IONIC EQUILIBRIUM

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 :

∴ $pH = -\log a_{H^+}$ (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. **Molar concentration / Molarity of water = 55.56 M.**
3. **Ionic product of water (K_w) :**

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

   $pH = 7 = pOH$ ⇒ neutral

   $pH < 7$ or $pOH > 7$ ⇒ acidic

   $pH > 7$ or $pOH < 7$ ⇒ Basic

4. **Degree of dissociation of water :**

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

5. **Absolute dissociation constant of water :**

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

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

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

⇒ **Note: for a conjugate acid- base pairs**

$pK_a + pK_b = pK_w = 14$ at 25°C.

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

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

If $N_2V_2 > N_1V_1$, then solution will be basic in nature and

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

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

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

if $\alpha << 1 \Rightarrow (1-\alpha) \approx 1$ ⇒ $K_a \approx C\alpha^2$

$\Rightarrow \quad \alpha = \sqrt{\frac{K_a}{C}}$ (is valid if $\alpha < 0.1$ or 10%)

On increasing the dilution

$\Rightarrow \quad C\downarrow \quad \Rightarrow \alpha\uparrow$ and $[H^+]\downarrow \Rightarrow pH\uparrow$

RELATIVE STRENGTH OF TWO ACIDS :

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

○ **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 $[Na_3PO_4] = C$.

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

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

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

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

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).

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

SOLUBILITY PRODUCT :

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

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).