Buffers: The solutions which maintain constant p^H value on addition of acid or base.

- Resisting change in p^H value on adding acid or base to a buffer is called Buffer action.
- Buffers posses reserve acidity and reserve alkality. Reserve acidity will nullify the effect of added base and reserve basicity will nullify the effect of added acid.
- Blood buffer is H_2CO_3 + $NaHCO_3$.

Types of buffers:

1) Acid buffers: It is the mixture of weak acid and it's salt of strong base.
   CH_3COOH + CH_3COONa
   H_2CO_3 + $NaHCO_3$
   Tetra boric acid + Borax $\rightarrow$ [$p^H > 7$]
   H_3PO_4 + NaH_2PO_4
   The p^H of acid buffers is usually less than 7 but not always.
2) Basic buffers: It is mixture of weak base and its salt of strong acid.
   NH_4 OH + NH_4Cl
   Glycine + Glycine hydro chloride
3) Normal salt of weak acid and its acidic salt
   Na_2CO_3 + NaH CO_3
   Na_3PO_4 + Na_2HPO_4
4) Salt of weak acid and weak base
   Eg : CH_3COONH_4 ; HCOONH$_4$
5) Ampholytes Amino acids proteins **:**
   Which of the following can act as buffer

Action of Acid buffers:

Eg : CH_3COOH + CH_3COONa

Acetic acid mostly remains as unionised and sodium acetate is almost completely ionised. Therefore the components present in the above buffer are

(CH_3COOH+CH_3COO^-+ Na^+)

If little strong acid (H^+) is added to the above buffer, the added strong acid will convert into weak acid. Thus the effect is nullified.

CH_3COO^- + $H^+ \rightarrow CH_3COOH$

If little strong base (OH^-) is added to buffer, the added strong base is converted into water (H_2O). Thus the effect of added base is nullified.

CH_3COOH + $H^- \rightarrow CH_3COO^-$ + H_2O

Thus acid buffer can resist change in p^H on addition of little amount of acid or little amount of base.

In the above buffer the reserve acidity is due to CH_3COOH and reserve basisity is due to CH_3COO^-.

Action of Basic buffer :

Eg : NH_4OH + NH_4Cl

NH_4OH ionizes to very small extent and NH_4Cl being a salt ionizes completely. Therefore the components present in the above buffer are [NH_4OH + NH_4^+ + Cl^-]

The reserve acidity of the above buffer is due to NH_4^+ and reserve bascity is due to NH_4OH.

- If strong acid [H^+] is added to buffer, it is converted into H_2O

  $H^+ + NH_4OH \rightarrow NH_4^+ + H_2O$

- If strong base [OH^-] is added to buffer, it will convert into weak base

  $NH_4^+ + OH^- \rightarrow NH_4OH$

  Thus an acid buffer or a basic buffer can maintain constant p^H value by adding acid as well as base.

- P^H of Buffers : [Henderson's equation]

  Deriving p^H expression for Acid buffer :

  $HA \rightleftharpoons H^+ + A^-$

  (weak acid)

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

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

$$[A^-] = K_a\left[\frac{Acid}{Salt}\right]$$

[∵most of the A^- concentration comes from salt]

By applying – log on both sides.

$$-log[H^+] = -log\,K_a - log\left[\frac{Acid}{salt}\right]$$

$$p^H = p^{K_a} - log\left[\frac{Acid}{salt}\right]$$

$$p^H = p^{K_a} + log\left[\frac{salt}{acid}\right]$$

- Deriving p^H expression for basic buffer:

  $BOH \rightleftharpoons B^+ + OH^-$

  (weak base)

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

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

$$[OH^-] = K_b\left[\frac{base}{salt}\right]$$

[∵most of the B^+ concentration come from salt]

By applying – log on both sides

$$-log[OH]^- = -log\,K_b - log\left[\frac{base}{salt}\right]$$

$$p^{OH} = p^{K_b} - log\left[\frac{base}{salt}\right]$$

$$p^{OH} = p^{K_b} + log\left[\frac{salt}{base}\right]$$

$$p^H = 14 - p^{OH}$$

$$p^H = p^{K_\omega} - p^{K_b} - log\left[\frac{salt}{base}\right]$$

$$\left.\begin{aligned} p^H &= p^{K_a} + log\left[\frac{salt}{acid}\right] \\ p^{OH} &= p^{K_b} + log\left[\frac{salt}{base}\right] \end{aligned}\right\} [Henderson'sequation]$$

Buffer capacity:

It is the capacity of a buffer to resist change in p^H by adding acid or base.

- A good buffer shows only a slight change in p^H on addition of acid or base.
- Buffer capacity is defined as the number of moles of acid or base added per litre of buffer to cause the change in its p^H by one unit

(or)

Buffer capacity is the ratio of number of moles of acid or base added per litre of buffer to the change in p^H

Buffer capacity =

$$\frac{no.ofmoleofacidorbaseaddedperlitreofbuffer}{changeinp^H}$$

- p^H range of buffer :
  It is the range of p^H values where a buffer can effectively resist the change in p^H on adding acid or base.
- For an acid buffer the p^H range.

$$p^H = p^{K_a} \pm 1$$

For example P^{K_a} of $CH_3COOH + CH_3COONa$ buffer is 4.5. Therefore it functions effectively between p^H values 3.5 and 5.5.

- The p^H range of basic buffer.

$$p^{OH} = p^{K_b} \pm 1$$

- Buffer capacity will maximum if $p^H = p^{K_a}$:[salt] =[acid]
  Buffer capacity will be more if the components are taken in higher concentrations.
- Any buffer has a definite p^H values. The p^H of buffer does not change on long standing.
- The p^H of buffer does not change on dilution.

Applications of buffers :

1) Buffers are used in various chemical industries
2) Buffers are used in various enzyme catalyses reaction.
3) used in softening of hard water.
4) used in various research programmes.
5) used in chemical analysis. [precipitation of radicals]

Salt of Hydrolysis :

Acid + base $\rightleftharpoons$ salt + H_2O

Salt hydrolysis is endothermic because t is reverse of neutralisation.

- The reaction of the salt with water to produce acid or base or both is called salt hydrolysis.

- Salt hydrolysis is of three types.

1) Cationic hydrolysis : Cation of the salt reacts with water to produce H^+ ions.

Eg: NH_4Cl, NH_4NO_3, $[NH_4]_2SO_4$, $AlCl_3$ etc.

In these salts cation is stronger because it is the conjugate of weak base therefore they undergo cationic hydrolysis.

Eg:$NH_4^+Cl^-$: $NH_4^+ + H_2O \rightleftharpoons$ $NH_4OH + H^+$

2) Anionic Hydrolysis : Anion of the salt reacts with water to produce OH^-.

Eg: CH_3COONa, HCOOK, Na_2CO_3, etc.

In these salts anion is stronger as it is the conjugate of weak acid.

Eg: CH_3COONa^+ :

$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$

3) Cationic and Anionic hydrolysis : Both cation and anion of the salt react with water to produce H^+ and OH^- ions. Therefore the solution is neutral.

Eg: CH_3COONH_4, $HCOONH_4$, $Al(CH_3COO)_3$

In these salts both cation and anion are stronger because they are the conjugates of weak base and weak acid respectively.

Eg: $CH_3COONH_4^+$:

$CH_3OO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$

$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$

there are four types of salts depending on the nature of acid and base involved in the titrations.

- **Salt of strong acid and weak base :**

Eg: NH_4Cl, NH_4NO_3, $(NH_4)_2SO_4$, $AlCl_3$, $MgCl_2$, $Al_2(SO_4)_3$ etc,…

- These salts undergo cationic hydrolysis to produce H^+ ions.
- Their aqueous solution is acidic and p^H is less than 7.
- Their aqueous solution will turn blue litmus to red and they can be used for titrating against bases.

Eg: $NH_4^+Cl^-$

Hydrolysis : $NH_4^+ + H_2O \rightleftharpoons$ $NH_4OH + H^+$

$$K = \frac{[NH_4OH][H^+]}{[NH_4^+][H_2O]}$$

$$K.[H_2O] = \frac{[NH_4OH][H^+]}{[NH_4^+]}$$

$$K_h = \frac{[NH_4OH][H^+]}{[NH_4^+]}$$

Ionisation of

NH_4OH : $NH_4OH \rightleftharpoons NH_4^+ + OH^-$

$K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]}$

Ion product of water = k_w = $[H^+]\,[OH^-]$

$\frac{K_w}{K_b} = \frac{[H^+][OH^-][NH_4OH]}{[NH_4^+][OH^-]}$

$$K_h = \frac{K_w}{K_b}$$

The degree of hydrolysis of the salt is inversely proportional to the square root of its molar concentration.

$\alpha = \sqrt{\frac{K_b}{C}} \Rightarrow \sqrt{\frac{K_w}{K_b.C}}$

$[H^+] = C\alpha$

$[H^+] = C\sqrt{\frac{K_w}{K_b.C}}$

$[H^+] = \sqrt{\frac{K_w.C}{K_b}}$

Appling – log on both sides

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

$$p^H = \frac{1}{2}p^{Kw} - \frac{1}{2}p^{K_b} - \frac{1}{2}log\,C$$

- **Salt of weak acid and strong base :**

Eg: CH_3COONa, HCOOK, Na_2CO_3, $NaHCO_3$, Na_3PO_4, Na_2HPO_4, KCN etc.

Anionic hydrolysis : CH_3COONa

$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$

$K = \frac{[CH_3COOH][OH^-]}{[CH_3OO^-][H_2O]}$

$$K[H_2O] = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$$

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

Ionisation of CH_3COOH :

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$

ionic product of water : $K_w = [H^+]\,[OH^-]$

$$\frac{K_w}{K_a} = \frac{[H^+][OH^-][CH_3COOH]}{[CH_3COO^-][H^+]}$$

$$K_h = \frac{K_w}{K_a}$$

The degree of hydrolysis of these salts is also inversely proportional to the square root of its concentration.

$\alpha = \sqrt{\frac{k_h}{C}} \Rightarrow \sqrt{\frac{k_w}{k_a.C}}$

$[OH^-] = C\sqrt{\frac{K_w}{K_a.C}} \Rightarrow \sqrt{\frac{K_w.C}{K_a}}$

applying – log on both sides

$$-log[OH^-] = -\frac{1}{2}log\, K_w + \frac{1}{2}log\, K_a - \frac{1}{2}log\, C$$

$$p^{OH} = \frac{1}{2}p^{K_w} - \frac{1}{2}p^{K_a} - \frac{1}{2}log\, C$$

- aqueous solution of these salts are basic they undergo anionic hydrolysis because the anion of the salt is stronger as it is the conjugate of weak acid.
  $[OH^-]$ is produced and solution is basic.

- **Salt of weak acid and weak base :**
  Eg: CH_3COONH_4, $HCOONH_4$, NH_4CN, $Al(CH_3COO)_3$ etc…
- The aqueous solution of these salts is all most neutral and p^H is all most equal to 7.
- The nature of the salt solution actually depends on K_a and K_b values of acid and base.
  i) If $K_a = K_b$, solution is exactly neutral.
  Eg: CH_3COONH_4
  K_a of CH_3COOH = K_b of NH_4OH
  ii) If $K_a > K_b$, solution is acidic
  Eg: $HCOONH_4$
  K_a of $HCOOH$ > K_b of NH_4OH
  iii) If $K_a < K_b$, solution is basic
  Eg: $Mg(CN)_2$
  K_b of $Mg(CN)_2$ > K_a of HCN

- These salts will undergo both cationic and anionic hydrolysis to produce both H^+ and OH^- ions.
  Eg: CH_3COONH_4
  $CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$
  $NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$

$$K = \frac{[CH_3COOH][NH_4OH][H^+][OH^-]}{[CH_3COO^-][NH_4^+][H_2O]^2}$$

$$K[H_2O]^2 = \frac{[CH_3COOH][NH_4OH][H^+][OH^-]}{[CH_3COO^-][NH_4^+]}$$

$$K_h = \frac{[CH_3COOH][NH_4OH][H^+][OH^-]}{[CH_3COO^-][NH_4^+]}$$

The $[H^+] = [OH^-]$ they get cancelled mutually

$$K_h = \frac{[CH_3COOH][NH_4OH]}{[CH_3COO^-][NH_4^+]}$$

ionic product of water $K_w = [H^+]\,[OH^-]$

$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]}$$

$$\frac{K_w}{K_a.k_b} = \frac{[H^+][OH^-][CH_3COOH][NH_4OH]}{[CH_3COO^-][H^+][NH_4^+][OH^-]}$$

$$\frac{K\omega}{K_a.k_b} = \frac{[CH_3COOH][NH_4OH]}{[CH_3COO^-][NH_4^+]}$$

$$K_b = \frac{K_w}{K_a.K_b}$$

- The degree of hydrolysis [α] is independent of concentration of the salt because both cation and anion of the salt are stronger as they are conjugate of weak base and weak acid respectively.

A = $\sqrt{K_h} \Rightarrow \sqrt{\frac{K_w}{K_a.K_b}}$

$[H^+] = K_a.\alpha \Rightarrow K_a\sqrt{\frac{K_w}{K_a.K_b}} \Rightarrow \sqrt{\frac{K_w.K_a}{K_b}}$

apply - log on both sides

$$-log[H^+] = -\frac{1}{2}log\,K_a - \frac{1}{2}log\,K_a + \frac{1}{2}log\,K_b$$

$$p^H = \frac{1}{2}p^{K_w} + \frac{1}{2}p^{K_a} - \frac{1}{2}p^{K_b}$$

$[OH^-]$ = K_b·

$=K_b\sqrt{\frac{k_w}{k_a.k_b}} = \sqrt{\frac{k_w \times k_b}{k_a}}$

apply – log on both sides

$-\log[OH^-] = -\frac{1}{2}\log k_w - \frac{1}{2}\log k_b + \frac{1}{2}\log k_a \; p^{OH} = \frac{1}{2}p^{kw} + \frac{1}{2}p^{k_b} - \frac{1}{2}p^{k_a}$

- **Salt of strong acid and strong base :**
  Eg: NaCl, KNO_3, Na_2SO_4, $BaCl_2$, $NaClO_4$, $Ba(NO_3)_2$, $Sr.(NO_3)_2$ etc.
- These salts do not undergo hydrolysis because both anion and cation are weak as they are conjugates of strong acid and strong base respectively.
- Therefore their aqueous solutions are exactly neutral and p^H is exactly .