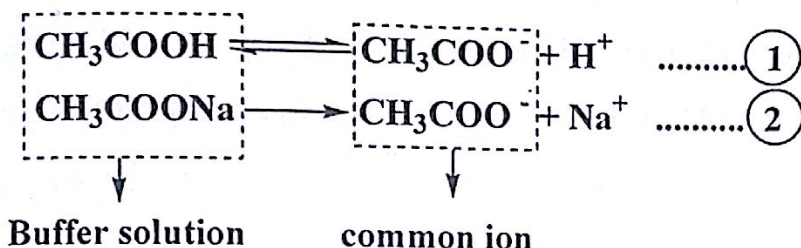
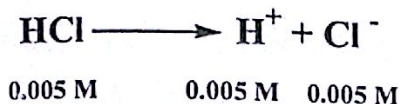
$$pH = pK_a + \log \frac{[\text{salt}]}{[\text{Acid}]}$$

$$pH = 4.74 + \log \frac{0.05}{0.05} = 4.74 + 0 = 4.74$$

when 1ml of 0.1 M HCl is added to this buffer:

$$1 \times 0.1 = 21 \times M_{\text{HCl}}$$

$$\therefore M_{\text{HCl}} = 0.005 \text{ M}$$



Therefore, the added acid will increase the concentration of unionised CH₃COOH according to Lechatelier principle, but decrease the concentration of the salt as a result of ^{the} combination of [H⁺] with [CH₃COO⁻] to form CH₃COOH.

$$\therefore [\text{CH}_3\text{COOH}] = 0.05 + 0.005 = 0.055 \text{ M}$$

$$[\text{CH}_3\text{COONa}] = 0.05 - 0.005 = 0.045 \text{ M}$$

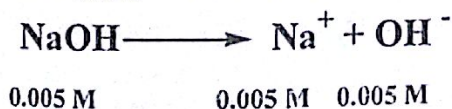
$$\therefore pH = 4.74 + \log \frac{0.045}{0.055} = 4.74 - 0.09 = 4.65$$

Therefore, the pH value is reduced by ^{number} the unit of 0.09 by ^{ing} addition of 1ml of 0.1 M HCl which is ^a very little change.

Now, when 1ml of 0.1 M NaOH is added.

$$1 \times 0.1 = 21 \times M_{\text{NaOH}}$$

$$\therefore M_{\text{NaOH}} = 0.005 \text{ M}$$



OH⁻ is combined with H⁺ to form water.

Therefore, the equilibrium (1) will be replaced to the right with increasing the ionisation of CH₃COOH. Thus, a decrease of [CH₃COOH] is

occurred ^{in addition to an} increase in $[\text{CH}_3\text{COONa}]$ as a result of addition ^{ing} more acetate to the solution.

$$\therefore [\text{CH}_3\text{COOH}] = 0.05 - 0.005 = 0.045 \text{ M}$$

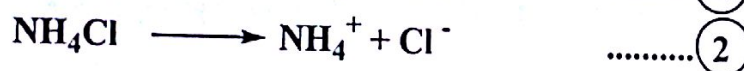
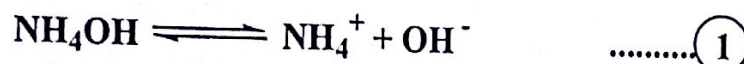
$$[\text{CH}_3\text{COONa}] = 0.05 + 0.005 = 0.055 \text{ M}$$

$$\therefore \text{pH} = 4.74 + \log \frac{0.055}{0.045} = 4.74 + 0.09 = 4.83$$

Therefore, a little increase in pH value is occurred which equals 0.09 units.

Example: A buffer solution of 0.1 M NH_4OH and 0.08 M of NH_4Cl ^{its has 9} volume = 100 ml. Calculate the pH of this solution. Also, calculate the change in pH when 1 ml of 1 M HCl and 1 ml of 1 M NaOH ^{are} added separately to this solution. $K_b_{\text{NH}_4\text{OH}} = 1.85 \times 10^{-5}$ at 25°C

The solution:



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

$$\text{pOH} = 4.74 + \log \frac{0.08}{0.1} = 4.74 - 0.1 = 4.64$$

$$\therefore \text{pH} = 14 - 4.64 = 9.36$$

Now, when 1 ml of 1 M HCl is added:

$$1 \times 1 = 101 \times M_{\text{HCl}}$$

$$M_{\text{HCl}} = 10^{-2} \text{ M}$$



$$10^{-2} \text{ M} \quad \quad 10^{-2} \text{ M} \quad 10^{-2} \text{ M}$$

H^+ will combine with OH^- to form water and the equilibrium (1) is replaced to right with ionisation of ^{new} amount of NH_4OH . Therefore, there will be a decrease in $[\text{NH}_4\text{OH}]$ which equals $= 0.1 - 0.01 = 0.09 \text{ M}$.

On ^{the} other hand, there will be an increase in salt of $[\text{NH}_4\text{Cl}]$:

$$0.08 + 0.01 = 0.09 \text{ M}$$

$$\therefore pOH = 4.74 + \log \frac{0.09}{0.09} = 4.74$$

$$\therefore pH = 14 - 4.74 = 9.26$$

Therefore, a little decrease in pH occurs when 1ml of 1 M HCl is added.

When 1ml of 1M NaOH is added:

$$1 \times 1 = 101 \times M_{\text{NaOH}}$$

$$M_{\text{NaOH}} = 10^{-2} \text{ M}$$

Therefore, OH^- is combined with NH_4^+ to form NH_4OH accompanied with ^{an} increase in $[\text{NH}_4\text{OH}]$ and ^a decrease in $[\text{NH}_4\text{Cl}]$.

$$\therefore [\text{NH}_4\text{OH}] = 0.1 + 0.01 = 0.11 \text{ M}$$

$$[\text{NH}_4\text{Cl}] = 0.08 - 0.01 = 0.07 \text{ M}$$

$$pOH = 4.74 + \log \frac{0.07}{0.11} = 4.74 - 2 = 4.54$$

$$pH = 14 - 4.54 = 9.46$$

Here, a little increase in pH value occurs which confirms approximately the constant value of pH of buffer solution.

the

6.7 Problems.

- 1- Calculate the pH of the following acidic solutions: (a) 0.0036 M HNO_3 .
(b) 0.0093 N H_2SO_4 . (c) 0.0153 M HCl .
- 2- Calculate the pH of the following basic solutions: (a) 0.036 N NaOH .
(b) 0.25 M $\text{Ba}(\text{OH})_2$. (c) 1 N KOH .
- 3- Calculate the number of millimoles of HCl which should be added to
250ml of water to get the following values of pH: (a) 2.43 . (b) 0.64 . (c)
4.33 . (d) 11.2 .
- 4- Calculate the number of millimoles of NaOH which should be added to
333ml of water to get the following values of pH: (a) 1.49 . (b) 4.73 . (c)
6.10 . (d) 0.50 .
- 5- Calculate the molar concentrations of HCl solutions that give the
following pH values: (a) 1.23 . (b) 2.34 . (c) 3.45 . (d) 5.67 .
- 6- Calculate the molar concentrations of NaOH solutions that give the
following pH values: (a) 7.89 . (b) 13.0 . (c) 8.97 . (d) 10.12 .
- 7- Calculate the pH of the following salts/ solutions: (a) 0.025 M
 CH_3COONa . (b) 0.2134 M potassium benzoate. (c) 0.105 N NaCl .
- 8- Calculate the pH of the following salts/ solutions: (a) 0.1 M NH_4NO_3 .
(b) 0.01 M NH_4Cl . (c) 0.125 M $(\text{NH})_2\text{SO}_4$. (d) 0.125 M AgNO_3 .
- 9- Calculate the pH of the following salts/ solutions: (a) 0.25 M NaHCO_3 .
(b) 0.074 M NaH_2PO_4 . (c) 0.1 M Na_2HPO_4 . (d) 0.125 M $\text{Na}_2\text{-EDTA}$.
- 10- Calculate the pH of the following buffer solutions: (a)
0.25 M NH_4OH + 0.05 M NH_4Cl . (b) 0.15 M Na_2HPO_4 + 0.25 M
 NaH_2PO_4 . (c) 0.01 M $\text{C}_6\text{H}_5\text{COOH}$ + 0.01 M $\text{C}_6\text{H}_5\text{COONa}$.
- 11- Calculate the pH of the following solutions:
a) 400ml containing 7.5g Na_2CO_3 + 6g NaHCO_3 .

b) A solution prepared by addition ¹⁰⁰ 50ml of 0.15 M NaOH to 50ml 0.15 M H_3PO_4 . /

c) A solution prepared by addition ¹⁰⁰ 10ml of 3 M HCl to 90ml M NH_4OH . X

12- Calculate the percentage of hydrolysis of 0.005 M CH_3COOK .

13- Calculate the increase in hydrolysis of 0.1 M NaNO_2 if it is diluted 10 times.

14- Calculate the pH of 0.1 M KHCO_3 .

15- Calculate the number of grams that should be dissolved in 100ml solution from the following chemicals to get pH value = 9.

(a) NH_3 . (b) NaOH . (c) KNO_3 .

16- Calculate the pH of the following buffer solutions:

a) 0.0405 M NH_4OH + 0.02 M $(\text{NH}_4)_2\text{SO}_4$.

b) 0.0176 M phenol + 0.0254 M sodium phenolate.

c) 1 M Cl_3CCOOH + 0.5 M Cl_3CCOONa .

d) 0.164 M ethylamine + 0.272 M ethylamine hydrochloride.

17- Calculate the ratio of $\frac{[\text{salt}]}{[\text{Acid}]}$ or $\frac{[\text{salt}]}{[\text{Base}]}$ for the following buffer

solutions which give pH = 9.8 :

a) NH_3 , NH_4Cl . (b) CH_3NH_2 , $\text{CH}_3\text{NH}_3\text{Cl}$. (c) HCN , NaCN .

b) HOCl , NaOCl .

18- Calculate the ratio of $\frac{[\text{salt}]}{[\text{Acid}]}$ or $\frac{[\text{salt}]}{[\text{Base}]}$ for the following buffer

solutions to give pH value = 4.75 :

a) HNO_2 , NaNO_2 .

b) $\text{CH}_3\text{CH}_2\text{COOH}$, $\text{CH}_3\text{CH}_2\text{COONa}$.

c) $\text{C}_5\text{H}_5\text{N}$, $\text{C}_5\text{H}_5\text{NHCl}$. d) $\text{C}_6\text{H}_6\text{NH}_2$, $\text{C}_6\text{H}_6\text{NH}_3\text{Cl}$.

- 19- A litre of solution contains 0.25 M HCOOH and 0.3 M HCOONa, calculate the pH of this solution. Calculate the change of pH of this solution when 10ml of 0.1 M HCl and 10ml of 0.1 M NaOH are added separately to this solution.

$$K_{a_{\text{HCOOH}}} = 1.75 \times 10^{-4}$$

- 20- A mixture of 0.123 M NH₄Cl and 0.246 M NH₄OH has volume of 20ml, calculate its pH value. 1ml of 1 M HCl and 1ml of 1 M NaOH are added separately to this solution. Calculate the change in pH value.