Ionic Equilibrium

1. Acid and Bases :

a) Arrhenius definition :

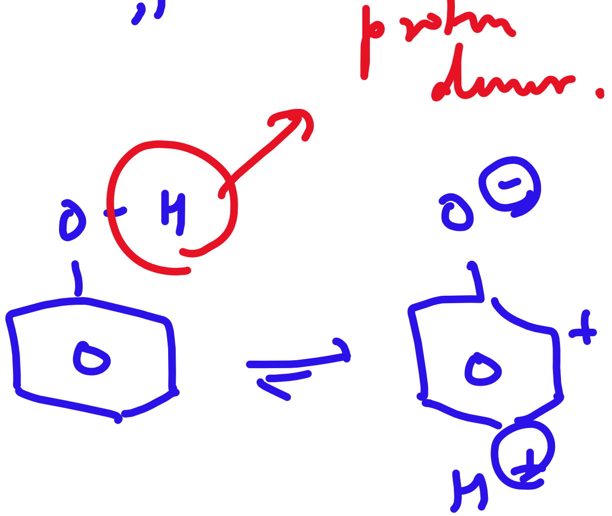
i) Acids give H^+ ions in aqueous solution.

ii) Bases ,, OH^- ,, ,, ,, ,,

b) Bronsted - Lowry definition :

i) Acid = Proton donor

ii) Base = ,, acceptor.



c) Lewis definition.

i) Acid = Electron pair acceptor

ii) Base = ,, ,, donor.

d) Concept of strong & weak acids.

Classification based on the extent of dissociation

a. Strong acid completely dissociate in aqueous soln.

b. Weak acid partially " " " "

Strong acid : HCl, H_2SO_4, HNO_3, KOH, $NaOH$.

Weak acid : CH_3COOH, NH_4OH

2. Dissociation constant:

$$AB \rightleftharpoons A^+ + B^{\ominus}$$

$$\frac{[A^+][B^-]}{[AB]} = \text{constant}$$

dissociation (electrolytes dissociate into ions)

$$\frac{[A^+][B^-]}{[AB]} = k = \text{dissociation constant.}$$

Dissociation of H_2O at 25°C

$$H_2O(l) \rightleftharpoons H^+(aq) + {}^{\ominus}OH(aq)$$

$$K_w = [H^+][\overset{\ominus}{O}H] = 1.0 \times 10^{-14}$$

3. **Ostwald's Dilution Law:-**

The degree of dissociation (α) of weak electrolytes increases with dilution & law of mass action can be applied to them.

$$AB \rightleftharpoons A^+ + B^-$$

$C \quad 0 \quad 0$ ---> Initial concentration

α = degree of dissociation

$c(1-\alpha) \quad c\alpha \quad c\alpha$ → At equilibrium.

Ionisation constant, $K = \dfrac{[A^+][B^-]}{[AB]}$

$$= \frac{c\alpha \times \cancel{c}\alpha}{\cancel{c}(1-\alpha)} = \frac{c\alpha^2}{1-\alpha}$$

$\therefore \alpha << 1$,

α can be neglected from the denominator.

$\therefore K = c\alpha^2$

$K = c\alpha^2 \Rightarrow \alpha^2 = \frac{K}{c}$

$\Rightarrow \alpha = \sqrt{\frac{K}{c}}$

$\Rightarrow \alpha \propto \sqrt{\frac{1}{c}}$

∴ As the dilution is increased, c decreases.

So, at infinite dilution, c is negligible.
or high "

$\alpha \rightarrow 1 \Rightarrow \alpha$ approaches unity with dilution.

4. Strength of acids & bases - Greater the value of K_a or K_b, stronger is the acid or base.

K_a = acid dissociation constant.

$$HA \rightleftharpoons H^{\oplus} + A^{\ominus}$$

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

$$BOH \rightleftharpoons B^+ + OH^{\ominus}$$

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

⑤ Levelling effect.

All the strong acids in soln. appear almost equally strong since H_2O acts as a strong base. For e.g. $HClO_4$, HBr, H_2SO_4, HCl, HNO_3 appear equally strong.

$$HA + H_2O \rightleftharpoons H_3O^{\oplus} + A^{\ominus}$$

Hence, relative strengths in aqueous soln- cannot be compared. This phenomenon is known as levelling effect.

c <u>Relation between Ka, Kb & Kw.</u>

$$\boxed{-\log} = p.$$

$$K_a \times K_b = K_w$$

$$-\log(K_a \cdot K_b) = -\log K_w$$

$$-\log K_a - \log K_b = -\log K_w = -\log(10^{-14})$$

$$= 14 \log 10$$

$$= 14$$

$$\Rightarrow pK_a + pK_b = pK_w$$

$$= 14$$

7. Common Ion Effect.

The degree of ionisation of an electrolyte is suppressed by the addition of another electrolyte having a common ion. This is known as common ion effect. For e.g.: ionisation of acetic acid is suppressed by addition of HCl or CH_3COONa.

Common ion effect helps in controlling the concentration of ions furnished by weak electrolytes.

It also affects the solubility of salts.

8. **Solubility Product K_{sp}.**

At constant temperature and pressure the saturated soln. of a sparingly soluble salt has an equilibrium between the excess of the solute & ions furnished by it -

$$\underset{\text{solid undissolved}}{AgCl} \rightleftharpoons \underset{\text{solid dissolved but not ionised}}{AgCl} \rightleftharpoons Ag^+ + Cl^-$$

Applying law of mass action,

$$K = \frac{[Ag^+][Cl^-]}{[AgCl]}$$

$$\Rightarrow K[AgCl] = [Ag^+][Cl^-]$$

$$\Rightarrow \boxed{K_{sp}} = [Ag^+][Cl^-]$$

$\downarrow$ solubility product = product of concentration of ions in saturated soln

When $K_{sp} > [Ag^+][Cl^-]$, soln. is not saturated.

When $K_{sp} < [Ag^+][Cl^-]$ soln. is super-saturated & precipitation takes place.

When $K_{sp} = [Ag^+][Cl^-]$ soln is saturated.

ⓔ N.B: Dissociation constant of water:

K_w $\wedge$ 10^{-14}

$$2H_2O \rightleftharpoons H_3O^{\oplus} + OH^{\ominus}$$

$$K = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$

$$\Rightarrow K[H_2O]^2 = [H_3O^+][OH^-]$$

⑨ Mathematical treatment of hydrolysis.

a) Salts of strong acid & weak base

i) Hydrolysis constant

$$A^+\underline{B^-} + H_2O \rightleftharpoons AOH + \underline{B}^{\ominus} + H^{\oplus}$$

or,

$$A^+ + H_2O \rightleftharpoons AOH + H^+$$

$$K = \frac{[AOH]\ [H^+]}{[A^+]\ [H_2O]}$$

As water is taken in excess, its active mass remains practically constant.

$$\therefore \quad K[H_2O] = \frac{[AOH]\,[H^+]}{[A^+]}$$

hydrolysis constant

$$\boxed{K_h} = \frac{[AOH]\,[H^+]}{A^+} \Rightarrow \frac{K_h}{[H^+]} = \frac{[AOH]}{[A^+]}$$

Relation betn. K_h, K_b & K_w.

The dissociation of the weak base produced in the hydrolysis of a strong acid & weak base:

$$AOH \longrightarrow A^+ + OH^-$$

$$K_b = \frac{[A^+]\,[OH^-]}{[AOH]}$$

$$K_b = \frac{[A^+][\overset{\ominus}{OH}]}{[AOH]} \longrightarrow ①$$

$$K_h = \frac{[AOH][H^+]}{[A^+]}$$

$$\Rightarrow \frac{K_h}{[H^+]} = \frac{[AOH]}{[A^+]} \longrightarrow ②$$

$$K_b = \frac{\boxed{[OH^-] \cdot [H^+]}}{K_h} \Rightarrow \frac{K_w}{K_h}$$

ionic product K_w

$$K_w = K_h \times K_b$$

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

Degree of hydrolysis :

$$A^{+} + H_2O \longrightarrow AOH + H^{\oplus}$$

$$c(1-h) \qquad \text{Excess} \qquad ch \qquad ch$$

$$K_h = \frac{\cancel{c}h \times ch}{\cancel{c}(1-h)} = \frac{ch^2}{1-h}$$

If the base is very weak,
h is very small as compared to unity

$\Rightarrow$ $1 - h$ may be replaced by 1

$\Rightarrow$ $h = \sqrt{\frac{K_h}{c}}$

$$h = \sqrt{\frac{K_h}{c}}$$

h = degree of hydrolysis

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

c = initial concentratio of salt.

$$\therefore \quad h = \sqrt{\frac{K_w}{K_b . c}}$$

The degree of hydrolysis of a salt of weak base & strong acid is

i) directly proportional to ionic product of H_2O.

ii) Inversely proportional to the value of K_b

iii) " " " " " " c.

Relationship between pH, pK_b & c :

$$h = \sqrt{\frac{K_w}{cK_b}} = \left(\frac{K_w}{c\cdot K_b}\right)^{1/2}$$

Recap.

$$A^+ + H_2O \longrightarrow AOH + H^+$$

c(1−h) excess ch ch

$$[H^+] = ch = c\sqrt{\frac{K_w}{c\cdot K_b}}$$

$$= \sqrt{\frac{c\cdot K_w}{K_b}}$$

$$[H^+] = \sqrt{\frac{c \cdot K_w}{K_b}} = \left(\frac{c \cdot K_w}{K_b}\right)^{1/2}$$

$$\Rightarrow \overset{p}{\boxed{-\log}}[H^+] = -\log\left[\frac{c \cdot K_w}{K_b}\right]^{1/2}$$

$$= -\frac{1}{2}\log c - \frac{1}{2}\log K_w + \frac{1}{2}\log K_b$$

$$\Rightarrow pH = -\frac{1}{2}\log c + \frac{1}{2}pK_w - \frac{1}{2}pK_b$$

$$\Rightarrow pH = \frac{1}{2}pK_w - \frac{1}{2}K_b - \frac{1}{2}\log c.$$

Henderson- Hasselbalch eqn.

Mathematical expression for pH of an acidic buffer.

Let us consider having a weak acid HA & its salt BA, with a strong base.

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

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

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

The salt BA is completely ionized. Thus high concn. of A^- ions provided by almost complete ionisation of BA will suppress the ionisation of weak acid, so that we may assume that free $A^{\ominus}$ ions are entirely due to the salt.

$$\therefore \quad [A^-] = [\text{salt}] \quad \& \quad [HA] = [\text{acid}]$$

$$[H^+] = K_a \cdot \frac{[\text{acid}]}{[\text{salt}]}$$

$$\log[H^+] = \log K_w + \log\frac{[acid]}{[salt]}$$

$$\Rightarrow -\log[H^+] = -\log K_a - \log\frac{[acid]}{salt}$$

$$\Rightarrow pH = pK_a + \log\frac{[salt]}{[acid]}$$

Henderson - Hasselbach eqn.

Basic buffer:

$$pOH = pK_a + \log\frac{[salt]}{[base]}$$

$$\therefore pH = 14 - pOH$$

$$\therefore \; pH = 14 - \left[pK_a + \log \frac{[salt]}{[base]} \right]$$

$$[H^+]\,[\overset{\ominus}{O}H] = K_w = 10^{-14}$$

$$\log K_w = -14 \log 10 = -14$$

$$\Rightarrow 14 = -\log K_w = pK_w$$

$$\therefore \; pH = pK_w - pK_a + \log \frac{[salt]}{base}.$$