6.IONIC EQUILIBRIUM

1. OSTWALD DILUTION LAW :

- Dissociation constant of weak acid (K_a) , $K_a = \frac{[H^+][A^-]}{[HA]} = \frac{[C\alpha][C\alpha]}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha}$

  If $\alpha << 1$, then $1 - \alpha \cong 1$ or $K_a = c\alpha^2$ or $\alpha = \sqrt{\frac{K_a}{C}} = \sqrt{K_a \times V}$

- Similarly for a weak base , $\alpha = \sqrt{\frac{K_b}{C}}$. Higher the value of K_a / K_b , strong is the acid / base.

Acidity and pH scale :

$\therefore$ pH = – log a_{H^+} (where a_{H^+} is the activity of H^+ ions = molar concentration for dilute solution).

[Note : pH can also be negative or > 14]

$pH = -\log [H^+]$; $[H^+] = 10^{-pH}$

$pOH = -\log [OH^-]$; $[OH^-] = 10^{-pOH}$

$pKa = -\log Ka$; $Ka = 10^{-pKa}$

$pKb = -\log Kb$; $Kb = 10^{-pKb}$

PROPERTIES OF WATER :

1. In pure water $[H^+] = [OH^-]$ so it is Neutral.

2. Moler concentration / Molarity of water = 55.56 M.

3. Ionic product of water (K_w) :

$K_w = [H^+][OH^-] = 10^{-14}$ at 25° (experimentally)

pH = 7 = pOH $\Rightarrow$ neutral

pH < 7 or pOH > 7 $\Rightarrow$ acidic

pH > 7 or pOH < 7 $\Rightarrow$ Basic

4. Degree of dissociation of water :

$$\alpha = \frac{\text{no. of moles dissociated}}{\text{Total No. of moles initially taken}} = \frac{10^{-7}}{55.55} = 18x10^{-10} \text{ or } 1.8x10^{-7}\%$$

5. Absolute dissociation constant of water :

$$K_a = K_b = \frac{[H^+][OH^-]}{[H_2O]} = \frac{10^{-7} \times 10^{-7}}{55.55} = 1.8 \times 10^{-16}$$

$pK_a = pK_b = -\log(1.8 \times 10^{-16}) = 16 - \log 1.8 = 15.74$

$\mathbf{K_a \times K_b = [H^+]\,[OH^-] = K_w}$

$\Rightarrow$ **Note: for a conjugate acid- base pairs**

$\mathbf{pK_a + pK_b = pK_w = 14}$ at 25ºC.

pK_a of H_3O^+ ions = –1.74

pK_b of OH^- ions = –1.74.

❍ pH Calculations of Different Types of Solutions :

(a) Strong acid solution :

(i) If concentration is greater than 10^{-6} M

In this case H^+ ions coming from water can be neglected,

(ii) If concentration is less than 10^{-6} M

In this case H^+ ions coming from water cannot be neglected

(b) Strong base solution :

Using similar method as in part (a) calculate first $[OH^-]$ and then use $[H^+] \times [OH^-] = 10^{-14}$

(c) pH of mixture of two strong acids :

Number of H^+ ions from I-solution = N_1V_1

Number of H^+ ions from II-solution = N_2V_2

$$[H^+] = N = \frac{N_1V_1 + N_2V_2}{V_1 + V_2}$$

(d) pH of mixture of two strong bases :

$$[OH^-] = N = \frac{N_1V_1 + N_2V_2}{V_1 + V_2}$$

(e) pH of mixture of a strong acid and a strong base :

If $N_1V_1 > N_2V_2$, then solution will be acidic in nature and $[H^+] = N = \dfrac{N_1V_1 - N_2V_2}{V_1 + V_2}$

If $N_2V_2 > N_1V_1$, then solution will be basic in nature and $[OH^-] = N = \dfrac{N_2V_2 - N_1V_1}{V_1 + V_2}$

(f) pH of a weak acid(monoprotic) solution :

$$K_a = \frac{[H^+]\,[OH^-]}{[HA]} = \frac{C\alpha^2}{1-\alpha}$$

if $\alpha << 1 \Rightarrow (1-\alpha) \approx 1$ $\Rightarrow$ $K_a \approx C\alpha^2$ $\Rightarrow$ $\alpha = \sqrt{\dfrac{K_a}{C}}$ (is valid if α < 0.1 or 10%)

On increasing the dilution $\Rightarrow$ $C\downarrow \Rightarrow \alpha\uparrow$ and $[H^+]\downarrow \Rightarrow pH\uparrow$

(g) pH of a solution of a polyprotic weak acid :

$$\mathbf{pH} = \frac{1}{2}\left(pK_{a_1} - \log C\right).$$

RELATIVE STRENGTH OF TWO ACIDS :

$$\frac{[H^+] \text{ furnished by I acid}}{[H^+] \text{ furnished by II acid}} = \frac{c_1\alpha_1}{c_2\alpha_2} = \sqrt{\frac{k_{a_1}c_1}{k_{a_2}c_2}}$$

(h) pH of a mixture of two weak acid(both monoprotic) solutions :

$$(\alpha_1 << 1) \text{ and } (\alpha_2 << 1) \Rightarrow \frac{K_{a1}}{K_{a2}} = \frac{\alpha_1}{\alpha_2}$$

$$[H^+] = C_1\alpha_1 + C_2\alpha_2 = \sqrt{C_1K_{a1} + C_2K_{a2}}$$

**** If water is again considered third weak acid in solution of two weak acid then**

$$[H^+] = \sqrt{K_{a1}C_1 + K_{a2}C_2 + K_w}$$

$$C_wK_{aw} = 10^{-14} = K_w$$

$$[H^+] = \sqrt{C_1K_{a1} + C_2K_{a2} + 10^{-14}}$$

(i) pH of a mixture of weak acid(monoprotic) and a strong acid solution :

If [SA] = C_1 and [WA] = C_2, then [H^+] from SA = C_1 and [H^+] from WA = C_2

Let HA is a weak acid.

$$[H^+] = \frac{C_1 + \sqrt{C_1^2 + 4K_a.C_2}}{2}$$

**** If a strong acid of low conc is added in water then [H^+] of solution can be calculated as**

$$[H^+] = \frac{C_1 + \sqrt{C_1^2 + 4K_w}}{2}.$$

❍ SALT HYDROLYSIS :

	Salt of	Type of hydrolysis	k_h	h	pH
(a)	weak acid & strong base	anionic	$\frac{k_w}{k_a}$	$\sqrt{\frac{k_w}{k_a c}}$	$7 + \frac{1}{2} pk_a + \frac{1}{2} \log c$
(b)	strong acid & weak base	cationic	$\frac{k_w}{k_b}$	$\sqrt{\frac{k_w}{k_b c}}$	$7 - \frac{1}{2} pk_b - \frac{1}{2} \log c$
(c)	weak acid & weak base	both	$\frac{k_w}{k_a k_b}$	$\sqrt{\frac{k_w}{k_a k_b}}$	$7 + \frac{1}{2} pk_a - \frac{1}{2} pk_b$
(d)	Strong acid & strong base	--------do not hydrolysed-------			pH = 7

Hydrolysis of ployvalent anions or cations

For [Na_3PO_4] = C.

$$K_{a1} \times K_{h3} = K_w$$

$K_{a1} \times K_{h2} = K_w$

$K_{a3} \times K_{h1} = K_w$

Generally pH is calculated only using the first step Hydrolysis

$$K_{h1} = \frac{Ch^2}{1-h} \approx Ch^2$$

$$h = \sqrt{\frac{K_{h1}}{c}} \quad \Rightarrow [OH^-] = ch = \sqrt{K_{h1} \times c} \quad \Rightarrow [H^+] = \sqrt{\frac{K_W \times K_{a3}}{C}}$$

So $\quad \mathbf{pH = \frac{1}{2}[pK_w + pK_{a3} + \log C]}$

Hydrolysis of Amphiprotic Anion. (Cation is not Hydrolysed e.g. $NaHCO_3$, NaHS, etc.)

$$pH\ (HCO_3^-) = \left(\frac{pK_{a_1} + pK_{a_2}}{2}\right)$$

(b) Similarly for $H_2PO_4^-$ and HPO_4^{2-} amphiprotic anions.

$$pH_{(H_2PO_4^-)} = \left(\frac{pK_{a_1} + pK_{a_2}}{2}\right) \quad \text{and} \quad pH_{(HPO_4^{2-})} = \left(\frac{pK_{a_2} + pK_{a_3}}{2}\right)$$

- $H_3PO_4 \xrightarrow{K_{a1}} H_2PO_4^- \xrightarrow{K_{a2}} HPO_4^{2-} \xrightarrow{K_{a3}} PO_4^{3-}$ ionisation.

  $\xleftarrow[K_{h_1}=\frac{K_w}{K_{a_1}}]{} \quad \xleftarrow[K_{h2}=\frac{K_w}{k_{a2}}]{} \quad \xleftarrow[K_{h1}=\frac{K_w}{K_{a3}}]{}$

The $\quad$ pH of $H_3PO_4 = \frac{1}{2}(pK_{a1} - \log C) \qquad \therefore K_{a1} >> K_{a2} >> K_{a3}$

pH of $NaH_2PO_4 = \frac{1}{2}(pK_{a1} + pK_{a2})$

pH of $Na_2HPO_4 = \frac{1}{2}(pK_{a2} + pK_{a3})$

pH of $Na_3PO_4 = \frac{1}{2}(pKw + pKa_3 + \log C) \quad \therefore$ Sec hydrolysis can neglect.

BUFFER SOLUTION :

(a) **Acidic Buffer :** e.g. CH_3COOH and CH_3COONa. (weak acid and salt of its conjugate base).

$$pH = pK_a + \log \frac{[Salt]}{[Acid]} \qquad \text{[Henderson's equation]}$$

(b) **Basic Buffer :** e.g. $NH_4OH + NH_4Cl$. (weak base and salt of its conjugate acid).

$$pOH = pK_b + \log \frac{[Salt]}{[Base]}$$

Buffer capacity (index) :

$$\text{Buffer capacity} = \frac{\text{Total no. of moles of acid / alkali added per litre}}{\text{Change in pH}}$$

$$\text{Buffer capacity} = \frac{dx}{d\Delta pH} = 2.303 \frac{(a+x)(b-x)}{a+b}$$

INDICATOR :

$$HIn \rightleftharpoons H^+ + In^-$$

or $[H^+] = K_{HIn} \times \frac{[HIn]}{[In^-]}$

$\therefore$ $pH = pK_{HIn} + \log \frac{[In^-]}{[HIn]}$ $\Rightarrow$ $pH = pK_{HIn} + \log \frac{[\text{Ionised form}]}{[\text{Unionised form}]}$

SIGNIFICANCE OF INDICATORS :

☞ Extent of reaction of different bases with acid (HCl) using two indicators :

	Phenolphthalein	**Methyl Orange**
NaOH	100% reaction is indicated $NaOH + HCl \rightarrow NaCl + H_2O$	100% reaction is indicated $NaOH + HCl \rightarrow NaCl + H_2O$
Na_2CO_3	50% reaction upto $NaHCO_3$ stage is indicated $Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl$	100% reaction is indicated $Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2$
$NaHCO_3$	No reaction is indicated	100% reaction is indicated $NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2$.

❍ **ISOELECTRIC POINT :**

$$[H^+] = \sqrt{K_{a1}K_{a2}}$$

$$pH = \frac{pK_{a1} + pK_{a2}}{2}.$$

SOLUBILITY PRODUCT :

$$K_{SP} = (xs)^x (ys)^y = x^x.y^y.(s)^{x+y}$$

CONDITION FOR PRECIPITATION :

If ionic product $K_{I.P} > K_{SP}$ precipitation occurs,

if $K_{I.P} = K_{SP}$ saturated solution (precipitation just begins or is just prevented).