p^H and Buffer Solution

p^H of the solution :- The p^H of the solution is the negative logrithm of the concentration of hydrogen ions which it contains.

$$\boxed{p^H = -\log[H^+]}$$

* The conc. of $[H^+]$ must be in moles/litre.

(i) If $p^H = 7$ - Solution is neutral.
(ii) If $p^H < 7$ - " " Acidic.
(iii) If $p^H > 7$ - " " Basic.

Similarly → $\boxed{p^{OH} = -\log[OH^-]}$

* $[OH^-]$ - must be in moles/litre.

$$\boxed{p^H + p^{OH} = 14}$$

$$\boxed{[H^+][OH^-] = 10^{-14}}$$

p^H Scale :- Given by "Sorensen" - It extends from 0 - 14.

Dissociation of water :- Very less.

$$\underset{1\text{ mole}}{H_2O} \rightleftharpoons \underset{10^{-7}}{H^+} + \underset{10^{-7}}{OH^-} \quad (\text{at } 25°C)$$

Water dissociates very less at 25°C.

* If the conc. of Acid or base is less than 10^{-6} (10^{-7} or 10^{-8} or less) - then only dissociation of H_2O is considered.

* If suppose HCl conc. is 10^{-3}M. then dissociation of water is not considered. As from water we get $10^{-7}[H^+]$ very less as compared to 10^{-3}.

As - $10^{-3} + \underbrace{10^{-7}}_{\text{very small as compared to } 10^{-3}} \approx 10^{-3}$

Buffer Solution :-

A buffer solution is one which can resist change in its pH on the addition of an acid or a base.

OR.

A buffer solution is one which maintains its pH fairly constant even upon the addition of small amount of Acid or base.

e.g. $CH_3COOH + CH_3COONa$ - Acidic buffer

$NH_4OH + NH_4Cl$ - Basic buffer.

$$\boxed{\text{Buffer capacity} = \frac{\text{No. of moles of acid or base added to 1 litre of buffer}}{\text{Change in pH}}}$$

Acidic Buffer & its Mechanism :-

Acidic buffer - $\underset{\text{(weak acid)}}{CH_3COOH} + \underset{\text{(salt)}}{CH_3COONa}$

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$ (very less)

$CH_3COONa \rightleftharpoons CH_3COO^- + Na^+$ (completely dissociated)

(i) Addition of Strong Acid [HCl] :- $HCl \rightleftharpoons H^+ + Cl^-$

The H^+ of the strong acid will be taken up immediately by CH_3COO^- to form CH_3COOH.

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

Thus H^+ ions added are neutralized by the CH_3COO^- present in the mixture, so their will be very little change in pH of mixture

* Dissociation constant of CH_3COOH at 25°c is 1.75×10^{-5}.
i.e from 1 mole of CH_3COOH we get only 1.75×10^{-5} moles of H^+.

$$\underset{1\,\text{mole}}{CH_3COOH} \rightleftharpoons \underset{1.75\times10^{-5}}{CH_3COO^-} + \underset{1.75\times10^{-5}}{H^+}$$

(ii) Addition of strong base - $NaOH \rightleftharpoons Na^+ + OH^-$

The OH^- ions ~~a~~ added are neutralized by the acetic acid present in the mixture.

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

Thus their is very small change in PH.

Basic buffer and its Mechanism :-

Basic buffer - $\underset{\text{(weak base)}}{NH_4OH} + \underset{\text{(Salt)}}{NH_4Cl}$

$NH_4OH \rightleftharpoons NH_4^+ + OH^-$ (very less)

$NH_4Cl \rightleftharpoons NH_4^+ + Cl^-$ (completely Dissociated).

(i) Addition of Strong Acid :- $HCl \rightleftharpoons H^+ + Cl^-$

The ~~o~~ H^+ ions added are neutralized by the NH_4OH present in the mixture.

$$H^+ + NH_4OH \longrightarrow NH_4^+ + H_2O.$$

Thus their is very small change in PH.

(ii) Addition of strong base :- $NaOH \rightleftharpoons Na^+ + OH^-$

The OH^- ions added are taken up by NH_4^+ ions forming NH_4OH. ~~ve~~ which dissociated to very less extent.

So their will be very less change in PH.

* $\underset{\text{1mole}}{NH_4OH} \rightleftharpoons \underset{1.81\times10^{-5}}{NH_4^+} + \underset{1.81\times10^{-5}}{OH^-}$ (at 25°C).

Henderson equation :-

(i) Acidic Buffer :- $CH_3COOH + CH_3COONa$.

let dissociation constant of CH_3COOH is Ka.

$$CH_3COOH \underset{}{\overset{K_a}{\rightleftharpoons}} CH_3COO^- + H^+$$

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

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

Since CH_3COOH dissociates to very less extent.

$$[CH_3COO^-] = [Salt] = [CH_3COONa].$$

$$\Rightarrow \quad [H^+] = K_a \frac{[Acid]}{[Salt]} \quad \rightarrow \text{Taking (-)ve log}$$

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

$$\boxed{p^H = p^{K_a} + \log\frac{[Salt]}{[Acid]}}$$

② Basic buffer :- $NH_4OH + NH_4Cl$

$$NH_4OH \overset{K_b}{\rightleftharpoons} NH_4^+ + OH^-$$

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

$$[OH^-] = K_b \frac{[NH_4OH]}{[NH_4^+]} \quad \text{taking (-)ve log.}$$

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

$$[NH_4^+] = [Salt]$$

$$-\log[OH^-] = -\log K_b - \log\frac{[Base]}{[Salt]}$$

$$\boxed{p^{OH} = p^{K_b} + \log\frac{[Salt]}{[Base]}}$$