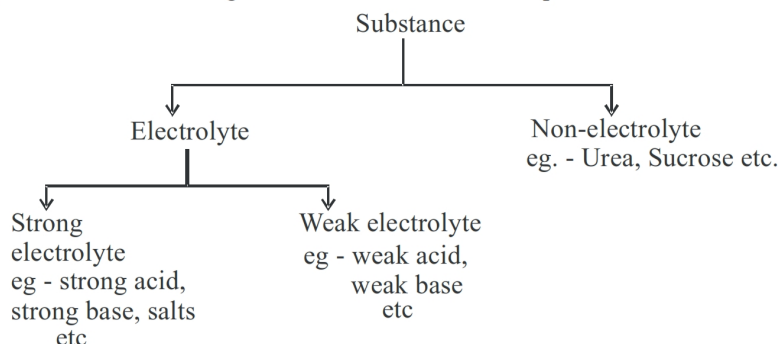# IONIC EQUILIBRIUM

The study of reactions involving ions is studied under ionic equilibrium.

DISSOCIATION OF WEAK ELECTROLYTES

Weak electrolytes are not completely ionized when dissolved in polar solvents. The equilibrium is set up between ionized and unioized molecule in soluton.

Degree of Dissociation

The degree of dissociation (α) of weak electrolytes is much less than unity.

$$\alpha = \frac{\text{No. of molecules dissociated as ions}}{\text{Total number of molecules of electrolytes dissolved}}$$

ACID AND BASE DISSOCIATION CONSTANT

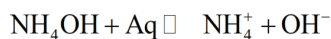Let us consider the dissociation of a weak acid,

$$H_3C-\overset{\displaystyle O}{\overset{\|}{C}}-O-H+H_2O \rightleftharpoons H_3O^+ + H_3C-\overset{\displaystyle O}{\overset{\|}{C}}-O^-$$

$$\boxed{K_a = \frac{\left[H_3O^+\right]\left[CH_3COO^-\right]}{\left[H_3C-COOH\right]}}, \text{ Here } K_a \text{ is acid dissociaton costant.}$$

Larger, is the $[H_3O^+]$ concentration, larger will be the Ka value and thus larger is the strength of acid.

BASE DISSOCIATION CONSTANT (K_b) :
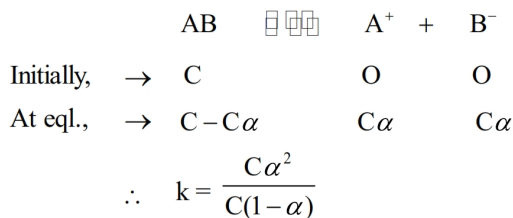
Let us consider the dissociation of weak base.

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

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

OSTWALD DILUTION LAW :

Let us consider the dissociation of weak electrolyte AB.

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

Initially,	$\rightarrow$	C	O	O
At eql.,	$\rightarrow$	$C - C\alpha$	$C\alpha$	$C\alpha$

$$\therefore \quad k = \frac{C\alpha^2}{C(1-\alpha)}$$

For very weak electrolytes

$$\alpha << 1$$

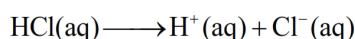$$\boxed{\therefore \alpha = \sqrt{\frac{k}{c}}} \quad \text{where k = dissociation constant.}$$

The degree of dissociation of weak electrolyte is proportional to square root of dilution.

$$\boxed{\alpha = \sqrt{\frac{Ka}{c}}} , \quad \boxed{\alpha = \sqrt{\frac{Kb}{c}}} \qquad \text{where, Ka = Acid dissociation constant}$$

$$\text{and} \qquad \text{Kb = Base dissociation constant}$$

CONCEPT OF ACID AND BASE

I. ARRHENIUS CONCEPT :

<u>Acid :</u> A substance which ionises in water to produce H^+ ion is acid.
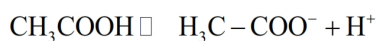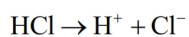
$$HCl(aq) \longrightarrow H^+(aq) + Cl^-(aq)$$

<u>Base :</u> A substance which produces $OH^-(aq)$ in water is called base.

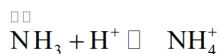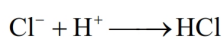$$NH_4OH(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

But the Arrhenius concept is limited to aqueous solutions and there are few other limitation in this theory.

II. THE BRONSTED-LOWRY'S CONCEPT

<u>Acid :</u> Proton (H^+) donor is acid

$$HCl \rightarrow H^+ + Cl^-$$

$$CH_3COOH \rightleftharpoons H_3C-COO^- + H^+$$

<u>Base :</u> Proton acceptor is base

$$Cl^- + H^+ \longrightarrow HCl$$

$$\overset{\cdot\cdot}{N}H_3 + H^+ \rightleftharpoons NH_4^+$$

Thus Cl^- and $\overset{\cdot\cdot}{N}H_3$ are Bronsted base.
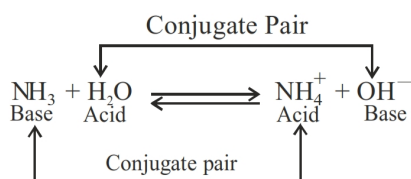
Conjugate acid-base pair

The acid base pair which differs by a proton (H^+) is called conjugate pair.

The conjugate pair of acid is always a base and that of a base it is always a acid.
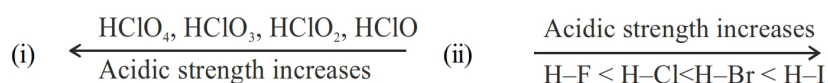
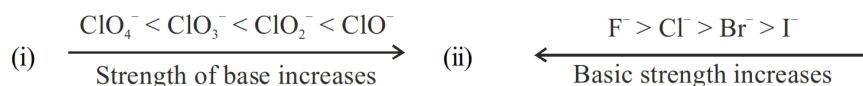$$\underset{\text{Base}}{NH_3} + \underset{\text{Acid}}{H_2O} \rightleftharpoons \underset{\text{Acid}}{NH_4^+} + \underset{\text{Base}}{OH^-}$$

Conjugate Pair (top)

Conjugate pair (bottom)

Amphoteric behaviour

Substance which can act as acid and base in different reaction is called amphoteric substance

$$\underset{\text{Acid}}{H-Cl} + \underset{\text{Base}}{H_2O} \rightleftharpoons H_3O^+ + Cl^-$$

$$\underset{\text{Base}}{NH_3} + \underset{\text{Acid}}{H_2O} \rightleftharpoons NH_4^+ + OH^-$$

Strength of Bronsted Acid and Base

(i) $\overleftarrow{\underset{\text{Acidic strength increases}}{HClO_4, HClO_3, HClO_2, HClO}}$

(ii) $\overrightarrow{\underset{H-F < H-Cl < H-Br < H-I}{\text{Acidic strength increases}}}$

The conjugate pair of strong acid is weak base and vice-versa.

(i) $\overrightarrow{\underset{\text{Strength of base increases}}{ClO_4^- < ClO_3^- < ClO_2^- < ClO^-}}$

(ii) $\overleftarrow{\underset{\text{Basic strength increases}}{F^- > Cl^- > Br^- > I^-}}$

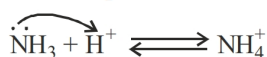## Hydrated protons and hydronium ions :

H^+ gets bonded to oxygen of H_2O to exist as H_3O^+ in aqueous solution. H_3O^+ is trigonal pyramidal.

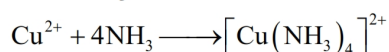Other hydrated species are $H_5O_2^+$, $H_7O_3^+$, $H_9O_4^+$.

III. Lewis Acid-Base Concept

Acid : Electron pair acceptor are Lewis acid

Base : Electron-pair donor is Lewis base

$$\overset{..}{N}H_3 + H^+ \rightleftharpoons NH_4^+$$

Since, NH_3 donates a electron pair, it is base.

$$Cu^{2+} + 4NH_3 \longrightarrow \left[Cu(NH_3)_4\right]^{2+}$$
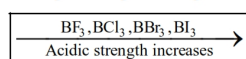
Here, Cu^{2+} accepts electron pair from NH_3 thus Cu^{2+} is acid.

Some Common Lewis Acids :

(a) Molecules in which central atom has incomplete octet due to the deficiency of at least a pair of electron are Lewis acid.

Examples - BF_3, BCl_3, $AlCl_3$, $MgCl_2$, $BeCl_2$ etc.

$\overrightarrow{\underset{\text{Acidic strength increases}}{BF_3, BCl_3, BBr_3, BI_3}}$

This can be explained by back-bonding concept.

(b) Simple Cations : H^+, Ag^+, Cu^+ etc.

(c) Molecules in which central atom has vacant d orbital : $SiCl_4, GeCl_4, TiCl_4, SnCl_4$, PCl_3, PCl_5, SF_4 etc

(d) Molecules having a multiple bond between atom of dissimilar electronegativity.

eg. - CO_2, SO_3, SO_2

Some Examples of Lewis base

(a) Neutral species having at least one lone pair of electron to donate are Lewis base.

$$eg. - \overset{\cdot\cdot}{N}H_3, \quad R - \overset{\cdot\cdot}{\underset{\cdot\cdot}{O}} - H \text{ etc.}$$
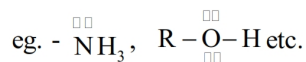
(b) Negatively charged species : Cl^-, Br^-, $\overset{\cdot\cdot}{N}H_2^-$

Ionic Product of water (kw) : Let us consider the self dissociation of H_2O.

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

$$\boxed{K_w = [H_3O^+][OH^-]}$$

The value of Kw increases with increase in temperature and at 25°C, Kw is 1×10^{-14}. since pure water is neutral, thus $[H_3O^+] = [OH^-]$

$$\therefore \left[H_3O^+\right] = \left[OH^-\right] = 10^{-7} \text{ moles litre}^{-1}$$

HYDROGEN ION CONCENTRATION AND pH SCALE :

This concept was given by sorenson in 1909.

$$pH = -\log[H_3O^+]$$

Thus pH is defined as the negative logarithm concentration (in moles per litre) of hydrogen ion.

Similarly, $pOH = -\log[OH^-]$

RELATION BETWEEN pH AND pOH :

$$\because [H_3O^+][OH^-] = Kw = 1 \times 10^{-14}$$

Taking negative log on both sides

$$\boxed{pH + pOH = pKw = 14}$$

where $pKw = -\log Kw$

pH Scale :

$[H^+]$	$[OH^-]$	pH	pOH	Nature of Solution
$10°$	10^{-14}	0	14	Strongly acidic
10^{-2}	10^{-12}	2	12	Acidic
10^{-5}	10^{-9}	5	9	Weakly acidic
10^{-7}	10^{-7}	7	7	Neutral
10^{-9}	10^{-5}	9	5	Weakly basic
10^{-11}	10^{-3}	11	3	Basic
10^{-14}	100	14	0	Strongly basic

BUFFER SOLUTION

A solution whose pH is not affected to great extent by the addition of few drop of either acid or base is called buffer solution.

(i) Acidic Buffer : $CH_3COOH + CH_3COONa$ - Weak acid its salts of any strong bases.

(ii) Alkaline Buffer : $NH_4OH + NH_4Cl$ - Weak acid and its salts of any strong acid.

HENDERSON EQUATION (pH OF A BUFFER):

For acidic buffer = $pH = -\log Ka - \log \dfrac{[Acid]}{[Salt]}$

or, $\boxed{pH = pKa + \log \dfrac{[Salt]}{[Acid]}}$

For Alkaline buffer : $\boxed{pOH = pKb + \log \dfrac{[salt]}{[Base]}}$

Buffer Capacity : The property of a buffer solution to resist any change in its pH value is called buffer capacity.

$$\text{Buffer Capacity} = \frac{\text{No. of moles of Acid or Base added to 1 litre}}{\text{Change in pH}}$$

HYDROLYSIS OF SALT

The reaction of salt with water is called its hydrolysis.

$$\text{Salt + water} \rightleftharpoons \text{Acid + Base}$$

1. **Hydrolysis of salt of Weak Acid with a strong Base**

    Examples : CH_3COONa , Na_2CO_3, KCN, Na_3PO_4, Na_2S, Borax etc.

    If K_h = hydrolysis constant of salt

    $\therefore \quad K_h = \dfrac{Kw}{Ka}$ ...(i)

    and degree of hydrolysis of salt is h

    $h = \sqrt{\dfrac{Kh}{C}}$ ...(ii)

    where C = initial molar concentration of salt

    Comparing Equation (i) and (ii)

    $\boxed{h = \sqrt{\dfrac{Kw}{Ka.C}}}$

    $\boxed{pH = 7 + \dfrac{1}{2}PKa + \dfrac{1}{2}\log C}$

2. **Hydrolysis of salt of strong acid and a weak base:**

    Examples : $(NH_4)_2 SO_4$, $CaNO_3$, $FeCl_3$ etc.

    $k_h = \dfrac{k_w}{k_b}$ and $\because h = \sqrt{\dfrac{K_h}{C}}$

    $\boxed{\therefore h = \sqrt{\dfrac{K_w}{K_b.C}}}$ and $\boxed{pH = 7 - \dfrac{1}{2}Pk_b - \dfrac{1}{2}\log C}$

3. Hydrolysis of salt of weak acid and a weak base
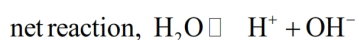
Examples : CH_3COONH_4, $BaCO_3$

$$K_h = \frac{K_w}{K_a \times K_b} \quad \text{and} \quad h = \sqrt{\frac{K_w}{K_a \times K_b}}$$

$$\boxed{pH = \frac{1}{2}(PK_w + Pk_a - Pk_b)}$$

4. Hydrolysis of salt of strong acid and strong base

Example   NaCl

$$Na^+ + Cl^- + H_2O \rightleftharpoons Na^+ + OH^- + H^+ + Cl^-$$

net reaction, $H_2O \rightleftharpoons H^+ + OH^-$

Thus, salt do not undergo hydrolysis.

SOLUBILITY PRODUCT

If a sparingly soluble salt (like AgCl, $BaSO_4$ etc) is put in water, very little amount of it dissolves in water and the solution becomes saturated. Equilibrium is established between the undissolved salt and the ions in solution.

$$\underset{\text{(Undissolved salt)}}{AB} \rightleftharpoons \underset{\text{(Ions in solution)}}{A^+ + B^-}$$

Applying the law of mass action, we get

$$K = \frac{\left[A^+\right]\left[B^-\right]}{\left[AB\right]} \quad \text{or} \quad K[AB] = [A^+][B^-]$$

But since only a little of the salt AB goes into solution, the concentration of undissolved salt nearly remains constant.

Hence, $K \times$ constant = Ksp

Where K_{sp} is another constant and is known as solubility product of the salt AB.

For general study let us discuss the sparingly soluble compound A_xB_y.

$$A_xB_y \rightleftharpoons x A^{y+} + yB^{x-}$$
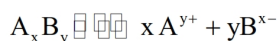
Hence the solubility product of such salt, $K_{sp} = [A^{y+}]^x \times [B^{x-}]^y$

From the above expression of solubility product, it is obvious that

(i) When the ionic product is equal to solubility product, the solution is just saturated, and no precipitation occurs.

(ii) When the ionic product is less than the solubility product, the solution is unsaturated and more of the salt can be dissolved in it, and thus no precipitation is observed.

(iii) When the ionic product exceeds the solubility product, the solution is super-saturated, and precipitation will occur.

Remember that solubility product of an electrolyte is a constant value at a particular temperature and it is the largest limit of ionic product of the electrolyte in solution.

Relation Between Solubility Product and Solubility

(i) For AB type : $\quad AB \rightleftharpoons \underset{S}{A^+} + \underset{S}{B^-}$

$$\therefore \; S = \sqrt{Ksp}$$

(ii) For ternary type (AB$_2$) : say Ag_2CrO_4, PbI_2, etc

$\quad K_{sp} = (2S)^2 \times S = 4S^3$

$\qquad S^3 = \dfrac{K_{sp}}{4}$

$$S = \left[\dfrac{K_{sp}}{4}\right]^{1/3}$$

(iii) For AB$_3$ type: e.g. Al(OH)$_3$

$\quad K_{sp} = [Al^{3+}]\,[OH^-]^3 = 27S^4$

$\qquad \Rightarrow S = \left(\dfrac{K_{sp}}{27}\right)^{1/4}$

(iv) For A$_3$B$_2$ type: e.g. Ca$_3$(PO$_4$)$_2$

$\quad K_{sp} = \left[Ca^{2+}\right]^3 \left[PO_4^{3-}\right]^2 = 108\,S^5$

$$S = \sqrt[5]{\dfrac{K_{sp}}{108}}$$