IONIC EQUILIBRIUM

INTRODUCTION

- **According to Conductivity Substances are of 2 types**

1. Non-Conductor : Those substances which do not show the flow of current or electricity.

Ex. Non - metals, plastic rubber, wood etc.

Exception – Graphite is a non-metal but show conductivity due to motion of free electrons.

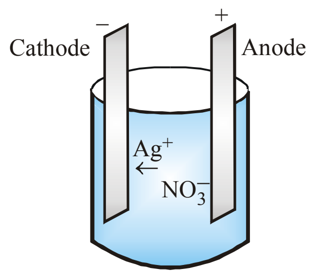
2. Conductors – Those substances which show conductivity or flow of current are called conductors and these are of 2 types :

(a) Metallic Conductor

Those conductor which show conductivity due to motion of free electrons.

Eg. All metals, Graphite

(b) Ionic Condutors : Those conductor which show conductivity due to movement of free ions. Ions are in free state in the solutions of ionic compounds. On passing electric current through the solution, ions move towards oppositely charged electrodes, i.e., the cation moves towards cathode (negative electrode) and the anion moves towards anode (positive electrode). Due to this reason, they are called cations and anions respectively. The current flows through the solution due to the movement of the ions.



Movement of ions through the solution of electrolyte ($AgNO_3$) towards oppositely charged electrodes

DEGREE OF DISSOCIATION

- When an electrolyte is dissolved in a solvent (H_2O), it spontaneously dissociates into ions.
- It may dissociate partially ($\alpha <<< 1$) or sometimes completely ($\alpha \cong 1$)

Ex.
$$NaCl + aq \longrightarrow Na^+(aq) + Cl^-(aq)$$
$$CH_3COOH \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$$

- The degree of dissociation (α) of an electrolyte is the fraction of one mole of the electrolyte that has dissociated under the given conditions.

$$\alpha = \frac{\text{No. of moles dissociated}}{\text{No. of moles taken initially}}$$

- **According to Strength Electrolyte are of 2 types :**

1. Strong Electrolyte : Those ionic conductors which are completely ionized in aqueous solution are called as strong electrolyte.

Ex. Na^+Cl^-, K^+Cl^-, etc.

For strong electrolyte ionisation is 100%.

i.e. $\alpha = 1$

Ex.

(a) Strong acid $\rightarrow$ H_2SO_4, HCl, HNO_3 $HClO_4$, H_2SO_5, HBr, HI

(b) Strong base $\rightarrow$ KOH, NaOH, $Ba(OH)_2$ CsOH, RbOH

(c) All water soluble salts $\rightarrow$ NaCl, KCl, $CuSO_4$..........

2. **Weak Electrolytes :** Those electrolytes which are partially ionized in aqueous solution are called as weak electrolytes. For weak electrolytes the value of α is less than one.

Ex.

(a) Weak acid $\rightarrow$ HCN, CH_3COOH, HCOOH, H_2CO_3, H_3PO_3, H_3PO_2, $B(OH)_3$,
$\downarrow$
H_3BO_3
(boric acid)

(b) Weak base $\rightarrow$ NH_4OH, $Cu(OH)_2$, $Zn(OH)_2$, $Fe(OH)_3$, $Al(OH)_3$

(c) All sparingly soluble salts like AgCl, AgBr, $PbSO_4$, etc.

FACTORS AFFECTING THE VALUE OF DEGREE OF DISSOCIATION

(1) Temperature $\rightarrow$ On increasing temperature ionization increases so, α increases

(2) Nature of electrolyte

(i) Strong electrolyte $\alpha = 100\ \%$ (ii) Weak elecrolyte $\alpha < 100\ \%$

(3) Nature of solvent

If Dielectric constant μ of solvent increases, then the value of α increases.

$H_2O \rightarrow \mu = 81$
$D_2O \rightarrow \mu = 79$
$C_6H_6 \rightarrow \mu = 2.5$
$CCl_4 \rightarrow \mu = 0$

Ex. Which one is greater α_1 or α_2 for the following equation :

(i) $NH_4OH + H_2O \rightarrow \alpha_1$ (ii) $NH_4OH + D_2O \rightarrow \alpha_2$

Sol. Dielectric constant of H_2O is more than that of D_2O , so $\alpha_1 > \alpha_2$

Ex. Which one is greater α_1 or α_2 for the following equations :

(i) $HCN + CCl_4 \rightarrow \alpha_1$ (ii) $HCN + C_6H_6 \rightarrow \alpha_2$

(A) $\alpha_1 > \alpha_2$ **(B)** $\alpha_2 > \alpha_1$ **(C)** $\alpha_1 = \alpha_2$ **(D)** None **Ans. (B)**

Sol. $\because$ $\mu(CCl_4) = 0$ and $\mu(C_6H_6) = 2.5$

So, $\alpha_2 > \alpha_1$

5. Mixing of Ions

Common Ion Effect	Odd Ion Effect
$NH_4OH \rightleftharpoons NH_4^+ + OH^-$	$NH_4OH \rightleftharpoons NH_4^+ + OH^-$
On mixing NH_4Cl	On mixing HCl
$NH_4Cl \rightarrow NH_4^+ + Cl^-$	$HCl \rightarrow H^+ + Cl^-$
Due to mixing of common ion concentration of ammonium ion will increase therefore equilibrium will shift in backward direction i.e. rate of backward reaction increases means α decreases.	Due to mixing of odd ions concentration of OH^- will decrease $\therefore$ Equilibrium will shift in forward direction i.e. rate of forward reaction increases, means a increases

Common Ion Effect : The decrease in degree of inonisation of a weak electrolyte in presence of a strong electrolyte having a common ion is called common ion effect.

For example when HCl is added in a solution containing CH_3COOH, the following equilibria exists :

$$\underset{C - C\alpha}{CH_3COOH(aq.)} \rightleftharpoons \underset{C\alpha}{CH_3COO^-(aq.)} + \underset{(C_1 + C\alpha)}{H^+(aq.)} \qquad ...(1)$$

$$\underset{C_1}{HCl(aq.)} \rightarrow \underset{C_1}{H^+(aq.)} + \underset{C_1}{Cl^-(aq.)} \qquad ...(2)$$

$$Ka = \frac{\alpha[C_1 + c\alpha]}{1-\alpha}$$

when HCl is added the concentration of H^+ will increase in solution and therefore equilibrium (1) will shift backward as a result of which the degree of ionisation of CH_3COOH will decrease

Ex. Calculate concentration of each species at equlibrium containing –

(i) 0.1 M NH_4OH only

(ii) 5.35 g/L NH_4Cl along with 0.1 M NH_4OH ($k_b = 1.8 \times 10^{-5}$)

Sol. (i) $$\underset{0.1 - 0.1\alpha}{NH_4OH(aq)} \rightleftharpoons \underset{0.1\alpha}{NH_4^+(aq)} + \underset{0.1\alpha}{OH^-(aq)}$$

$$k_b = \frac{0.1\alpha^2}{(1-\alpha)} \Rightarrow \therefore \alpha = \sqrt{\frac{k_b}{C}} = \sqrt{\frac{1.8\times10^{-5}}{0.1}} = \sqrt{1.8\times10^{-4}} = 1.34 \times 10^{-2}.$$

$\therefore \quad \alpha = 0.0134$

$[NH_4^+] = [OH^-] = c\alpha$

$= 0.1 \times 1.34 \times 10^{-2} = 1.34 \times 10^{-3}$

(ii) $$\underset{0.1 - 0.1\,\alpha}{NH_4OH} \rightleftharpoons \underset{(0.1\,\alpha + 0.1)}{NH_4^+} + \underset{0.1\alpha}{OH^-}$$

$$\underset{0.1\ M}{NH_4Cl} \longrightarrow \underset{0.1}{NH_4^+} + \underset{0.1}{Cl^-}$$

$$\frac{5.35\ g/L}{53.5\ g}$$

$$k_b = \frac{0.1(1+\alpha)\times 0.1\alpha}{0.1(1-\alpha)}$$

$$k_b = \frac{0.1(1+\alpha).1\alpha}{(1-\alpha)}$$

$a << 1 \qquad \therefore\ 1 + \alpha \approx 1 \quad$ and $\quad 1 - \alpha \approx 1$

$k_b = 0.1 \times \alpha = 1.8 \times 10^{-5}$

$\alpha = 1.8 \times 10^{-4}$

$\alpha = 0.00018$

Ex. The solubility product of $Mg(OH)_2$ is 1.2 x 10¯11. What minimum OH^- concentration must be attained (for example, by adding NaOH) to decrease the Mg^{2+} concentration in a solution of $Mg(NO_3)^2$ to less than 1.1×10^{-10} M?

Sol. K_{sp} expression:

$K_{sp} = [Mg^{2+}] [OH^-]^2$

We set $[Mg^{2+}] = 1.1 \times 10^{-10}$ and $[OH^-] = x$. Substituting into the K_{sp} expression:

$1.2 \times 10^{-11} = (1.1 \times 10^{-10}) (x)^2$

$x = 0.33$ M

Any sodium hydroxide solution greater than 0.33 M will reduce the $[Mg^{2+}]$ to less than 1.1×10^{-10} M.

Ex. Calculate the number of moles of Ag_2CrO_4 that will dissolve in 1.00 L of 0.010 M K_2CrO_4 solution. K_{sp} for $Ag_2CrO_4 = 9.0 \times 10^{-12}$.

Sol. 1) Concentration of dichromate ion from potassium chromate : 0.010 M

2) Calculate solubility of Ag+:

$K_{sp} = [Ag^+]^2 [CrO_4^{2-}]$

$9.0 \times 10^{-12} = (x)^2 (0.010)$

$x = 3.0 \times 10^{-5}$ M

Since there is a 2:1 ratio between the moles of aqueous silver ion and the moles of silver chromate that dissolved, 1.5×10^{-5} M is the molar solubility of Ag_2CrO_4 in 0.010 M K_2CrO_4 solution.

Since we were asked for the moles of silver chromate that would disolve in 1.00 L, the final answer is:

1.5×10^{-5} mol

Weak Electrolyte : A weak electrolyte is a substance which forms ions in an aqueous solution but does not dissociate completely. When dissolved, a weak electrolyte does not disperse completely into ions. The solution instead contains both ions and molecules. Some examples of weak electrolytes are carbonic acid, acetic acid and ammonia

OSTWALD'S DILUTION LAW (for weak electrolyte's)

- For a weak electrolyte A^+B^- dissolved in water, if α is the degree of dissociation then

	AB $\rightleftharpoons$	A^+	+ B^-
initial conc.	C	0	0
conc-at eq.	$C(1-\alpha)$	$C\alpha$	$C\alpha$

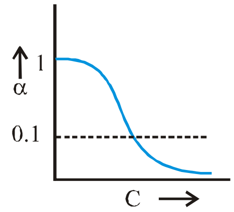
Then according to law of mass action,

$$K_a = \frac{[A^+][B^-]}{[AB]} = \frac{C\alpha.C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)} = \text{dissociation constant of the weak electrolyte}$$

If α is negligible in comparison to unity $1 - \alpha \simeq 1$. so $k_{eq} = \alpha^2 C \Rightarrow$ $\boxed{\alpha = \sqrt{\frac{k_{eq}}{C}}}$

$$\alpha \propto \frac{1}{\text{concentration}} \propto \text{volume} \qquad \left[\text{as concentration} = \frac{\text{mass}}{\text{volume}}\right]$$

- **as concentration increases ⇒ α decreases**
- **at infinite dilution α reaches its maximum value, unity i.e. A weak electrolyte will as a strong electrolyte at infinite dilution.**



ACIDS BASES AND SALTS

Arrhenius Concept

Arrhenius Acid : Substance which gives H^+ ion on dissolving in water (H^+ donor)

Ex. HNO_3, $HClO_4$, HCl, HI, HBr, H_2SO_4, H_3PO_4 etc.

- H_3BO_3 is not Arrhenius acid. (it is a lewis base)
- H^+ ion in water is extremely hydrated (in form of H_3O^+, $H_5O_2^+$, $H_7O_3^+$, general form $H^+(H_2O)_n$
- The structure of solid $HClO_4$ is studied by X-ray, It is found to be consisting of H_3O^+ and ClO_4^-

$$HClO_4 + H_2O \rightleftharpoons H_3O^+ + ClO_4^- \text{ (better representation)}$$

Arrhenius Base : Any substance which releases OH^- (hydroxyl) ion in water (OH^- ion donor)

- OH^- ion is present also in hydrated form of $H_3O_2^-$, $H_7O_4^-$, $H_5O_3^-$ .general form $OH^-(H_2O)_n$
- First group elements (except Li.) form strong bases

Limitation of Ostwald Dilution Law

(1) It is not applicable for strong electrolyte

(2) It is not applicable for saturated solution.

Modified Arrhenius Concept

It rectifies most of the above limitations

(i) Water is weak electrolyte and ionises to a very weak extent.

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

$$H^+ + H_2O \rightleftharpoons H_3O^+$$

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

Above reaction is called Autoionisation or selfionisation of water.

(ii) Water is neutral in nature i.e.

$$[H_3O^+] = [OH^-]$$

(iii) The substances which increase the H_3O^+ ion concentration act as acids and while those which increase OH^- ion concentration act as bases.

Ex.

(a) $SO_2 + H_2O \longrightarrow H_2SO_3 \xrightleftharpoons{H_2O} H_3O^+ + HSO_3^-$

Acid

(b) $NH_3 + H_2O \longrightarrow NH_4OH \xrightleftharpoons{H_2O} NH_4^+ + OH^-$

Base

Basicity or Protocity of an Acid

Types of bases

- Mono acidic base
  - Gives single OH^- per molecule e.g CsOH, RbOH NH_4OH
- Di acidic base
  - Gives two OH^- per molecule e.g $Ba(OH)_2$, $Ca(OH)_2$
- Tri acidic basic
  - Gives three OH^- per molecule e.g $Fe(OH)_3$

It is number of H^+ ions furnished by a molecule of an acid. An acid may be classified according to its basicity. Thus we may have,

(i) Mono basic or Mono protic acids like HCl, HNO_3, CH_3COOH, HCN etc.

(ii) Dibasic or Diprotic acids like, H_2SO_4, H_2CO_3, H_2SO_3, H_2S etc.

(iii) Tribasic or Triprotic acids like H_3PO_4,H_3AsO_4 etc.

Acidity or Hydroxity of a Base

Types of acids

- Mono basic acid
  - Gives single H^+ per molecule e.g HA (HNO_3, $HClO_4$, HCl)
- Di basic acid
  - Gives two H^+ per molecule e.g H_2A (H_2SO_4, H_3PO_3)
- Tri basic acid
  - Gives three H^+ per molecule e.g H_3A (H_3PO_4)

It may be defined as the number of OH^- ions furnished by a molecule of a base. A base can be,

(i) Mono acidic or Monohydroxic like NaOH, NH_4OH, AgOH etc.

(ii) Diacidic or dihydroxic like $Ba(OH)_2$, $Mg(OH)_2$, $Ca(OH)_2$, $Sr(OH)_2$ etc.

(iii) Triacidic or trihydroxic like $Fe(OH)_3$, $Al(OH)_3$ etc.

Strength of Acid or Base

(i) Strength of Acid or Base depends on the extent of its ionisation. Hence equilibrium constant K_a or K_b respectively of the following equilibria give a quantitative measurement of the strength of the acid or base.

(ii) $HA + H_2O \rightleftharpoons H_3O^+ + A^-$;

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

(iii) Similarly

$$B + H_2O \rightleftharpoons BH^+ + OH^-;$$

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$ here H_2O is szolvent.

KEY POINTS

(i) The other ways to represent above equilibrium is :

(a) $HA \xrightleftharpoons{H_2O} H^+ + A^-$; $K_a = \dfrac{[H^+][A^-]}{[HA]}$

(b) $BOH \xrightleftharpoons{H_2O} B^+ + OH^-$; $K_b = \dfrac{[B^+][OH^-]}{[BOH]}$

(ii) The larger the value of K_a or K_b, the more complete the ionisation, the higher the concentration of H_3O^+ or OH^- and stronger is the acid or base.

EXAMPLE BASED ON : ARRHENIUS CONCEPT

Ex. The characteristics of an acid is :

(A) turns blue litmus to red. **(B)** turns phenolphthalein pink from colourless.

(C) decompose carbonates **(D)** oxy compounds of non-metals

Sol. **(A)**, Statement **(A)** indicates characteristic of acid.

Ex. Arrhenius theory of acid-base is not applicable in :

(A) aqueous solution **(B)** in presence of water **(C)** non-aqueous solutions **(D)** none of the above

Sol. **(C)**, since Arrhenius theory is only applicable to aqueous medium.

Ex. Select the suitable reason (s) for higher strength of an acid or base :

(A) higher value of K_a or K_b **(B)** higher extent of ionisation

(C) **(A)** and **(B)** both **(D)** Larger number of replaceable H atoms.

Sol. **(C)**, K_a or K_b and degree of ionisation are the measure of strength of an acid or base.

Ex. The basicity of phosphorous acid is :

(A) 1 **(B)** 2 **(C)** 3 **(D)** 4

Sol. **(B)**, Phosphorous acid has two replaceable H^+ ions.

- **BRONSTED - LOWERY CONCEPT : (CONJUGATE ACID - BASE CONCEPT) (PROTONIC CONCEPT)**

Acid : substances which donate H^+ are Bronsted Lowery acids (H^+ donor)

Base : substances which accept H^+ are Bronsted Lowery bases (H^+ acceptor)

- **Conjugate Acid - Base Pairs**

These are the species which differ by one H^+ ion.

Conjugate acid are the species fromed after adding one H^+ to a base or removal of one OH^-

Ex. $NH_3 + H^+ \rightarrow NH_4^+$

base Conjugate acid

Ex. $NaOH \rightarrow Na^+ + OH^-$

base Conjugate acid

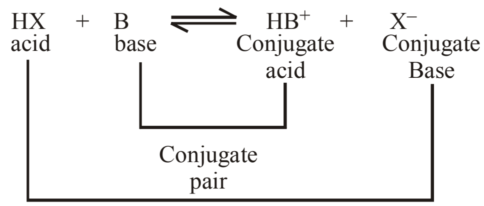
Conjugate base are the species fromed after removal of one H^+ ion from an acid

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

acid Conjugate base

Ex. $H_2SO_4 \rightarrow H^+ + HSO_4^-$
acid Conjugate base
In a typical acid base reaction

$$HX + B \rightleftharpoons X^- + HB^+$$



- Forward reaction - Here HX being a proton donor is an acid
  B being a proton acceptor is a base.
- Backward reaction - Here HB^+ being a proton donor is an acid
  X^- being a proton acceptor is a base.

	Acid		Base		Conjugate Acid		Conjugate Base
•	HCl	+	H_2O	$\rightleftharpoons$	H_3O^+	+	Cl^-
•	HSO_4^-	+	NH_3	$\rightleftharpoons$	NH_4^+	+	SO_4^{-2}
•	$[Fe(H_2O)_6]^{3+}$	+	H_2O	$\rightleftharpoons$	H_3O^+	+	$[Fe(H_2O)_5(OH)]^{2+}$

- Conjugate acid - base pair differ by only one proton.
- Strong acid will have weak conjugate base and vise versa.
- Reaction will always proceed from strong acid to weak acid or from strong base to weak base.

	Acid	Conjugate base	Base	Conjugate acid
Ex :	HCl	Cl^-	NH_3	NH_4^+
	H_2SO_4	HSO_4^-	H_2O	H_3O^+
	HSO_4^-	SO_4^{2-}	RNH_2	RNH_3^+
	H_2O	OH^-		

Amphoteric : Substances which can act as acid as will as base are known as amphoteric

$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$$
base

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$
acid

Amphiprotic : An amphiprotic molecule (or ion) can either donate or accept a proton, thus acting either as an acid or a base. Water, amino acids, hydrogen carbonate ions and hydrogen sulfate ions are common examples of amphiprotic species. Since they can donate a proton, all amphiprotic substances contain a hydrogen atom.

Ex. $H_2O + S^{2-} \rightleftharpoons OH^- + HS^-$

$H_2O + HSO_4^- \rightleftharpoons H_3O^+_{(aq)} + SO_4^{2-}{}_{(aq)}$

- According to this concept, neutralisation is a process of transfer of a proton from an acid to a base.

(a) $CH_3COOH + NH_3 \rightleftharpoons NH_4^+ + CH_3COO^-$

(b) $NH_4^+ + S^{2-} \rightleftharpoons HS^- + NH_3$

(c) $[Fe(H_2O)_6]^{3+} + H_2O \rightleftharpoons H_3O^+ + [Fe(H_2O)_5(OH)]^{2+}$

- An acid–base reaction always proceeds in the direction of formation of the weak acid and the weak base. In the equilibrium,

  $$\underset{\text{Strong acid}}{HA} + \underset{\text{Strong base}}{H_2O} \rightleftharpoons \underset{\text{Weak acid}}{H_3O^+} + \underset{\text{Weak base}}{A^-}$$

  In general "The conjugate base of a strong acid is always a weak base and the conjugate base of a weak acid is always a strong base."

- A number of organic compounds containing oxygen, can accept protons and thus act as bases.

  Ex.

  (a) $$\underset{\text{Ethanol}}{C_2H_5\ddot{O}H} + H_2SO_4 \rightleftharpoons \underset{\text{(Oxonium ion)}}{C_2H_5\overset{+}{\ddot{O}}H_2} + HSO_4^-$$

  (b) $$\underset{\text{Ethylether}}{(C_2H_5)_2\ddot{O}:} + HCl \rightleftharpoons \underset{\text{Oxonium ion}}{(C_2H_5)_2\overset{+}{\ddot{O}}:H} + Cl^-$$

- Bronsted lowery concept does not differ appreciably from the Arrhenius theory for aqueous solution only.
- Autoionisation or Autoprotolysis or Self ionisation

  $$\underset{\text{acid}}{H_2O} + \underset{\text{base}}{H_2O} \rightarrow H_3O^+ + OH^-$$

  $$\underset{\text{acid}}{NH_3} + \underset{\text{base}}{NH_3} \rightarrow NH_4^+ + NH_2^-$$

  $$\underset{\text{acid}}{H_2SO_4} + \underset{\text{base}}{H_2SO_4} \rightarrow H_3SO_4^+ + HSO4^-$$

- A **limitation** of the Bronsted Lowery theory is that the extent to which a dissolved substance can act as an acid or a base depends largly on the solvent.

  (a) $$\underset{\text{Acid}}{HClO_4} + \underset{\text{Base}}{HF} \rightleftharpoons \underset{\text{Acid}}{H_2F^+} + \underset{\text{Base}}{ClO_4^-}$$ ($HClO_4$ acts as a acid in HF)

  (b) HNO_3 behaves as base in $HClO_4$ and HF

  $$\underset{\text{(base)}}{HNO_3} + \underset{\text{(acid)}}{4HF} \rightleftharpoons H_3O^+ + NO_2^+ + 2HF_2^-$$

  (c) Urea is weak acidic in liquid NH_3

  $$\underset{\text{Acid}}{NH_2CONH_2} + \underset{\text{Base}}{NH_3} \longrightarrow \underset{\text{Acid}}{NH_4^+} + \underset{\text{Base}}{NH_2CONH^-}$$

Note: H_2SO_4 also acts as base in HF solvent.

Classification of Bronsted - Lowery Acids and Bases

Bronsted - Lowery acids and bases can be

(i) Molecular (ii) Cationic and (iii) Anionic

Table - 1

Type	Acid	Base
Molecular	HCl, HNO_3, $HClO_4$, H_2SO_4, H_3PO_4, H_2O etc.	NH_3, N_2H_4, Amines, H_2O, Alcohol, Ethers etc.
Cationic	NH_4^+, $N_2H_5^+$, PH_4^+, Na^+, Ba^{2+} (All cations) $[Fe(H_2O)_6]^{3+}$, $[Al(H_2O)_6]^{3+}$ etc.	$[Fe(H_2O)_5OH]^{2+}$ $[Al(H_2O)_5OH]^{2+}$ etc.
Anionic	HS^-, HSO_3^-, $H_2PO_4^-$, HSO_4^- HCO_3^-, HPO_4^{2-} etc. all amphiprotic anions	Cl^-, Br^-, OH^-, HSO_4^-, CN^-, CO_3^{2-}, SO_4^{2-}, NH_2^-, CH_3COO^- etc. all anions.

Reactions in Non-Aqueous Solvents

(i) Solvents like C_6H_6, CCl_4, THF (Tetrahydrofuran), DMF (N, N-dimethyl formamide) etc. are used in organic chemistry. In inorganic chemistry reactions are generally studied in water. However a large number of non–aqueous solvents (such as Glacial acetic acid, Hydrogen halides, SO_2 etc.) have been introduced in inorganic chemistry.

(ii) The physical properties of a solvent such as M.P., B.P., Dipole moment and Dielectric constant are of importance in deciding its behaviour.

Classification of Solvents

There are two types of solvents

(i) Protonic (protic) and (ii) Aprotic

(i) Protonic or Protic Solvents

(i) They are characterized by the presence of a transferable hydrogen and the formation of "Onium" ions Autoionisation taking place in them.

Ex. (a) $H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$

(b) $NH_3 + NH_3 \rightleftharpoons NH_4^+ + NH_2^-$

(c) $3HX \rightleftharpoons H_2X + HX_2^-$

(d) $2H_2SO_4 \rightleftharpoons H_3SO_4^+ + HSO_4^-$

(ii) Protonic solvents may be

(a) Acidic (Anhydrous sulphuric acid, liquid HF, Glacial acetic acid etc.)

(b) Basic (liquid NH_3)

(c) Amphiprotic (H_2O, proton containing anions)

(ii) Aprotic Solvents

Such solvents do not have replaceable hydrogen in them. These can be classified into three categories

(a) Non polar or very weakly polar, nondissociated liquids, which do not solvate strongly.

Ex. CCl_4, hydrocarbons, C_6H_6, C_6H_{12} etc.

(b) Non-ionised but strongly solvating, generally polar solvents.

Ex. Acetonitrile CH_3CN, DMF, DMSO (dimethyl sulfoxide), THF and SO_2.

(c) Highly polar, autoionising solvents.

Ex. Inter halogen compounds (BrF_3, IF_5 and trichloro phosphine)

(a) $2\,BrF_3 \rightleftharpoons BrF_2^+ + BrF_4^-$

(b) $2\,IF_5 \rightleftharpoons IF_4^+ + IF_6^-$

(c) $2Cl_3PO \rightleftharpoons Cl_2PO^+ + Cl_4PO^-$

Levelling Solvents

(i) The Bronsted - Lowery theory can be extended to acid - base reactions in non-aqueous solvents. It can be used in differentiating the acid strength of a particular acid and in titration of weak bases.

(ii) In water solvent, mineral acids appear to be equally strong because of their complete ionisation, water is called here a **levelling solvent** because it levels all the acids to the same strength.

(iii) If instead of water solvent, we take mineral acids in pure acetic acid solvent (which is poor proton acceptor as compared to water) it is found acids become weak and can be differentiated.

Ex. $HCl + CH_3COOH \rightleftharpoons Cl^- + CH_3COOH_2^+$

Acid Base Base Acid

In above example acetic acid and Cl^- ions both compete for protons and the former being a poor proton acceptor does it much less effectively than water. Thus HCl in acetic acid solvent appears to be a much weaker acid than that in water.

(iv) Mineral acids in acetic acid solvent follow the following order of their strengths.

$HNO_3 < HCl < H_2SO_4 < HBr < HClO_4$

(v) A weak base like acetamide or acetanilide in aqueous medium can not be titrated with acids. If how ever, the weak base is taken in glacial acetic acid solvent, the former behaves as a strong base and can be titrated. This is because acetic acid (which acts as a better proton donor) exerts a levelling effect on the base.

Lux - Flood Concept (1939 & 1947)*

(i) The proton plays an important role in explaining the acid-base behaviour in the Bronsted-Lowery concept. **Lux** observed that acid - base reactions are also feasible in oxide systems without the aid of protons.

(ii) Above approach was extended by **Flood** and applied to non-protonic systems, which were not covered by the Bronsted Lowery concept.

(iii) According to this concept a base (like CaO, BaO or Na_2O) is an oxide ion (O^{2-}) donor and an acid (like SiO_2, CO_2 or P_4O_{10}) is an oxide ion (O^{2-}) acceptor.

Ex. Base Acid

(a) $CaO + SiO_2 \longrightarrow CaSiO_3$

(b) $6Na_2O + P_4O_{10} \longrightarrow 4Na_3PO_4$

(iv) Substances are termed amphoteric if they show a tendency of losing as well as accepting an oxide ion.

Ex. $ZnO, Al_2O_3, BeO, Ga_2O_3$

KEY POINTS

(i) The concept is particularly applicable to reactions which take place at high temperature i.e. in metallurgical operations or during the manufacture of ceramics and glass.

(ii) The approach can be extended to include other negative ion systems (like halides, sulphide or carbanion).

Example based on : Bronsted - Lowery Concept

Ex. Select the aprotic solvent from the following is :

(A) H_2O **(B)** C_6H_6 **(C)** HF **(D)** NH_3

Sol. **(B)** according to the classification of solvents.

Ex. The strongest conjugate base is -

(A) Cl^- **(B)** CH_3COO^- **(C)** SO_4^{2-} **(D)** NO_2^-

Sol. **(B)** CH_3COOH is weakest acid among HCl, CH_3COOH, HSO_4^- and HNO_2.

Ex. Which is the strongest Bronsted base in the following anions :

(A) ClO^- **(B)** ClO_2^- **(C)** ClO_3^- **(D)** ClO_4^-

Sol. **(A)**, HClO is weakest acid among HClO, $HClO_2$, $HClO_3$ and $HClO_4$.

Ex. Give appropriate equation and label acid and base.

Sol. $NH_2CONH_2 + NH_3 \longrightarrow NH_4^+ + NH_2CONH^-$

Acid base Acid base

In liquid NH_3 solution urea can show weak acidic nature.

Ex. Ammonium ion is-

(A) A Lewis acid **(B)** Lewis base **(C)** Bronsted acid **(D)** Bronsted base **Ans. (C)**

Sol. Correct answer is **(C)**

Self Practice Problem

1. (a) Write conjugate acids of

SO_4^{2-}, RNH_2, NH_2^-, F^-

(b) Write conjugate base of

HNO_2, OH^-, H_2CO_3, $HClO_4$.

(c) Write conjugate acids and conjugate base of amphoteric species.

HS^-, NH_3, H_2O, HSO_4^-

2. Which of the following is the strongest base-

(A) NH_2^- **(B)** CH_3COO^- **(C)** $C_2H_5O^-$ **(D)** OH^- **Ans. (A)**

Lewis Concept (Electronic Concept)

- An acid is a molecule/ion which can accept an electron pair with the formation of a coordinate bond.

  Acid $\rightarrow$ e^- pair acceptor

  Ex. Electron deficient molecules : BF_3, $AlCl_3$

  Cations : H^+, Fe^{2+}, Na^+

  Molecules with vacant orbitals : SF_4, PF_3

- A base is any molecule/ion which has a lone pair of electrons which can be donated.

  Base $\rightarrow$ (One electron pair donate)

  Ex. Molecules with lone pairs : NH_3, PH_3, H_2O, CH_3OH

Ex. In which of the following reaction does NH_3 act as an acid ?

(A) $NH_3 + H^+ \longrightarrow NH_4^+$ **(B)** $NH_3 + Na \longrightarrow NaNH_2 + \frac{1}{2} H_2$

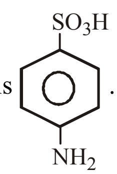
(C) $NH_3 + HCl \longrightarrow NH_4Cl$ **(D)** none of these

Sol. **(B)**

In the following reaction, NH_3 changes of $NaNH_2$ which contains NH_2 ion. This means that NH_3 has donated a proton to Na and hence acts as an acid.

Ex. Sulphanilic acid is a/an

(A) Arrhenius acid **(B)** Lewis base **(C)** Neither (A) or (B) **(D)** Both (A) and (B)

Sol. **(D)** Sulphanilic acid is 

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The SO_3H group is capable of donating H^+ and hence it acts as arrhenius acid while nitrogen in the NH_2 group contains lone pair of electrons and hence can act as lewis base by donating it.

Properties of Water

Amphoteric (Amphiprotic) Acid/Base Nature

Water - an acid as well as base according to Bronsted - Lowry theory but according to Lewis concept it can only be taken as base only.

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

Molar Concentration / Molarity of Water

Molarity $= \text{No. of moles/litre} = \dfrac{1000\,g / \text{litre}}{18\,g / \text{mole}} = 55.55$ mole/litre $= 55.55$ M (density $= 1$ g/cc)

Ionic Product of Water

According to arrhenius concept

$$H_2O \rightleftharpoons H^+ + OH^- \quad \text{so, ionic product of water,} \quad k_w = [H^+][OH^-] = 10^{-14} \text{ at } 25° \text{ (exp.)}$$

Dissociation of water is endothermic, so on increasing temperature K_{eq} increases.

K_w increases with increase in temperature.

- Ionic product of water is always a constant whatever has been dissolved in water since its an equilibrium constant so will be dependent only on temperature.

• Degree of Dissociation of Water

$$H_2O \rightleftharpoons H^+ + OH^- \Rightarrow \alpha = \frac{\text{no. of moles dissociated}}{\text{Total no. of moles initially taken}}$$

$$= \frac{10^{-7}}{55.55} = 18 \times 10^{-10} \text{ or } 1.8 \times 10^{-7}\%$$

• Absolute Dissociation Constant of Water

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

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

Acidity and pH Scale

- Acidic strength means the tendency of an acid to give H_3O^+ or H^+ ions in water.
  So greater then tendency to give H^+, more will be the acidic strength of the substance.
- Basic strength means the tendency of a base to give OH^- ions in water.
  So greater the tendency to give OH^- ions, more will be basic strength of the substance.
- The concentration of H^+ ions is written in a simplified form introduced by Sorenson known as pH scale. pH is defined as negative logarithm of activity of H^+ ions.

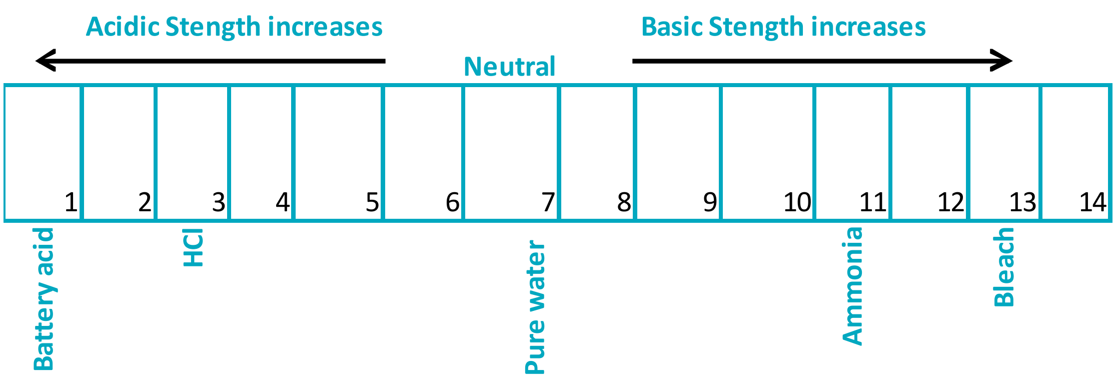
activity (a) = $\gamma \cdot \frac{C}{C_o}$ $\qquad$ C → unitless, C_o → standard concentration

$a = \gamma . C$

for dilute solution: $\gamma = 1$, $\therefore a = C = [H^+]$

for concentrated solution: $\gamma \neq 1$

$\therefore$ $pH = -\log a_{H^+}$ (where a_{H^+} is the activity of H^+ ions)



- Activity of H^+ ions is the concentration of free H^+ ions or H_3O^+ ions in a solution.
- The pH scale was marked from 0 to 14 with central point at 7 at 25 °C taking water as solvent.
- If the temperature and the solvent are changed, the pH range of the scale will also change. For example

0 - 14	at 25 °C ($K_w = 10^{-14}$)	Neutral point, pH = 7
0 - 13	at 80 °C ($K_w = 10^{-13}$)	Neutral point, pH = 6.5

- pH can also be negative or > 14

– pH Calculation 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,
so $[H^+]$ = normality of strong acid solution

(ii) If concentration is less than 10^{-6} M
In this case H^+ ions coming from water cannot be neglected.
So $[H^+]$ = normality of strong acid + H^+ ions coming from water in presence of this strong acid

– **Solved Examples**

Ex. Calculate pH of 10^{-8} M HCl solution.

Sol. $H_2O \rightleftharpoons H^+ + OH^-$

$10^{-8}+x \qquad x$

$k_w = [H^+][OH^-]$

$10^{-14} = x(x+10^{-8})$

$\Rightarrow x^2 + x \times 10^{-8} - 10^{-14} = 0$

$$x = \frac{-10^{-8} \pm \sqrt{10^{-16} + 4 \times 10^{-14}}}{2} = \frac{-10^{-8} + 10^{-7}\sqrt{4 + \frac{1}{100}}}{2} = \frac{(\sqrt{401}-1)10^{-8}}{2} = 0.95 \times 10^{-7}$$

$[H^+] = 10.5 \times 10^{-8} = 1.05 \times 10^{-7}$

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

$pH = 7 - \log 1.05 \approx 6.98$

10^{-9} M HCl pH ≈ 7

10^{-16} M HCl pH ≈ 7

(b) **Strong Base Solution :** Calculate the $[OH^-]$ which will be equal to normality of the strong base solution and then use $K_w = [H^+] \times [OH^-] = 10^{-14}$, to calculate $[H^+]$

Ex. Calculate pH of 10^{-7} M of NaOH solution

Sol. $[OH^-]$ from NaOH $= 10^{-7}$

$[OH^-]$ from water $= x < 10^{-7}$ M (due to common ion effect)

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

$- \qquad (x + 10^{-7}) \qquad x$

$K_w = [H^+][OH^-] = 10^{-14} = x(x+10^{-7})$

$x^2 + 10^{-7}x - 10^{-14} = 0$

$$\Rightarrow x = \frac{\sqrt{5}-1}{2} \times 10^{-7} = 0.618 \times 10^{-7} \qquad (\sqrt{5} = 2.236)$$

$[OH^-] = 10^{-7} + 0.618 \times 10^{-7} = 1.618 \times 10^{-7}$

$pOH = 7 - \log(1.618) = 6.79$

$pH = 14 - 6.79 = 7.21$

Self Practice Problem

1. Calculate pH of a KOH solution having

(a) 5.6 g of KOH mixed in 50mL water

(b) if it is further diluted to make 100 mL.

Ans. (a) 14.3 (b) 14

(c) **pH of Mxture of Two Strong Acids :** If V_1 volume of a strong acid solution of normality N_1 is mixed with V_2 volume of another strong acid solution of normality N_2, then

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

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

If final normality is N and final volume is V, then

$NV = N_1V_1 + N_2V_2$

[dissociation equilibrium of none of these acids will be disturbed as both are strong acid]

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

(d) **pH of Mixture of Two Strong Bases**

similar to above calculation

$$[OH^-] = N = \frac{N_1V_1 + N_2V_2}{V_1 + V_2} \qquad [H^+] = \frac{10^{-14}}{[OH^-]}$$

Ex. Calculate pH of mixture of (400 mL, $\frac{1}{200}$ M H_2SO_4) + (400 mL, $\frac{1}{100}$ M HCl) + (200 mL of water)

Sol. **Normality Method**

$N_1V_1 = \frac{1}{100} \times \frac{400}{1000} = \frac{4}{1000}$, $N_2V_2 = \frac{4}{1000}$, H^+ ions from water will be neglected

$N_1V_1 + N_2V_2 = 8 \times 10^{-3}$ $\quad [H^+] = \frac{8 \times 10^{-3}}{1} = 8 \times 10^{-3}$

pH = 3 – log 8 = 2.1

Molarity Method :

$H_2SO_4 \longrightarrow 2H^+ + SO_4^{2-}$

2m mole $\qquad$ 4m mole

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

4m mole $\qquad$ 4m mole

$$\left[H^+\right]_{total} = \frac{8\text{ m mole}}{1000\text{ mL}} = 8 \times 10^{-3}$$

pH = –log [H^+] = – log [8×10^{-3}] = 2.1 **Ans.**

Ex. 500 mL of 10^{-5} M NaOH is mixed with 500 mL of 2.5×10^{-5} M of $Ba(OH)_2$. To the resulting solution 99 L water is added. Calculate pH.

Sol. $[OH^-] = \frac{500 \times 10^{-5} + 500 \times 2 \times 2.5 \times 10^{-5}}{1000}$

$= 3 \times 10^{-5}$ M

$M_1 = 3 \times 10^{-5}$ M

$V_2 + V_1 = 1$ L

$V_1 = 100\ L$

no. of moles of $[OH^-]$ initially = no. of moles of $[OH^-]$

$3 \times 10^{-5} = M_2 \times 100$

$\because \quad M_2 = 3 \times 10^{-7} < 10^{-6}$

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

$$\qquad x \qquad (x + 3 \times 10^{-7})$$

$K_w = x\,(x + 3 \times 10^{-7}) = 10^{-14}$

$$\because \quad x = \left(\frac{\sqrt{13} - 3}{2}\right) \times 10^{-7}$$

$x = 0.302 \times 10^{-7}$

$$[OH^-]_{Net} = \left[3 + \frac{\sqrt{13} - 3}{2}\right] \times 10^{-7} = \left[\frac{3 + \sqrt{13}}{2}\right] \times 10^{-7} = 3.302 \times 10^{-7}$$

Self Practice Problem

1. Calculate the pH for-

(a) 50 mL of 0.1 M HCl, 25 mL of 0.1M H_2SO_4, 25 mL of 0.2 M HNO_3 + 100 mL of H_2O

(b) 50 mL of 0.2 M NaOH + 100 mL of 0.1 M RbOH the resulting solution is diluted by 350 mL H_2O.

Ans. **(a)** 1.123 **(b)** 12.6

(e) pH of Mixture of a Strong Acid and a Strong Base

- Acid Base neutralisation reaction will take place.
- The solution will be acidic or basic depending on which component has been taken in excess.
- If V_1 volume of a strong acid solution of normality N_1 is mixed with V_2 volume of a strong base solution of normality N_2, then

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

Number of OH^- ions from II-solution = N_2V_2

If $N_1V_1 > N_2V_2$

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

Solution will be acidic in nature

If $N_2V_2 > N_1V_1$

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

Solution will be basic in nature

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

Ex. Calculate pH of mixture of (400 mL, $\frac{1}{200}$ M $Ba(OH)_2$) + (400 mL, $\frac{1}{50}$ M HCl) + (200 mL of water)

Sol. $$[H^+] = \frac{400 \times \frac{1}{50} - 400 \times \frac{1}{200} \times 2}{1000} = 4 \times 10^{-3}, \text{ so } pH = 3 - 2\log 2 = 2.4$$

Ex. What will be the resultant pH when 150 mL of an aqueous solution of HCl (pH = 2.0) is mixed with 350 mL of an aqueous solution of NaOH (pH = 12.0) ?

Sol. pH of HCl = 2

$\therefore$ [HCl] = 10^{-2} M

pH of NaOH = 12, pOH = 2 $\therefore$ [NaOH] = 10^{-2} M

	HCl	+	NaOH	$\longrightarrow$	NaCl	+	H_2O
Meq. initial	150×10^{-2} = 1.5		350×10^{-2} = 3.5		0		0
Meq. final	0		0.2		1.5		1.5

$\therefore$ [OH^-] from NaOH = $\frac{2}{500} = 4\times10^{-3}$ M

pOH = – log[OH^-] = –log (4×10^{-3})

$\therefore$ pOH = 2.3979

$\therefore$ pH = 14 – pOH = 14 – 2.3979 = 11.6021

Self Practice Problem

1. Calculate pH of mixture 200 mL of 0.2 M H_2SO_4 + 300 mL of 0.2 M NaOH + 200 mL of 0.1 M KOH.

2. Calculate the pH when 200 mL of 0.25 M H_2SO_4 is mixed with 200 mL of 0.2 M $Ba(OH)_2$

Ans. **1.** 7 **2.** 1.30

(f) pH of a Weak Acid (Monoprotic) Solution

- Weak acid does not dissociated 100 % therefore we have to calculate the percentage dissociation using K_a dissociation constant of the acid.
- We have to use Ostwald's Dilution law (as have been derived earlier)

	HA	$\rightleftharpoons$	H^+	+	A^-
t = 0	C		0		0
t_{eq}	$C(1-\alpha)$		$C\alpha$		$C\alpha$

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

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

$[H^+] = C\alpha = C\sqrt{\frac{K_a}{C}} = \sqrt{K_a \times C}$ So $\boxed{pH = \frac{1}{2}(pK_a - \log C)}$ valid only if $\alpha <<< 1$.

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

Ex. Calculate pH of **(a)** 10^{-1} M CH_3COOH **(b)** 10^{-3} M CH_3COOH **(c)** 10^{-6} M CH_3COOH

Take $K_a = 2\times10^{-5}$

Sol. **(a)**

CH_3COOH	$\rightleftharpoons$	CH_3COO^-	+	H^+
C		0		0
$C(1-\alpha)$		$C\alpha$		$C\alpha$

$$K_a = \frac{C\alpha^2}{1-\alpha} \Rightarrow \alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{2\times10^{-5}}{10^{-1}}} = \sqrt{2\times10^{-4}} \quad (\alpha << 0.1)$$

So, $[H^+] = 10^{-1}\times\sqrt{2}\times10^{-2} \Rightarrow pH = 3 - \frac{1}{2}\log 2 = 2.85$

(b) $\alpha = \sqrt{\frac{K_a}{C}} \Rightarrow \alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{2\times10^{-5}}{10^{-3}}} = \sqrt{2\times10^{-2}} \quad (\alpha > 0.1)$

So we have to do the exact calculations

$K_a = \frac{C\alpha^2}{1-\alpha} \Rightarrow 2\times10^{-5} = \frac{10^{-3}\times\alpha^2}{1-\alpha} \Rightarrow \alpha = 13.14\,\%$

$[H^+] = 10^{-3}\times 0.1314 = 1.314\times10^{-4} \Rightarrow pH = 4 - \log(1.314) \approx 3.8$

(c) If approximation is used the, $\alpha = \sqrt{\frac{2\times10^{-5}}{10^{-6}}} = \sqrt{20} > 1,$

so we have to do the exact calculation, $2\times10^{-5} = 10^{-6}\frac{\alpha^2}{1-\alpha} \Rightarrow \alpha \approx 0.95$ or 95%

$[H^+] = 0.95\times10^{-6} = 9.5\times10^{-7} \Rightarrow pH = 7 - \log(9.5) = 6.022$

- **At very low concentration (at infinite dilution) weak electrolyte will be almost 100% dissociate, so behave as strong electrolyte**

  (pH) of 10^{-6} M HCl $\simeq$ pH of 10^{-6} M $CH_3COOH \simeq 6$)

(g) pH of a Mixture of Weak Acid (Monoprotic) and a Strong Acid Solution

- Weak acid and Strong acid both will contribute H^+ ion.
- For the first approximation we can neglect the H^+ ions coming from the weak acid solution and calculate the pH of the solution from the concentration of the strong acid only.
- To calculate exact pH, we have to take the effect of presence of strong acid on the dissociation equilibrium of the weak acid.
- If $[SA] = C_1$ and $[WA] = C_2$, then $[H^+]$ from SA $= C_1$

  the weak acid will dissociate as follows.

HA $\rightleftharpoons$	H^+	+ A^-
C_2	0	0
$C_2(1-\alpha)$	$C_2\alpha + C_1$	$C_2\alpha$

$K_a = \frac{(C_2\alpha + C_1)C_2\alpha}{C_2(1-\alpha)} \quad (\alpha <<< 1)$

(The weak acids dissociation will be further suppressed because of presence of strong acid, common ion effect)

$$K_a = (C_2\alpha + C_1)\alpha$$

Total H^+ ion concentration $= C_1 + C_2\alpha$

- If the total $[H^+]$ from the acid is more than 10^{-6} M, then contribution from the water can be neglected, if not then we have to take $[H^+]$ from the water also.

Relative Strength of Weak Acids and Bases

The relative strength of weak acids and bases are generally determined by their dissociation constants K_a and K_b respectively. For weak acid, i.e. CH_3COOH

$$\begin{array}{lll} CH_3COOH \rightleftharpoons & CH_3COO^- & + \quad H^+ \\ C & 0 & \quad 0 \\ C(1-\alpha) & C\alpha & \quad C\alpha \end{array}$$

$$K_a = \frac{C\alpha . C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)} \Rightarrow K_a = C\alpha^2 \qquad (\text{if } \alpha << 1)$$

Similarly, for weak base, i.e. NH_4OH

$$\begin{array}{lll} NH_4OH \rightleftharpoons & NH_4^+ & + \quad OH^- \\ C & 0 & \quad 0 \\ C(1-\alpha) & C\alpha & \quad C\alpha \end{array}$$

$K_b = C\alpha^2$

K_a and K_b are just the equilibrium constants and hence depends only on temperature. Greater the value of dissociation constant of the acid (K_a), more is the strength of the acid and similarly greater the value of dissociation constant of the base, more is the strength of the base. For two acids of different concentrations.

$$\frac{\text{Strength of acid (I)}}{\text{Strength of acid (II)}} = \sqrt{\frac{K_{a_1}.c_1}{K_{a_2}.c_2}}$$

Similarly for bases, $\dfrac{\text{Strength of base (I)}}{\text{Strength of base (II)}} = \sqrt{\dfrac{K_{b_1}.c_1}{K_{b_2}.c_2}}$

The modern method is to convert K_a as a power of 10 and express acid strength by power of 10 with sign changed and call this new unit pK_a. Thus, if K_a for acid is equal to 10^{-4}, $pK_a = 4$. So higher pK_a value means lower acid strength,

that is, $pK_a = -\log K_a$

Also, $pK_b = -\log K_b$

Total $[H^+]$ in a mixture of two weak Acids.

$$[H^+] = \sqrt{K_{a_1}c_1 + K_{a_2}c_2}$$

Similarly for two weak bases

$$[OH^-] = \sqrt{K_{b_1}c_1 + K_{b_2}c_2}$$

(h) pH of a Mixture of Two Weak Acid (Both Monoprotic) Solution

- Both acids will dissociate partially.
- Let the acid are HA_1 & HA_2 and their final concentrations are C_1 & C_2 respectively, then

$$\begin{array}{lllll} & HA_1 \rightleftharpoons & H^+ & + \ A_1^- \\ t=0 & C_1 & 0 & \ 0 \\ \text{At eq.} & C_1(1-\alpha_1) & C_1\alpha_1 + C_2\alpha_2 & \ C_1\alpha_1 \end{array} \qquad \begin{array}{lll} HA_2 \rightleftharpoons & H^+ & + \ A_2^- \\ C_2 & 0 & \ 0 \\ C_2(1-\alpha_2) & C_2\alpha_2 + C_1\alpha_1 & \ C_2\alpha_2 \end{array}$$

$$K_{a_1} = \frac{C_1\alpha_1(C_1\alpha_1 + C_2\alpha_2)}{C_1(1-\alpha_1)} \qquad K_{a_2} = \frac{(C_2\alpha_2 + C_1\alpha_1)C_2\alpha_2}{C_2(1-\alpha_2)}$$

(Since α_1, α_2 both are small in comparision to unity)

$$K_{a_1} = (C_1\alpha_1 + C_2\alpha_2)\alpha_1 \ ; \ K_{a_2} = (C_1\alpha_1 + C_2\alpha_2)\alpha_2 \Rightarrow \frac{K_{a_1}}{K_{a_2}} = \frac{\alpha_1}{\alpha_2}$$

$$[H^+] = C_1\alpha_1 + C_2\alpha_2 = \frac{C_1K_{a_1}}{\sqrt{C_1K_{a_1} + C_2K_{a_2}}} + \frac{C_2K_{a_2}}{\sqrt{C_1K_{a_1} + C_2K_{a_2}}} \Rightarrow [H^+] = \sqrt{C_1K_{a_1} + C_2K_{a_2}}$$

- If the dissociation constant of one of the acid is very much greater than that of the second acid then contribution from the second acid can be neglected.

  So, $[H^+] = C_1\alpha_1 + C_2\alpha_2 \approx C_1\alpha_1$

Ex. K_a for acid HA is 2.5×10^{-8} calculate for its decimolar solution at 25°C.

(i) % dissociation

(ii) pH

(iii) OH^- ion concentration

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

C	0	0
C(1–α)	α	α

$$K_a = \frac{[H^+][A^-]}{[HA]} \Rightarrow K_a = \frac{C\alpha.C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)} \approx C\alpha^2$$

(i) $\therefore \alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{2.5 \times 10^{-8}}{1/10}}$ (C = 1/10 M)

$= 5 \times 10^{-4} = 0.05\%$

(ii) $[H^+] = C\alpha = \frac{1}{10} \times 5 \times 10^{-4} = 5 \times 10^{-5}$ mol/L $\Rightarrow$ So pH = 5 – log 5 = 4.30

(iii) $[H^+][OH^-] = 1 \times 10^{-14}$

$\therefore [OH^-] = \frac{10^{-14}}{5 \times 10^{-5}} = 2 \times 10^{-10}$ mol/L

Ex. Determine the degree of dissociation of 0.05 M NH_3 at 25°C in a solution of pH = 10.

Sol. $NH_4OH \rightleftharpoons NH_4^+ + OH^-$

C	0	0

Given, pH = 10

$[H^+] = 10^{-10}$

$[H^+][OH^-] = 1 \times 10^{-14}$

$\therefore [OH^-] = \frac{1 \times 10^{-14}}{10^{-10}} = 10^{-4} = C\alpha$

$\therefore \alpha = \frac{[OH^-]}{C} = \frac{10^{-4}}{0.05} = 2 \times 10^{-3}$ or 0.2 %

Ex. Two weak monobasic organic acids HA and HB have dissociation constants as 1.6×10^{-5} and 0.4×10^{-5} respectively at 25° C. If 500 mL of 1 M solutions of each of these two acids are mixed to produce 1 litre of mixed solution, what is the pH of the resulting solution ?

Sol. In such cases, we have to consider H^+ from both HA and HB simultaneously. The concentration of HA and HB in the mixture = 0.5 M [equal volumes are mixed] = say 'c'

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

$HB \rightarrow H^+ + B^-$

Let, $x = [H^+]$ from HA and $y = [H^+]$ from HB

$\Rightarrow [H^+]_{final} = x + y$

$$K_{HA} = \frac{(x+y)x}{c} \text{ and } K_{HB} = \frac{(x+y)y}{c}$$

$$\frac{[H^+]_{HA}}{[H^+]_{HB}} = \frac{x}{y} = \sqrt{\frac{k_{HA} \times C}{k_{HB} \times C}}$$

$$\frac{x}{y} = \sqrt{\frac{1.6 \times 10^{-5}}{0.4 \times 10^{-5}}} = 2$$

$$x = 2y \Rightarrow y = \frac{x}{2}$$

Substitute for $y = \frac{x}{2}$ in $K_{HA} = \frac{x^2 + xy}{c}$

$$1.6 \times 10^{-5} = \frac{2x^2 + 3x^2}{2 \times 0.5}$$

$3x^2 = 1.6 \times 10^{-5} \Rightarrow x^2 = 5.33 \times 10^{-6}$

$x = 2.30 \times 10^{-3}$ M, $y = 1.15 \times 10^{-3}$ M

$[H^+]_{Final} = x + y = 2.30 \times 10^{-3} + 1.15 \times 10^{-3} = 3.45 \times 10^{-3}$ M

$pH = -\log_{10}(3.45 \times 10^{-3})$

$pH = 2.462$

Ex. Saccharin ($K_a = 2 \times 10^{-12}$) is a weak acid represented by formula HSaC. A 8×10^{-4} mole amount of saccharin is dissolved in 400 cm^3 water of pH = 3. Assuming no change in volume, calculate the concentration of SaC^- ions in the resulting solution at equilibrium.

Sol. $[HSaC] = \frac{\text{mole}}{\text{litre}} = \frac{8 \times 10^{-4}}{400/1000} = 2 \times 10^{-3}$ M

The dissociation of HSaC takes place in presence of $[H^+] = 10^{-3}$

	HSaC $\rightleftharpoons$	H^+ +	SaC^-
Conc. Before dissociation	2×10^{-3}	10^{-3}	0

In presence of H^+, the dissociation of HSaC is almost negligible because of common ion effect. Thus, at equilibrium $[HSaC] = 2 \times 10^{-3}$; $[H^+] = 10^{-3}$ M

$$\because K_a = \frac{[H^+][SaC^-]}{[HSaC]}$$

$$\therefore 2 \times 10^{-12} = \frac{[10^{-3}][SaC^{-1}]}{2 \times 10^{-3}}$$

$\therefore [SaC^-] = 4 \times 10^{-12}$ M

Ex. A solution contains 0.08 M HCl, 0.08 M $CHCl_2COOH$ and 0.1 M CH_3COOH. The pH of this solution is 1. If K_a for acetic acid is 10^{-5}, calculate K_a for $CHCl_2COOH$.

Sol. pH will be decided by $[H^+]$ furnished by HCl and $CHCl_2COOH$.

	$CHCl_2COOH \rightleftharpoons$	$CHCl_2COO^-$	$+ \; H^+$	
Initial conc.	0.08	0	0.08	(from HCl)
Final conc.	(0.08 – x)	x	(0.08 + x)	

$\therefore [H^+] = 0.08 + x$;

but pH = 1,

$\therefore [H^+] = 10^{-1} = 0.1$

$\therefore 0.08 + x = 0.1$ M

$\therefore x = 0.02$

K_a for $CHCl_2COOH$ can be given as

$$K_a = \frac{[H^+][CHCl_2COO^-]}{[CHCl_2COOH]} = \frac{0.1 \times 0.02}{(0.08 - 0.02)} = 3.33 \times 10^{-2}$$

ISOHYDRIC SOLUTIONS

(i) Solutions of electrolytes are said to be isohydric if the concentration of the common ion present in them is the same and on mixing such solutions, there occurs no change in the degree of dissociation of either of the electrolyte.

(ii) Let the isohydric solution is made by HA_1 and HA_2 acids, then $[H^+]$ of both acids should be equal i.e.

$$\sqrt{K_{a_1} C_1} = \sqrt{K_{a_2} C_2} \quad \text{or} \quad \frac{K_{a_1}}{K_{a_2}} = \frac{C_2}{C_1}$$

Example Based on : Dissociation of Acid and Base and pH Calculation

Ex. The degree of dissociation of pure water at 25°C is found to be 1.8×10^{-9}. Find K_W and K_d at 25°C.

(A) 3.24×10^{-18} ; 5.83×10^{-20} **(B)** 1×10^{-14} ; 1.8×10^{-16}

(C) 1.8×10^{-16} ; 1×10^{-14} **(D)** 1×10^{-14} ; 1×10^{-14}

Sol. (B)

Since $\alpha = 1.8 \times 10^{-9}$

and for water $c = \frac{1000}{18} = 55.56$

$[H^+] = [OH^-] = c\alpha = 55.56 \times 1.8 \times 10^{-9} = 1 \times 10^{-7}$ M

$K_W = [H^+] \times [OH^-] = (1 \times 10^{-7})^2 = 10^{-14}$

$$\text{and } K_d = \frac{[H^+][OH^-]}{[H_2O]} = \frac{K_W}{[H_2O]} = \frac{10^{-14}}{55.56} = 1.8 \times 10^{-16}$$

Ex. The concentration of $[H^+]$ and $[OH^-]$ of the 10^{-1} M aqueous solution of 2% ionised weak acid is :

(A) 2×10^{-3} M and 5×10^{-12} M **(B)** 1×10^{-3} M and 3×10^{-11} M

(C) 2×10^{-4} M and 5×10^{-11} M **(D)** 3×10^{-2} M and 4×10^{-13} M

Sol. (A)

$[H^+] = C\alpha = 2 \times 10^{-3}$ M

$$\text{or } [OH^-] = \frac{10^{-14}}{[H^+]} = 5 \times 10^{-12} \text{ M}$$

Ex. When a 0.1 N solution of an acid at 25°C has a degree of ionisation of 4%, the concentration of OH^- present is :

(A) 2.5×10^{-3} **(B)** 2.5×10^{-11} **(C)** 2.5×10^{-12} **(D)** 2.5×10^{-13}

Sol. **(C)**

$[H^+] = C\alpha = 0.1 \times 4 \times 10^{-2} = 4 \times 10^{-3}$ M

or $[OH^-] = \dfrac{10^{-14}}{[H^+]} = 2.5 \times 10^{-12}$ N

Ex. Calculate the molar concentration of a solution of acetic acid (HOAc) that has a pH of 4.00.
($K_a = 1.8 \times 10^{-5}$) :

(A) 1.0×10^{-3} **(B)** 1.0×10^{-6} **(C)** 0.057×10^{-2} **(D)** 0.010

Sol. **(C)**

$$K_a = \frac{[H^+][OAc^-]}{[HOAc]}$$

or $1.8 \times 10^{-5} = \dfrac{(10^{-4})^2}{[HOAc]}$

or $[HOAc] = 5.56 \times 10^{-4}$ M

Ex. Select the correct option from the following ?

(A) pK_W increases with increase of temperature

(B) pK_W decreases with increase of temperature

(C) $pK_W = 14$ at all tempera tures

(D) $pK_W = pH$ at all temperatures

Sol. **(B)**

Ex. How much water must be added to 200 mL of 0.2 M solution of CH_3COOH for the degree of dissociation of the acid to double ? K_a for the acetic acid = 1.8×10^{-5}:

Sol. $C_1\alpha_1^2 = C_2\alpha_2^2$ or $C_2 = C_1\left(\dfrac{\alpha_1}{\alpha_2}\right)^2 = \dfrac{C_1}{4}$

so $M_1 = 0.2$ M ; $M_2 = \dfrac{0.2}{4}$ M

$V_1 = 200$ mL, $V_2 = ?$

$M_1V_1 = M_2V_2$

or $V_2 = \dfrac{M_1V_1}{M_2} = \dfrac{0.2 \times 200 \times 4}{0.2} = 800$ mL

so 800 – 200 = 600 mL water should be added.

Ex. The degree of dissociation of acetic acid in a 0.1 M solution is 1.32×10^{-2}. Calculate dissociation constant of acid and its pK_a value :

Sol.

	$CH_3COOH \rightleftharpoons$	CH_3COO^-	+ H^+
Initially	0.1	0	0
at equilibrium	0.1(1–0.0132)	0.1×0.0132	0.1×0.0132

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{0.1 \times 0.0132 \times 0.1 \times 0.0132}{0.1(1 - 0.0132)} = 1.76 \times 10^{-5}$$

$pK_a = -\log K_a = -\log(1.76 \times 10^{-5}) = 4.75$

Ex. A solution having pH = 13, calculate the no. of H^+ ions present in 1 mL of this solution :

Sol. pH = 13 so $[H^+] = 10^{-13}$ M

moles of H^+ in one mL $= \frac{10^{-13}}{10^3} = 10^{-16}$ mol.

$\therefore$ No. of H^+ ions $= 10^{-16} \times 6.022 \times 10^{23}$

$= 6.022 \times 10^7$

Ex. Calculate pH of solution obtained by mixing equal vol. of 0.02 M HOCl & 0.2 M CH_3COOH solution given that

K_{a_1} (HOCl) $= 2 \times 10^{-4}$

K_{a_2} (CH_3COOH) $= 2 \times 10^{-5}$

also calculate OH^-, OCl^-, CH_3COO^-

Sol. Final solution volume become double

$C_1 = 0.01, \quad C_2 = 0.1$

$[H^+] = \sqrt{K_{a_1}C_1 + K_{a_2}C_2}$

$= \sqrt{2\times10^{-4}\times0.01 + 2\times10^{-5}\times0.1} = \sqrt{2\times10^{-6} + 2\times10^{-6}} = 2\times10^{-3}$

pH = 3 – log2 = 3 – 0.3010 = 2.69

$\alpha_1 = \frac{2\times10^{-4}}{2\times10^{-3}} = 10^{-1} \quad \alpha_2 = \frac{2\times10^{-5}}{2\times10^{-3}} = 10^{-2}$

$HOCl \rightleftharpoons H^+ + OCl^-$

$C_1(1-\alpha_1) \quad C_1\alpha_1 + C_2\alpha_2 \quad C_1\alpha_1$

$[OCl^-] = C_1\alpha_1$

$= 0.01 \times 10^{-1}$

$= 1 \times 10^{-3}$

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

$C_2(1-\alpha_2) \quad C_1\alpha_1 + C_2\alpha_2 \quad C_2\alpha_2$

$[CH_3COO^-] = C_2\alpha_2$

$= 0.1 \times 10^{-2}$

$= 1 \times 10^{-3}$

$[OH^-] = \frac{K_w}{[H^+]} = \frac{10^{-14}}{2\times10^{-3}} = 0.5 \times 10^{-11}$

$= 5 \times 10^{-12}$ M

$[HOCl] = 10^{-2}(1-0.1) = 9 \times 10^{-3}$ M

$[CH_3COOH] = 10^{-1}(1-0.01) \approx 10^{-1}$

(i) pH of a Solution of a Polyprotic Weak Acid

- Diprotic acid is the one, which is capable of giving 2 protons per molecule in water. Let us take a weak diprotic acid (H_2A) in water whose concentration is c M.

  In an aqueous solution, following equilbria exist.

If

α_1 = degree of ionization of H_2A in presence of HA^-

α_2 = degree of ionisation of HA^- in presence of H_2A

K_{a_1} = first ionisation constant of H_2A

K_{a_2} = second ionisation constant of H_2A

$$H_2A + H_2O \rightleftharpoons HA^- + H_3O^+ \qquad\qquad HA^- + H_2O \rightleftharpoons A^{2-} + H_3O^+$$

at eq. $C - x \quad\quad x - y \quad\quad x + y$ at eq. $x - y \quad\quad y \quad\quad x + y$

$$(K_{eq})_1 [H_2O] = \frac{[H_3O^+][HA^-]}{[H_2A]} = K_{a_1} \qquad\qquad (K_{eq})_2 [H_2O] = \frac{[H_3O^+][A^{2-}]}{[HA^-]} = K_{a_2}$$

$$\therefore \; K_{a_1} = \frac{(x-y)(x+y)}{(C-x)} \qquad\qquad K_{a_2} = \frac{(y)(x+y)}{(x-y)}$$

Approximation

For diprotic acids, $K_{a_2} << K_{a_1}$ and y would be even smaller than x.

$\therefore \; y <<< x \Rightarrow x - y \cong x$ and $x + y \cong x$

Thus, equation (i) can be reduced to $K_{a_1} = \dfrac{x^2}{C-x}$, $K_{a_2} = y$

This is expression similar to the expression for a weak monoprotic acid.

- Hence, for a diprotic acid (or a polyprotic acid) the $[H_3O^+]$ can be calculated from its first equilibrium constant expression alone provided $K_{a_2} << K_{a_1}$

Ex. Calculate pH of $[HS^-]$, $[S^{2-}]$, $[Cl^-]$ in a solution which is 0.1 M HCl & 0.1 M H_2S given that $K_{a_1}(H_2S) = 10^{-7}$, $Ka_2(H_2S) = 10^{-14}$ also calculate α_1 & α_2.

Sol. $HCl + H_2S$

0.1 0.1

$C_1 = C_2 = 0.1$

$\therefore$ pH = 1 (most of $[H^+]$ comes from HCl)

$$H_2S \rightleftharpoons H^+ + HS^-$$

$0.1(1 - \alpha_1) \quad\quad 10^{-1} \quad\quad C\alpha_1 = 0.1\,\alpha_1$

$$Ka_1 = \frac{C\alpha_1 \times 10^{-1}}{C(1-\alpha_1)} = \frac{10^{-7}}{10^{-1}} = \alpha_1$$

$\Rightarrow \alpha_1 = 10^{-6}$

$$HS^- \rightleftharpoons S^{2-} + H^+$$

$C\alpha_1(1 - \alpha_2) \quad\quad C\alpha_1\alpha_2 \quad\quad 0.1$

$10^{-14} = 0.1 \times \alpha_2$

$\Rightarrow \alpha_2 = 10^{-13}$

$[S^{2-}] = C\alpha_1\alpha_2$

$= 10^{-6} \times 10^{-1} \times 10^{-13} = 10^{-20}$ M

(j) pH of a Mixture of a Polyprotic Weak Acid and a Strong Acid

- pH can be calculated by taking the concentration of strong acid only (for first approximation)
- For precise calculation we should take only the first dissociation constant of the weak polyprotic acid. (As can be predicted from the equations we have presented so far for different cases.)
- All these steps can be followed for the calculation of pOH for weak base and their mixtures (we just have to replace Ka with Kb)

(k) pH of a Mixture of a Weak Acid/Weak Base with Weak/Strong Base/Acid Respectively.

For this type of mixtures there can be two cases in general,

(i) if the acids and bases are mixed in equal amounts (equivalents)

(ii) if the acids and bases are mixed in different amounts (equivalents)

First case will lead to phenomenon of **Salt hydrolysis** and second case will lead to formation of **Buffer Solution.**

Relation Between K_a and K_b for Conjugate Acid Base Pair

For conjugate-acid base pairs, the acid dissociation constant K_a and base ionizsation constnat K_b are related by the following equations :

$K_a \cdot K_b = K_w$ where Kw is the autoionization constant

$pK_a + pK_b = 14$ at 25°C

Weak acids, generically abbreviated as HA, donate H^+ (or proton) to water to form the conjugate base A^- and H_3O^+ :

$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$

acid base acid base

Similarly, a base (abbreviated as B) will accept a proton in water to form the conjugate acid, HB^+, and OH^- :

$B(aq) + H_2O(l) \rightleftharpoons HB^+(aq)^+ + OH^-(aq)$

base acid acid base

For a weak acid or base, the equilibrium constant for theionization reaction quantities the relative amount of each species. In this ariticle, we will discuss the relationship between the equilibrium constants K_a and K_b for a conjugate acid-base pair.

Let's look more closely at the dissociation reaction for a monoprotic weak acid HA :

$HA(aq) + H_2O(l) \rightleftharpoons H3O^+(aq) + A^-(aq)$

The products of this reversible reaction are A^-, the conjugate base of HA, and H_3O^+. We can write the following expressin for the equilibrium constant K_a :

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

Finding Kb for A– Reacting as a Base

Since A^- is a base, we can also write the reversible reaction for A^- acting as a base by accepting a proton from water :

$A^-(aq) + H_2O(l) \rightleftharpoons HA(aq) + OH^-(aq)$

The products of this reaction are HA and OH^-. We can write out the equilibrium constnat K_b for the reaction where A^- acts as a base :

$$K_b = \frac{[HA][OH^-]}{[A^-]}$$

Even though this almost looks like the reverse of HA acting as an acid, they are actually very different reactions. When HA acts as an acid, one of the products is H_3O^+. When the conjugate base A^- acts as a base, one of the products is OH^-.

Relationship between Ka and Kb for conjugate acid-base pair

If we multiply K_a for HA with the K_b of its conjugate base A^-, that gives :

$$K_a \cdot K_b = \left(\frac{[H_3O^+][A^-]}{[HA]}\right)\left(\frac{[HA][OH^-]}{[A^-]}\right)$$

$$= [H3O^+][OH^-]$$

$$= K_w$$

where K_w is the water dissociation constant. This relationship is very useful for reating K_a and K_b for a conjugate acid-base pair. We can also use the value of K_w at 25°C to derive other handy equations.

$K_a . K_b = K_w$

$= 1.0 \times 10^{-14}$ at 25°C (Eq. 1)

If we take the negativbe $\log_{10}$ of both sides of the Eq. 1, we get :

$pK_a + pK_b = 14$ at 25°C (Eq. 2)

We can use these equations to determine K_b (or pK_b) of a weak base given K_a of the conjugate acid. We can also calculate the K_a (or Pk_a) of a weak acid given K_b of the conjugate base.

An inportant thing to remember is that these equations only work for conjugate acid-base pairs.

SALTS

(i) Salts are the ionic compounds formed when its positive part (Cation) come from a base and its negative part (Anion) come from an acid.

(ii) Salts may taste salty, bitter, astringent or sweet or tasteless.

(iii) Solution of salts may be acidic, basic or neutral.

(iv) Fused salts and their aqueous solutions conduct electricity and undergo electrolysis.

(v) The salts are generally crystalline solids.

1. Classification of Salts

The salts may be classified into four categories.

1.1 Simple Salts

The salts formed by the neutralisation process between acid and base. These are of three types.

(i) Normal Salt

(i) The salt formed by the loss of all possible protons (replaceable H^+ ions)

Ex. $NaCl$, $NaNO_3$, K_2SO_4, $Ca_3(PO_4)_2$, Na_3BO_3, Na_2HPO_3, NaH_2PO_2 etc.

(ii) Acid Salts

(i) Salts formed by incomplete neutralisation of polybasic acids. Such salts contain one or more replaceable H atom.

Ex. $NaHCO_3$, $NaHSO_4$, NaH_2PO_4, Na_2HPO_4 etc. (these are salts containing amphiprotic ions)

(ii) Above salts when neutralized by base form normal salts.

(iii) Basic Salts

(i) Salts formed by in complete neutralisation of poly acidic bases are called basic salts. These salt contain one or more hydroxyl groups.

Ex. $Zn(OH)Cl$, $Mg(OH)Cl$, $Fe(OH)_2Cl$, $Bi(OH)_2Cl$ etc.

(ii) Above salts when neutralised by acids form normal salts.

1.2 Double Salts

(i) The addition compounds formed by the combination of two simple salts are termed as double salts.

Ex. $FeSO_4 (NH_4)_2SO_4 . 6H_2O$ (Ferrous ammonium sulphate), $K_2SO_4 Al_2 (SO_4)_3.24H_2O$ (Alum) and other alums.

(ii) Above salts are stable in solid state only.

(iii) When dissolved in water, it furnishes all the ions present in the simple salt from which it has been constituted.

(iv) The solution of double salt shows the properties of the simple salts from which it has been constituted.

1.3 Complex Salts

(i) These are formed by combination of simple salts or molecular compounds.

Ex. $K_4Fe(CN)_6$, $Co(NH_3)_6SO_4$ etc.

(ii) $\underbrace{FeSO_4 + 6KCN}_{\text{simple salt}} \longrightarrow \underset{\text{complex salt}}{K_4Fe(CN)_6} + K_2SO_4$

(iii) $CoSO_4 + 6NH_3 \longrightarrow Co(NH_3)_6SO_4$

Simple salt — Molecular compound — complex salt

(iv) These are stable in solid states as well as in solutions.

(v) On dissolving in water, if furnishes a complex ion.

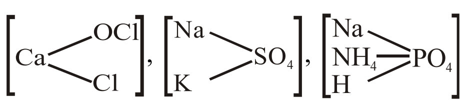
$$K_4Fe(CN)_6 \xrightleftharpoons{H_2O} 4K^+ + \underset{\text{complex ion}}{[Fe(CN)_6]^{4-}}$$

(vi) The properties of the solution are different from the properties of the substance from which it has been constituted.

1.4 Mixed Salts

(i) The salt which furnishes more than one cation or more than one anion when dissolved in water is called mixed salt.

Ex. $CaOCl_2$, $NaKSO_4$, $NaNH_4HPO_4$ etc.



Hydrolysis of Salt

Salt Hydrolysis

Salt hydrolysis is defined as the process in which water reacts with salt to form acid & base.

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

$\Delta H = +ve$

It is always an endothermic process because it is reverse of acid – base neutralization reaction which is always exothermic.

$$\text{Hydrolysis constant} \quad K_h = \frac{[\text{Acid}]\,[\text{Base}]}{[\text{Salt}]}$$

Here H_2O is a solvent (in excess) so active mass of H_2O is 1.

– Types of Salt Hydrolysis

(1) Hydrolysis of Strong Acid - Weak Base [SA - WB] Type Salt –

Ex. $CaSO_4$, NH_4Cl, $(NH_4)_2SO_4$, $Ca(NO_3)_2$, $ZnCl_2$, $CuCl_2$, $CaCl_2$

$$NH_4Cl + H_2O \rightleftharpoons NH_4OH + HCl$$

$$NH_4^+ + Cl^- + H_2O \rightleftharpoons NH_4OH + H^+ + Cl^-$$

$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$$

(1) In this type of salt hydrolysis, cation reacts with H_2O, therefore called as cationic hydrolysis.
(2) Solution is acidic in nature (SA WB) as $[H^+]$ is increased.
(3) pH of the solution is less than 7.

(a) Relation between K_h , K_W & K_b

$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$$

Hydrolysis constant K_h

$$K_h = \frac{[NH_4OH][H^+]}{[NH_4^+]} \quad \text{..... (1)}$$

For weak Base $\quad NH_4OH \rightleftharpoons NH_4^+ + OH^-$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]} \quad \text{..... (2)}$$

For water $\quad H_2O \rightleftharpoons H^+ + OH^-$

$$K_w = [OH^-][H^+] \quad \text{..... (3)}$$

Now multiplying Eq. (1) & (2) = Eq. (3)

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

i.e. $\quad K_h \times K_b = K_w$

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

(b) Degree of hydrolysis – Represented by h

$NH_4^+ + H_2O$	$\rightleftharpoons$	NH_4OH	H^+	
C		0	0	(initial concentration at equilibrium)
C – x		x	x	

nx = aα
1x = Ch
x = Ch

C – Ch		Ch	Ch

$$K_h = \frac{[NH_4OH][H^+]}{[NH_4^+]} = \frac{Ch \times Ch}{C - Ch}$$

$$= \frac{C^2h^2}{C(1-h)} = \frac{Ch^2}{(1-h)}$$

Since h <<<< 1

then $(1 - h) \approx 1$

$\therefore \quad K_h = Ch^2$

$$h^2 = \frac{K_h}{C} \quad \Rightarrow \quad h = \sqrt{\frac{K_h}{C}}$$

$$\therefore \ K_h = \frac{K_w}{K_b} \quad \Rightarrow \quad h = \sqrt{\frac{\frac{K_w}{K_b}}{C}} \quad \Rightarrow \quad \boxed{h = \sqrt{\frac{K_w}{K_b \times C}}}$$

(c) pH of the solution :

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

$$[H^+] = Ch = C\sqrt{\frac{K_w}{K_b \times C}} \quad \Rightarrow \quad [H^+] = \sqrt{\frac{K_w \times C}{K_b}}$$

On taking – log on both sides

$$-\log[H^+] = -\log\sqrt{\frac{K_w \times C}{K_b}} \quad \Rightarrow \quad pH = -\log\left(\frac{K_w \times C}{K_b}\right)^{1/2}$$

$$pH = -\frac{1}{2}[\log K_w + \log C - \log K_b]$$

$$pH = -\frac{1}{2}\log K_w - \frac{1}{2}\log C - \frac{1}{2}(-\log K_b)$$

$$pH = \frac{1}{2}pK_w - \frac{1}{2}\log C - \frac{1}{2}pK_b$$

$$\boxed{pH = 7 - \frac{1}{2}pK_b - \frac{1}{2}\log C}$$

KEY POINTS

Summary

(1) $K_h = \frac{K_w}{K_b}$

(2) $h = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{K_w}{K_b \times C}}$

(3) $\left[H^+\right] = Ch = \sqrt{\frac{K_w \times C}{K_b}}$

(4) $pH = -\log[H^+]$

$$pH = 7 - \frac{1}{2}pK_b - \frac{1}{2}\log C$$

Ex. Find out the K_h of centi normal $[10^{-2}$ N]solution of NH_4Cl (SA - WB) if dissociation constant of NH_4OH is 10^{-6} and $K_w = 10^{-14}$. Find out degree of hydrolysis and also find $[H^+]$ and pH of solution ?

Given : $K_w = 10^{-14}$; $K_b = 10^{-6}$

Sol. (1) $K_h = \frac{K_w}{K_b} = \frac{10^{-14}}{10^{-6}} = 10^{-8}$

(2) $h = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{10^{-8}}{10^{-2}}} = \sqrt{10^{-6}} = 10^{-3}$

(3) $[H^+] = Ch$
$= 10^{-2} \times 10^{-3}$
$= 10^{-5}$

(4) $pH = -\log [H^+]$
$= -\log [10^{-5}]$
$= +5 \log 10$
$= +5 \times 1$
$= 5$

Ex. Find out the K_h at 363 K (90°C) of a salt of [Strong Acid – Weak Base] if the value of K_b is 10^{-5} [At 90°C $K_w = 10^{-12}$]

Sol. $K_h = \frac{K_w}{K_b} = \frac{10^{-12}}{10^{-5}} = 10^{-7}$

Ex. How many grams of NH_4Cl should be dissolved per litre of solution to have a pH of 5.13 ? K_b for NH_3 is 1.8×10^{-5}.

Sol. NH_4Cl is a salt of strong acid and weak base for solutions of such salts.

$pH = \frac{1}{2} [pK_w - \log C - pK_b]$

$\Rightarrow 10.26 = 14 - \log C - 4.74$

$\Rightarrow \log C = 9.26 - 10.26 = -1.0$

$\therefore C = 10^{-1}$ M

$[NH_4Cl] = 10^{-1}$ M

$W_{NH_4NO_3} = 10^{-1} \times 53.5 \text{ gL}^{-1} = 5.35 \text{ gL}^{-1}$

Ex. What is the pH of 0.4 M aqueous NaCN solution? (Given pK_b of $CN^- = 4.70$)

Sol. pK_a for HCN = 14 – 4.7 = 9.30

$NaCN + H_2O \rightleftharpoons NaOH + HCN$

C	0	0
C(1–h)	Ch	Ch

$\therefore [OH^-] = Ch = C\sqrt{\frac{K_h}{C}} = \sqrt{K_hC} = \sqrt{\frac{K_wC}{K_a}}$

$pOH = \frac{1}{2} (pK_w - pK_a - \log C) = \frac{1}{2} [14 - 9.30 - \log (0.4)] = 2.548$

$\therefore pH = 14 - 2.5 = 11.45$

Ex. The acid ionization constant for

$Zn^{2+} + H_2O \rightleftharpoons Zn(OH)^+ + H^+$

is 1.0×10^{-9}. Calculate the pH of 0.10 M solution of $ZnCl_2$. Also calculate basic dissociation constant of $Zn(OH)^+$.

Sol. $Zn^{2+} + H_2O \rightleftharpoons Zn(OH)^+ + H^+$

$\therefore\ [H^+] = C.h = C\sqrt{\dfrac{K_h}{C}} = \sqrt{K_h C}$

$= \sqrt{\dfrac{K_w C}{K_b}}$ $\left[\begin{array}{l}\text{where } K_b \text{ is basic dissociation constant of } Zn(OH)^+ \\ \text{i.e. } Zn(OH)^+ \rightleftharpoons Zn^{2+} + OH^-\end{array}\right]$

We know Zn^{2+} and $Zn(OH)^+$ are conjugate acid and base.

$\therefore \quad K_a \times K_b = 10^{-14}$

or $\quad K_b = \dfrac{10^{-14}}{10^{-9}} = 10^{-5}$

Now, $\quad [H^+] = \sqrt{\dfrac{10^{-14} \times 0.1}{10^{-9}}} = \sqrt{10^{-6}} = 10^{-3}$

$pH = 3$

(2) Hydrolysis of [WA – SB] Type Salt –

Ex. KCN, NaCN, K_2CO_3, $BaCO_3$, K_3PO_4

$$NaCN + H_2O \rightleftharpoons NaOH + HCN$$

$$Na^+ + CN^- + H_2O \rightleftharpoons Na^+ + OH^- + HCN$$

$$CN^- + H_2O \rightleftharpoons HCN + OH^-$$

(1) In this type of salt hydrolysis anion reacts with water therefore called as anionic hydrolysis.

(2) Solution is basic in nature as $[OH^-]$ increases.

(3) pH of the solution is greater than 7.

(a) Relation between K_h, K_w, K_a

$$CN^- + H_2O \rightleftharpoons HCN + OH^-$$

$$K_h = \frac{[HCN]\left[OH^-\right]}{\left[CN^-\right]} \quad \text{..... (1)}$$

For weak acid $\quad HCN \rightleftharpoons CN^- + H^+$

$$K_a = \frac{\left[CN^-\right]\left[H^+\right]}{[HCN]} \quad \text{..... (2)}$$

For water $\quad H_2O \rightleftharpoons H^+ + OH^-$

$$K_w = [OH^-][H^+] \quad \text{..... (3)}$$

eq. (1) × eq. (2) = eq. (3)

$$\frac{[HCN][OH^-]}{[CN^-]} \times \frac{[CN^-][H^+]}{[HCN]} = [H^+][OH^-]$$

$$K_h \times K_a = K_w$$

$$\boxed{K_h = \frac{K_w}{K_a}}$$

(b) Degree of hydrolysis :

$$CN^- + H_2O \rightleftharpoons HCN + OH^-$$

C	0	0	Initial concentration at equlibrium
$C - x$	x	x	

$nx = a\alpha$

$1x = Ch$

$x = Ch$

$C - Ch$	Ch	Ch

$$K_h = \frac{[HCN][OH^-]}{[CN^-]} = \frac{Ch \times Ch}{C - Ch} = \frac{C^2h^2}{C(1-h)}$$

$$K_h = \frac{Ch^2}{(1-h)}$$

Since $h <<<< 1$

therefore $(1 - h) \approx 1$

$\therefore$ $K_h = Ch^2$

$$h^2 = \frac{K_h}{C} \Rightarrow \boxed{h = \sqrt{\frac{K_h}{C}}}$$

$$\boxed{h = \sqrt{\frac{K_w}{K_a \times C}}}$$

(c) pH of the solution

$$[OH^-] = Ch$$

$$[OH^-] = C \times \sqrt{\frac{K_w}{K_a \times C}}$$

$$[OH^-] = \sqrt{\frac{K_w \times C}{K_a}}$$

$\because$ $K_w = [OH^-][H^+]$

$\therefore$ $[H^+] = \dfrac{K_w}{[OH^-]}$

$$\left[H^+\right] = \frac{K_w}{\sqrt{\frac{K_w \times C}{K_a}}}$$

$$\boxed{\left[H^+\right] = \sqrt{\frac{K_w \times K_a}{C}}}$$

On taking – log on both sides

$$-\log [H^+] = -\log \sqrt{\frac{K_w \times K_a}{C}}$$

$$pH = -\log \left(\frac{K_w \times K_a}{C}\right)^{1/2}$$

$$pH = -\frac{1}{2}[\log K_w + \log K_a - \log C]$$

$$pH = -\frac{1}{2}\log K_w - \frac{1}{2}\log K_a + \frac{1}{2}\log C$$

$$pH = \frac{1}{2}\,pK_w + \frac{1}{2}\,pK_a + \frac{1}{2}\,\log C$$

$$pH = 7 + \frac{1}{2}\,pK_a + \frac{1}{2}\,\log C$$

KEY POINTS

Summary

(1) $K_h = \frac{K_w}{K_a}$

(2) $h = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{K_w}{K_a \times C}}$

(3) $[OH^-] = Ch = \sqrt{\frac{K_w \times C}{K_a}}$

(4) $[H^+] = \sqrt{\frac{K_w \times K_a}{C}}$

(5) $pH = -\log [H^+]$

$$pH = 7 + \frac{1}{2}\,pK_a + \frac{1}{2}\,\log C$$

Ex. Find out pH, h and $[OH^-]$ of milli molar solution of KCN 10^{-3} M, if the dissociation constant of HCN is 10^{-7}.

Sol. (1) $pH = 7 + \frac{1}{2}\,pK_a + \frac{1}{2}\,\log C = 7 + \frac{1}{2} \times 7 + \frac{1}{2}\log 10^{-3}$

$$= 7 + \frac{7}{2} - \frac{3}{2}\log 10 = \frac{14 + 7 - 3}{2} = \frac{21 - 3}{2} = \frac{18}{2} = 9$$

(2) $h = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{K_W}{K_a \times C}} = \sqrt{\frac{10^{-14}}{10^{-7} \times 10^{-3}}} = \sqrt{10^{-14} \times 10^{10}} = \sqrt{10^{-4}} = 10^{-2}$

(3) $[OH^-] = \sqrt{\frac{K_W \times C}{K_a}} = \sqrt{\frac{10^{-14} \times 10^{-3}}{10^{-7}}} = \sqrt{10^{-17} \times 10^{+7}} = \sqrt{10^{-10}} = 10^{-5}$

Ex. Calculate the pH and degree of hydrolysis of 0.01 M solution of NaCN, K_a for HCN is 6.2×10^{-12}.

Sol. NaCN is a salt of strong base NaOH and weak acid HCN. K^+ does not react with water whereas CN^- reacts with water as here under

$$CN^- + H_2O \rightleftharpoons HCN + OH^-$$

$$K_h = \frac{[HCN][OH^-]}{[CN^-]} = \frac{K_w}{K_a} = \frac{10^{-14}}{6.2 \times 10^{-12}} = 1.6 \times 10^{-3}$$

Let, x moles of salt undergo hydrolysis then concentrations of various species would be

$[CN^-] = (0.01 - x) \approx 0.01, [HCN] = x$

$[OH^-] = x$

$\therefore K_h = \frac{x.x}{0.01} = 1.6 \times 10^{-3}$

$\therefore x^2 = 1.6 \times 10^{-5}$

$\therefore x = 4 \times 10^{-3}$

$[OH^-] = x = 4 \times 10^{-3}$ M

$[H_3O^+] = \frac{K_W}{[OH^-]} = \frac{10^{-14}}{4 \times 10^{-3}} = 0.25 \times 10^{-11}$

$pH = -\log(0.25 \times 10^{-11}) = 11.6020$

Degree of hydrolysis $= \frac{x}{0.01} = \frac{4 \times 10^{-3}}{0.01} = 4 \times 10^{-11}$

Ex. Calculate for 0.01 N solution of sodium acetate

(i) Hydrolysis constant (ii) Degree of hydrolysis (iii) pH

Given K_a of $CH_3COOH = 1.9 \times 10^{-5}$.

Sol.

For	CH_3COONa	+	H_2O	$\rightleftharpoons$	CH_3COOH	+	NaOH
Initial	C				0		0
After	C(1–h)				Ch		Ch

(i) $K_h = \frac{K_w}{K_a} = \frac{10^{-14}}{1.9 \times 10^{-5}} = 5.26 \times 10^{-10}$

(ii) $h = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{5.26 \times 10^{-10}}{0.01}} = 2.29 \times 10^{-6} M$

(iii) $[OH^-]$ from NaOH, a strong base = Ch = $0.01 \times 2.29 \times 10^{-4} = 2.29 \times 10^{-6}$ M

pOH = 5.64

$\therefore$ pH = 14 – 5.64 = 8.36

3. Hydrolysis of (WA - WB) Type Salt

Ex. $NH_4CN, CaCO_3, (NH_4)_2CO_3, ZnHPO_3$

$$NH_4CN + H_2O \rightleftharpoons NH_4OH + HCN$$

$$NH_4^+ + CN^- + H_2O \rightleftharpoons NH_4OH + HCN$$

(1) Solution is almost neutral but it may be acidic or basic depending upon the nature of acid & base & pH of the solution is near to 7.

(a) Relation between K_h, K_w, K_a & K_b

$$NH_4^+ + CN^- + H_2O \rightleftharpoons NH_4OH + HCN$$

$$K_h = \frac{[NH_4OH][HCN]}{[NH_4^+][CN^-]} \qquad ..... (1)$$

For weak base $NH_4OH \rightleftharpoons NH_4^+ + OH^-$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]} \qquad ..... (2)$$

For weak acid $HCN \rightleftharpoons H^+ + CN^-$

$$K_a = \frac{[H^+][CN^-]}{[HCN]} \qquad ..... (3)$$

For water $H_2O \rightleftharpoons H^+ + OH^-$

$$K_w = [OH^-][H^+] \qquad ..... (4)$$

Multiply Eq. (1) × Eq. (2) × Eq. (3) = Eq. (4)

$$\frac{[NH_4OH][HCN]}{[NH_4^+][CN^-]} \times \frac{[NH_4^+][OH^-]}{[NH_4OH]} \times \frac{[H^+][CN^-]}{[HCN]} = [H^+][OH^-]$$

$$K_h \times K_b \times K_a = K_w$$

$$\boxed{K_h = \frac{K_w}{K_a \times K_b}}$$

(2) Degree of Hydrolysis –

NH_4^+	+ CN^- + $H_2O \rightleftharpoons$	NH_4OH	+ HCN	
C	C	0	0	Initial concentration
C – x	C – x	x	x	at equilibrium

$\because$ nx = aα

$\therefore \quad x = Ch$

$$K_h = \frac{[NH_4OH][HCN]}{[NH_4^+][CN^-]} = \frac{\overset{C-Ch}{}\;\overset{C-Ch}{}\;\; Ch \times Ch}{(C-Ch)(C-Ch)} = \frac{C^2h^2}{C(1-h) \times C(1-h)} = \frac{h^2}{(1-h)^2}$$

Since $h <<<< 1$

Then $(1-h) \approx 1$

$$\therefore \quad \boxed{K_h = h^2}$$

or $$h^2 = \frac{K_W}{K_a \times K_b}$$

$$h = \sqrt{\frac{K_W}{K_a \times K_b}} \qquad \text{..... (5)}$$

(b) pH of the solution

From eq. (3)

$$K_a = \frac{[H^+][CN^-]}{[HCN]}$$

$$[H^+] = \frac{K_a \times [HCN]}{[CN^-]}$$

$$[H^+] = \frac{K_a \times Ch}{C - Ch} = \frac{K_a \times h}{1 - h}$$

Since $h <<<< 1$

$(1-h) \approx 1$

$[H^+] = K_a \times h$ [Now put the value of h from eq. (5)]

$$= K_a \times \sqrt{\frac{K_w}{K_a \times K_b}}$$

$$\boxed{[H^+] = \sqrt{\frac{K_w \times K_a}{K_b}}}$$

On taking – log on both sides

$$-\log [H^+] = -\log \left(\frac{K_w \times K_a}{K_b}\right)^{1/2}$$

$$pH = -\frac{1}{2} \; [\log (K_w \times K_a) - \log K_b]$$

$$pH = -\frac{1}{2}[\log K_w + \log K_a - \log K_b]$$

$$pH = -\frac{1}{2}[\log K_w] - \frac{1}{2}[\log K_a] - \frac{1}{2}[-\log K_b]$$

$$pH = +\frac{1}{2}pK_w + \frac{1}{2}pK_a - \frac{1}{2}pK_b$$

$$pH = 7 + \frac{1}{2}pK_a - \frac{1}{2}pK_b$$

KEY POINTS

Summary

(1) $K_h = \dfrac{K_w}{K_a \times K_b}$

(2) $h = \sqrt{K_h} = \sqrt{\dfrac{K_w}{K_a \times K_b}}$

(3) $[H^+] = \sqrt{\dfrac{K_w \times K_a}{K_b}} = K_a.h$

(4) $pH = -\log[H^+]$

$$pH = 7 + \frac{1}{2}pK_a - \frac{1}{2}pK_b$$

Note : Degree of hydrolysis of [WA – WB] type salt does not depend on the concentration of salt.

Ex. Salt of weak acid and weak base

(i) Calculate pH of the mixture (25 mL of 0.1 M NH_4OH + 25 mL of 0.1 M CH_3COOH).

Given that $K_a : 1.8 \times 10^{-5}$, and $K_b = 1.8 \times 10^{-5}$

Sol.

	NH_4OH +	CH_3COOH →	CH_3COONH_4 +	H_2O
Initial milli moles	25 × 0.1 = 2.5	25× 0.1 = 2.5	0	0 –
Final milli moles	0	0	2.5	2.5

As salt is formed (salt of weak acid and weak base) and pH will be decided by salt hydrolysis

$$pH = \frac{pK_w + pK_a - pK_b}{2} = \frac{1}{2}(-\log 10^{-14} - \log 1.8 \times 10^{-5} + \log 1.8 \times 10^{-5}) = 7$$

Ex. In the following which one has highest / maximum degree of hydrolysis.

(1) 0.01 M NH_4Cl

(2) 0.1 M NH_4Cl

(3) 0.001 M NH_4Cl

(4) Same

Sol. **[3]** $\left(h = \sqrt{\dfrac{K_h}{C}} \quad \text{if C decreases, h increases}\right)$

Ex. In the following which one has lowest value of degree of hydrolysis.

(1) 0.01 M CH_3COONH_4

(2) 0.1 M CH_3COONH_4

(3) 0.001 M CH_3COONH_4

(4) Same

Sol. **[4]**

Ex. Find out the concentration of $[H^+]$ in 0.1M CH_3COONa solution ($K_a = 10^{-5}$)

Sol. Salt is [WA – SB] type

$$\therefore\ [H^+] = \sqrt{\frac{K_w \times K_a}{C}} = \sqrt{\frac{10^{-14} \times 10^{-5}}{10^{-1}}} = \sqrt{10^{-19} \times 10^{+1}} = \sqrt{10^{-18}} = 10^{-9}$$

Ex. Calculate the degree of hydrolysis of a mixture containing 0.1N NH_4OH and 0.1N HCN

$K_a = 10^{-5}$ & $K_b = 10^{-5}$

Sol. Salt is [WA – WB]

$$h = \sqrt{\frac{K_w}{K_a \times K_b}} = \sqrt{\frac{10^{-14}}{10^{-5} \times 10^{-5}}} = \sqrt{10^{-14} \times 10^{+10}} = \sqrt{10^{-4}} = 10^{-2}$$

(4) Hydrolysis of [SA – SB] Type Salt –

Ex. NaCl, $BaCl_2$, Na_2SO_4, $KClO_4$ etc.

$$NaCl + H_2O \rightleftharpoons NaOH + HCl$$

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

$$H_2O \rightleftharpoons H^+ + OH^- \text{ (It is not salt hydrolysis)}$$

(1) Hydrolysis of salt of [SA – SB] is not possible (2) Solution is neutral in nature (pH = pOH = 7)

(3) pH of the solution is 7

Hydrolysis of Polyvalent Anions or Cations

- The hydrolysis of these species will take place in steps (just like dissociation of weak acids).
- Out of different steps generally first step hydrolysis dominants mainly because of two reasons
- The hydrolysis constant of second and further steps is generally negligible in comparison to first step hydrolysis constant.
- The second and further step hydrolysis will be suppressed in presence of ions produced due to first step hydrolysis.

For a polyprotic acid (H_2S, H_3PO_4, H_2CO_3, $H_2C_2O_4$) we already know that the disscociation always takes place in steps, so for example for H_3PO_4

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^- \qquad K_{a_1} = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]} \qquad \text{..... (1)}$$

$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{-2} \qquad K_{a_2} = \frac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]} \qquad \text{..... (2)}$$

$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{-3}$ $\qquad K_{a_3} = \dfrac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]}$ ..... (3)

For all acids we always have $K_{a_1} >> K_{a_2} >> K_{a_3}$

pH of the solution can be calculated from Ist step only because $[H^+]$ from IInd & IIIrd step can be neglected as

(a) $K_{a_1} >> K_{a_2} >> K_{a_3}$

(b) $[H^+]$ from Ist dissociation will suppress the dissociation of IInd & IIIrd step.

Now for the hydrolysis of polyvalent ions of salts (like K_3PO_4, $Na_2C_2O_4$, $ZnSO_4$, $FeCl_3$, $(NH_4)_2C_2O_4$ or ions like PO_4^{3-}, $C_2O_4^{2-}$, Zn^{2+}, Fe^{3+} etc).

Consider the hydrolysis in step

$$\begin{array}{llll} PO_4^{3-} + H_2O & \rightleftharpoons & HPO_4^{2-} & + OH^- \\ C & & 0 & 0 \\ C(1-h) & & Ch & Ch \end{array}$$

$K_{h_1} = \dfrac{[OH^-][HPO_4^{2-}]}{[PO_4^{3-}]}$ ..... (4)

$HPO_4^{2-} + H_2O \rightleftharpoons H_2PO_4^- + OH^-$ $\qquad K_{h_2} = \dfrac{[OH^-][H_2PO_4^-]}{[HPO_4^{2-}]}$ ..... (5)

$H_2PO_4^- + H_2O \rightleftharpoons H_3PO_4 + OH^-$ $\qquad K_{h_3} = \dfrac{[OH^-][H_3PO_4]}{[H_2PO_4^-]}$ ..... (6)

$H_2O \rightleftharpoons H^+ + OH^-$ $\qquad K_w = [H^+][OH^-]$ ..... (7)

From above equations we get.

$K_{a_1} \times K_{h_3} = K_w$

$K_{a_2} \times K_{h_2} = K_w$

$K_{a_3} \times K_{h_1} = K_w$

Genarally pH is calculated only using the first step hydrolysis

$$K_{h_1} = \frac{ChCh}{C(1-h)} = \frac{Ch^2}{1-h} \approx Ch^2$$

$$h = \sqrt{\frac{K_{h_1}}{C}} \Rightarrow [OH^-] = Ch = \sqrt{K_{h_1} \times C} \Rightarrow [H^+] = \frac{K_w}{[OH^-]} = K_w\sqrt{\frac{K_{a_3}}{K_w C}} = \sqrt{\frac{k_w \times K_{a_3}}{C}}$$

So $pH = \dfrac{1}{2}[pK_w + pK_{a_3} + \log C]$

Ex. What is the pH of 1.0 M Na_3PO_4 in aqueous solution ?

$PO_4^{3-} + H_2O \rightleftharpoons HPO_4^{2-} + OH^-$; $K_b = 2.4 \times 10^{-2}$

Sol. $K_a(HPO_4^{2-}) = \dfrac{10^{-14}}{2.4 \times 10^{-2}} = 4.17 \times 10^{-13}$

$pK_a = -\log K_a = 12.38$

or $pH = 7 + \frac{1}{2} pK_a + \frac{1}{2} \log C = 7 + \frac{1}{2}(12.38) + \frac{1}{2}\log(1) = 13.19$

Hydrolysis of Amphiprotic Anion

(Cation is not Hydrolysed)

$NaHCO_3$, NaHS, etc., can undergo ionisation to from H^+ ion and can undergo hydrolysis to from OH^- (Na^+ ion is not hydrolysed)

(a) (i) $HCO_3^- + H_2O \xrightleftharpoons{\text{ionisation}} CO_3^{2-} + H_3O^+$ (acid)

(ii) $HCO_3^- + H_2O \xrightleftharpoons{\text{hydrolysis}} H_2CO_3 + OH^-$ (base)

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

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

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

Cation is Also Hydrolysed

(i) Salts like NH_4HCO_3, NH_4HS in which HCO_3^- and HS^- are amphiprotic respectively but NH_4^+ will also hydrolysed.

(ii) Equilibria in such solutions will be :

(Hydrolysis of anion)

$HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^-$

(Hydrolysis of cation)

$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$

so, $$[H^+] = \sqrt{K_{a_1}\left(\frac{K_w}{K_b} - K_{a_2}\right)}$$

Example Based on : Salt Hydrolysis

Ex. Select the compound whose 0.1 M solution is basic :

(A) ammonium chloride **(B)** ammonium acetate **(C)** ammonium sulphate **(D)** sodium acetate

Sol. **(D),** since sodium acetate is salt of (WA + SB) so its pH > 7.

Ex. If one equivalent of a strong acid is added to one equivalent of a weak base, the resulting solution will be.

(A) neutral **(B)** acidic **(C)** alkaline **(D)** none of these

Sol. **(B),** since after neutralisation salt of (SA + WB) will form and its pH < 7.

Ex. Which is the correct option for hydrolysis constant of NH_4CN ?

(A) $\sqrt{\frac{K_w}{K_a}}$ **(B)** $\frac{K_w}{K_a \times K_b}$ **(C)** $\sqrt{\frac{K_b}{K_c}}$ **(D)** $\frac{K_a}{K_b}$

Sol. **(B),** Since NH_4CN is a salt of (WA + WB).

Equilibrium constant of hydrolysis of WA + WB is $\frac{K_w}{K_a \times K_b}$

Ex. Increasing order of pH of 0.1 M solution of the following salts is :

(A) $NaCl < NH_4Cl < NaCN$ **(B)** $NH_4Cl < NaCl < NaCN$

(C) $NaCN < NH_4Cl < NaCl$ **(D)** $NaCl < NaCN < NH_4Cl$

Sol. **(B),** Since NH_4Cl is the salt of (WB + SA) so pH < 7, NaCl is salt of (SA + SB) so pH = 7 and NaCN is salt of (WA + SB) so pH < 7.

Ex. When a solution of 0.01 M CH_3COOH is titrated with a solution of 0.01 M NaOH. Calculate the pH at the equivalence point. (pK_a of CH_3COOH is 4.74)

Sol. $CH_3COOH + NaOH \rightleftharpoons CH_3COONa + H_2O$

Let acid be = V mL

V mL of 0.01 M CH_3COOH will require V mL of 0.01 M NaOH. But CH_3COONa formed will make solution alkaline due to hydrolysis

$CH_3COONa + H_2O \rightleftharpoons CH_3COOH + NaOH$

$$[CH_3COONa] = \frac{0.01}{2} = 0.005\ M$$

for pH of salt of weak acid and strong base

$$pH = 7 + \frac{pK_a}{2} + \frac{\log C}{2}$$

$$= 7 + \frac{4.74}{2} + \frac{\log 0.005}{2} = 8.22$$

Ex. Calculate the pH of 0.5 M Na_3PO_4 in aqueous solution ?

$PO_4^{3-} + H_2O \rightleftharpoons HPO_4^{2-} + OH^-$; $K_b(PO_4^{-3}) = 2.4 \times 10^{-2}$

Sol. HPO_4^{2-} and PO_4^{-3} are conjugate acid and base so $K_a \times K_b = 10^{-14}$

$$K_a(HPO_4^{2-}) = \frac{10^{-14}}{2.4 \times 10^{-2}} = 4.17 \times 10^{-13}$$

$pK_a = -\log K_a = 12.38$

or $pH = 7 + \frac{1}{2}\ pK_a + \frac{1}{2}\ \log C$

pH = 13.04

Ex. What is degree of hydrolysis, K_h and pH of 1 M urea hydrochloride solution in water. K_b (urea) = 1.5×10^{-14}.

Sol. $NH_2CONHCl$ is a salt of (SA + WB)

$$\text{so } h = \sqrt{\frac{K_w}{K_b.C}} = \sqrt{\frac{10^{-14}}{1.5 \times 10^{-14} \times 1}}$$

or h = 81.65 %

$$K_h = \frac{K_w}{K_b} = \frac{10^{-14}}{1.5 \times 10^{-14}} = 6.667 \times 10^{-1}$$

$$pH = 7 - \frac{1}{2}pK_b - \frac{1}{2}\log C$$

$$= 7 - \frac{1}{2}(13.82) - \frac{1}{2}\log(1) \text{ or } pH = 0.09$$

BUFFER SOLUTIONS

A solution that resists change in pH value upon addition of small amount of strong acid or base (less than 1 %) or when solution is diluted is called buffer solution.

The capacity of a solution to resist alteration in its pH value is known as buffer capacity and the mechanism of buffer solution is called buffer action.

Types of Buffer Solutions

(A) Simple buffer solution

(B) Mixed buffer solution

(A) Simple Buffer Solution

A salt of weak acid and weak base in water e.g. CH_3COONH_4, $HCOONH_4$, AgCN, NH_4CN.

Buffer Action of Simple Buffer Solution

Consider a simple buffer solution of CH_3COONH_4 ,since it is a salt will dissociated completely.

$$CH_3COONH_4 \longrightarrow CH_3COO^- + NH_4^+$$

If a strong acid such as HCl is added then

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

The H^+ ions from the added acid (HCl) combine with CH_3COO^- ions to form CH_3COOH, which is a weak acid so will not further ionized.

Thus there is no rise in H^+ ion concentration and the pH remains constant.

$$CH_3COO^- + H^+ \rightleftharpoons CH_3COOH \text{ (Weak acid)}$$

- If a strong base is added as NaOH

$$NaOH \longrightarrow Na^+ + OH^-$$

$$NH_4^+ + OH^- \rightleftharpoons NH_4(OH) \text{ (Weak base)}$$

Thus change in OH^- ion concentration is resisted by NH_4^+ ions by forming NH_4OH which is a weak base. So it will not further ionized and pH remains constant.

pH of a simple buffer solution :-

$$\boxed{pH = 7 + \frac{1}{2}pk_a - \frac{1}{2}pk_b}$$

(B) Mixed Buffer Solutions

(a) Acidic Buffer Solution

An acidic buffer solution consists of solution of a weak acid and its salt with strong base. The best known example is a mixture of solution of acetic acid and its salt with strong base (CH_3COONa). Other example :

$$HCN + KCN, (H_2CO_3 + NaHCO_3) \longrightarrow \text{blood}$$

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+ \text{ (Weakly ionised)}$$

$$CH_3COONa \longrightarrow CH_3COO^- + Na^+ \text{ (Highly ionised)}$$

When a few drops of an acid (HCl) are added to it, the H^+ ions from the added acid (HCl) combine with the CH_3COO^- ions to form CH_3COOH. Thus there is no rise in H^+ ion concentration and the pH of solution remains constant. On the other hand, when a few drops of base(NaOH) are added, the OH^- of the added base reacts with acetic acid to form unionise water and acetate ions.

$CH_3COOH + OH^- \rightleftharpoons H_2O + CH_3COO^-$. Thus there is no increase in OH^- ion concentration and hence the pH of the solution remains constant.

pH of an Acidic Buffer Solution (Handerson Equation)

Consider a buffer mixture (acidic buffer)

HA + NaA ($CH_3COOH + CH_3COONa$) where $A = CH_3COO$, $A^- = CH_3COO^-$

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

$$NaA \longrightarrow Na^+ + A^-$$

Applying law of mass action to dissociation equilibrium of HA

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

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

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

$$pH = pK_a + \log\frac{[A^-]}{[HA]}$$

$[A^-]$ = Initial concentration of salt as it is mainly comes from salt.

[HA] = Initial concentration of the acid.

$$pH = pK_a + \log\frac{[Salt]}{[Acid]}$$ (it is known as Handerson-Hasselbalch equation.)

KEY POINTS

A solution can act as buffer only if ratio of concentration of salt to acid is between 0.1 to 10.

CH_3COOH	:	CH_3COONa	
1		10	$pH = pK_a + 1$
10		1	$pH = pK_a - 1$

Thus pH range of an acidic buffer solution is $pK_a + 1$ to $pK_a - 1$

$$\text{pH range} = pK_a \pm 1$$

Maximum buffer capacity when concentration of salt is equal to that of acid.

$$[Salt] = [Acid]$$

Maximum buffer action will be only when ratio of concentration of acid and salt is 1. So for maximum buffer action.

$$pH = pK_a + \log 1/1 \Rightarrow pH = pK_a$$

Ex. Calculate the pH after the addition of 80 mL and 100 mL respectively of 0.1 N NaOH to 100 mL, 0.1 N CH_3COOH. (Given pK_a for $CH_3COOH = 4.74$)

Sol. If 80 mL of 0.1 N NaOH is added to 100 mL of 0.1 N CH_3COOH, acidic buffer will form as

	H_3CCOOH	+ NaOH	$\longrightarrow$ $H_3CCOONa$	+ H_2O
Initial	0.01 eq.	0.008 eq.	0	0
Final	0.002 eq.	0	0.008 eq.	

$$pH = pK_a + \log\frac{[CH_3COO^-]}{[CH_3COOH]} = 4.74 + \log\frac{8}{2} = 4.74 + 0.6020 = 5.342$$

If 100 mL of 0.1 N NaOH is added is added to 100 mL of 0.1 N CH_3COOH, complete neutralization takes place and the

concentration of $H_3CCOONa = \frac{0.1}{2}M = 0.05\ M$

Now, $pH = 7 + \frac{1}{2}pK_a + \frac{1}{2}\log C$

$pH = 8.72$

Ex. How much volume of 0.2 M solution of acetic acid should be added to 100 mL of 0.2 M solution of sodium acetate to prepare a buffer solution of pH = 6.00? (pK_a for acetic acid is 4.74)

Sol. $pH = pK_a + \log\frac{[Salt]}{[Acid]}$

$\log\frac{[Salt]}{[Acid]} = pH - pK_a = 6.00 - 4.74 = 1.26 \therefore \frac{[Salt]}{[Acid]} = 18.2$

Moles of CH_3COONa in solution $\frac{100\times0.2}{1000} = 0.02$

Let, volume of 0.2 acetic acid added = V mL

$\therefore$ Moles of acetic acid $= \frac{V\times0.2}{1000}$

$$\therefore \frac{0.02}{V\times\frac{0.2}{1000}} = 18.2$$

$\therefore V = 5.49$ mL

Ex. Calculate the pH of a solution when 0.20 moles of HCl is added to one litre solution containing ?

(a) 1 M each of acetic acid and acetate ion ? (b) 0.1 M each of acetic acid and acetate ion ?

Given K_a for acetic acid is 1.8×10^{-5}.

Sol. (a) Initially [Acetic acid] =1 M

[Acetate] = 1 M

Now 0.2 moles of HCl are added to it.

	HCl	+ CH_3COO^-	$\rightarrow$ CH_3COOH	+ Cl^-
Mole before reaction	0.2	1	1	0
Mole after reaction	0	0.8	1.2	0.2

$\therefore$ New $[CH_3COOH] = 1.2$; $[CH_3COO^-] = 0.8$

$\therefore\ pH = pk_a + \log \frac{[\text{conjugate}]}{[\text{acid}]}$

$\therefore\ pH = -\log 1.8 \times 10^{-5} + \log \frac{0.8}{1.2} = 4.5686$

(b) In II case initially [Acetic acid] = 0.1 M

[Acetate] = 0.1 M

Now 0.2 mole of HCl are added to it

	HCl	+	CH_3COO^-	→	CH_3COOH	+	Cl^-
Mole before reaction	0.2		0.1		0.1		0
Mole after reaction	0.1		0		0.2		0.1

$\therefore\ [H^+]$ from free HCl = 0.1 = 10^{-1}M

$\therefore\ pH = 1$

Note : CH_3COOH no doubt gives H^+ but being weak acid as well as in presence of HCl does not dissociate appreciably and thus, H^+ from CH_3COOH may be neglected.

Ex. Calculate the ratio of pH of a solution containing 1 mole of CH_3COONa + 1 mole of HCl per litre and of other solution containing 1 mole CH_3COONa + 1 mole of acetic acid per litre.

Sol. **Case I :** pH when 1 mole CH_3COONa and 1 mole HCl are present.

	CH_3COONa	+	HCl	→	CH_3COOH	+	NaCl
Before reaction	1		1		0		0
After reaction	0		0		1		1

$\therefore\ [CH_3COO] = 1$ M

$\therefore\ [H^+] = C.\alpha = C\sqrt{\left(\frac{K_a}{C}\right)} = \sqrt{(K_a.C)} = \sqrt{(K_a)}$ $\quad \because C = 1$

$\therefore\ pH_1 = -\frac{1}{2}\log K_a$

Case II : pH when 1 mole CH_3COONa and 1 mole of CH_3COOH ; a buffer solution

$\therefore\ pH_2 = -\log K_a + \log \frac{[\text{salt}]}{[\text{acid}]}$ $\quad \because$ [Salt] = 1M

$pH_2 = -\log K_a$ $\quad \because$ [Acid] = 1M

$\therefore\ \frac{pH_1}{pH_2} = \frac{1}{2}$

(b) Basic Buffer Solution

A basic buffer solution consists of a mixture of a weak base and its salt with strong acid. The best known example is a mixture of NH_4OH and NH_4Cl.

$NH_4OH \rightleftharpoons NH_4^+ + OH^-$ (Weakly ionised)

$NH_4Cl \rightarrow NH_4^+ + Cl^-$ (Highly ionised)

When a few drops of a base (NaOH) are added, the OH^- ions from NaOH combine with NH_4^+ ions to form feebly ionised NH_4OH thus there is no rise in the concentration of OH^- ions and hence the pH value remains constant.

$NH_4^+ + OH^- \longrightarrow NH_4OH$

If a few drops of a acid (HCl) are added the H^+ from acid combine with NH_4OH to form H_2O and NH_4^+ ions.

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

Thus the addition of acid does not increase the H^+ ion concentration and hence pH remains unchanged.

Ex. Calculate the amount of NH_3 and NH_4Cl required to prepare a buffer solution of pH = 9 when total concentration of buffering reagents is 0.3 mol L^{-1}. (pK_b for NH_3 = 4.7, log 2 = 0.30)

Sol. $pOH = -\log K_b + \log \frac{[salt]}{[Base]}$

$$5 = 4.7 + \log \frac{a}{b} \Rightarrow \frac{a}{b} = 2$$

$\therefore$ a = 2b

Given a + b = 0.3

2b + b = 0.3

$\therefore$ 3b = 0.3

or b = 0.1 mole/L

Amount of base = 0.1 × 17 = 1.7 g/L

$\therefore$ a = 0.2 mole/L

Amount of salt = 0.2 × 53.5 = 10.7 g/L

Thus, [Salt] = 0.2 M and [Base] = 0.1 M

- **pH of Basic Buffer Solution**

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

$NH_4Cl \longrightarrow NH_4^+ + Cl^-$

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

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

(NH_4^+ mainly comes from salt)

taking –log on both side

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

$$pOH = pK_b + \log \frac{[Salt]}{[Base]} \Rightarrow pH = 14 - pOH$$

- **pOH Range**

A solution can act as buffer solution only if ratio of concentration of salt to base is from 0.1 to 10.

NH_4OH	:	NH_4Cl	
1		10	$pOH = pK_b + 1$
10		1	$pOH = pK_b - 1$

So pOH range is $pK_b \pm 1$

- **Condition for Maximum Buffer Action**

$[NH_4OH]$: $[NH_4Cl]$ i.e. [Salt] = [Base]

1 : 1

$$pOH = pK_b + \log\frac{1}{1}$$

$pOH = pK_b$ and $pH = 14 - pK_b$

Maximum buffer action because pH remains constant.

Ex. A solution of weak base LiOH was titrated with 0.1 N HCl. The pH of the solution was found to be 10.04 and 9.14 after the addition of 5 mL and 20 mL of the acid respectively. Find the dissociation constant of the base.

Sol. **Case I :**

	LiOH	+ HCl	⟶ LiCl	+ H_2O
Millimole before reaction	a	0.1× 5=0.5	0	0
Millimole after reaction	(a–0.5)	0	0.5	0.5

$$\therefore pOH = -\log K_b + \log\frac{[LiCl]}{[LiOH]} \quad ....(i)$$

$\because$ pH = 10.04 so pOH = 3.96

$$\therefore 3.96 = -\log K_b + \log\frac{0.5}{(a-0.5)} \quad ....(ii)$$

Case II :

	LiOH	+ HCl	⟶ LiCl	+ H_2O
Millimole before reaction	a	0.1× 20=2	0	0
Millimole after reaction	(a–2)	0	2	2

$$\therefore pOH = -\log K_b + \log\frac{[LiCl]}{[LiOH]} \quad ....(iii)$$

$\because$ pH = 9.14 $\therefore$ pOH = 4.86

$$\therefore 4.86 = -\log K_b + \log\frac{2}{(a-2)} \quad ....(iv)$$

Solving Eqs. (ii) and (iv), $K_b = 1.81 \times 10^{-5}$

Ex. An organic base B has K_b value equal to 1×10^{-8}. In what amounts should 0.01 M HCl and 0.01 M solution of B be mixed to prepare 1 L of a buffer solution having pH = 7.0 ?

Sol. $B + H_2O \rightleftharpoons BH^+ + OH^-$

$$K_b = \frac{[XH^+][OH^-]}{[B]} = 1 \times 10^{-8}$$

$$pOH = pK_b + \log\frac{[BH^+]}{[B]}$$

$\Rightarrow 7 = -\log(10^{-8}) + \log\frac{[BH^+]}{[B]} \Rightarrow 7 = 8 + \log\frac{[BH^+]}{[B]}$

$\log\frac{[BH^+]}{[B]} = -1$

$\therefore \frac{[BH^+]}{[B]} = 10^{-1} = 0.1$

Let, volume of HCl taken = xL

$\therefore$ Volume of base taken = (1 – x) L

After the reaction, millimole of BH^+ formed = 0.01 × (x)

Millimoles of base left = 0.01 (1 – 2x)

$\therefore \frac{[BH^+]}{[B]} = \frac{x}{[1-2x]} = 0.1$

$\therefore$ x = 0.083 L = Volume of HCl

$\therefore$ Volume of base = 0.0917 L

BUFFER CAPACITY

It is defined as the number of moles of acid (or base) require by one litre of a buffer solution for changing its pH by one unit.

$$\text{Buffer capacity} = \frac{\text{No.of moles of acid or bases added per litre}}{\text{change in pH}}$$

Buffer capacity gives the tendency of buffer to resist change in its pH.

Higher is the buffer capacity, smaller will be the change in pH and more efficient will be the buffer.

Ex. When 2 moles of HCl is added to 1 lit. of an acidic buffer solution, its pH changes from 3.4 to 3.9. Find its buffer capacity.

Sol. $B.C. = \frac{2}{0.5} = 4$

EXAMPLE BASED ON : Buffer solutions

Ex. Which of the following buffers containing NH_4OH and NH_4Cl show the lowest pH value?

	Conc. of NH_4OH (mol L^{-1})	Conc. of NH_4Cl (mol L^{-1})
(A)	0.50	0.50
(B)	0.10	0.50
(C)	0.50	1.50
(D)	0.50	0.10

Sol. **(B)** $pOH = pk_b + \log\frac{[salt]}{[base]}$ for $NH_4Cl = 0.5$ and $NH_4OH = 0.1$

pOH will be maximum and so pH will be minimum.

Ex. pH of a mixture containing 0.2 M X^- (base) and 0.4 M HX with $pK_b(X^-) = 4$ is :

(A) 4 + log 2 **(B)** 4 – log 2 **(C)** 10 + log 2 **(D)** 10 – log 2

Sol. **(D).** $HX \rightleftharpoons H^+ + X^-, K_a = \frac{10^{-14}}{K_b} = 10^{-10}$

$$[H^+] = K_a \frac{[HX]}{[X^-]} = \frac{10^{-10} \times 0.4}{0.2}$$

or $pH = 10 - \log 2$

Ex. pH of a mixture of 1 M benzoic acid ($pK_a = 4.2$) and 1 M sodium benzoate is 4.5, in 150 mL buffer, benzoic acid is :

(A) 200 mL **(B)** 150 mL **(C)** 100 mL **(D)** 50 mL

Sol. **(D)** $pH = pK_a + \log \frac{[salt]}{[Acid]}$

$$4.5 = 4.2 + \log \left[\frac{(150 - x)}{x}\right]$$ where x is the volume of benzoic acid

$$0.3 = \log \left[\frac{(150 - x)}{x}\right] \text{ or } 2.0 = \left[\frac{(150 - x)}{x}\right]$$

or $x = 50$ mL

Ex. Buffering action of a mixture of CH_3COOH and CH_3COONa is maximum when the ratio of salt to acid is equal to :

(A) 1.0 **(B)** 100.0 **(C)** 10.0 **(D)** 0.1

Sol. **(A).** The buffer action of a buffer mixture is effective in the pH range $pK_a \pm 1$. It is maximum when $pH = pK_a$.

Ex. What amount of sodium propanoate should be added to one litre of an aqueous solution containing 0.02 mole of propanoic acid to obtain a buffer solution of pH 4.74 ? What will be the pH of 0.01 mol of HCl is dissolved in the above buffer solution ? Compare the last pH value with the pH of 0.01 molar HCl solution. Dissociation constant of propanoic acid at 25°C is 1.34×10^{-5}.

Sol. Using Henderson's expression

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

We get $4.74 = -\log(1.34 \times 10^{-5}) + \log \frac{[Salt]}{0.02}$

Which gives $4.74 = 4.87 + \log \frac{[Salt]}{0.02}$ or $\frac{[Salt]}{0.02} = 0.74$ or $[Salt] = 1.48 \times 10^{-2}$ M

Hence, amount of sodium propanoate to be added $= 1.48 \times 10^{-2} \times 96$ g $= 1.42$ g

The addition of 0.01 mol of HCl converts the equivalent amount of sodium propanoate into propanoic acid. Hence, we will have

$$pH = 4.87 + \log \frac{(0.01482 - 0.01)\,mol\,L^{-1}}{(0.02 + 0.01)\,mol\,L^{-1}}$$

$pH = 4.87 + \log(0.160) = 4.87 - 0.79 = 4.08$

(The pH of 0.01 molar HCl solution would be $pH = -\log(0.01) = 2$)

Ex. A solution of a weak acid was titrated with NaOH the equivalence point was reached when 25.06 mL of 0.1 N NaOH have been added. Now 12.53 mL of 0.1 N HCl were added to the titrated solution, the pH was found to be 4.92. What is K_a of the acid.

Sol. For complete neutralisation, meq. of acid = meq. of NaOH

$$= 25.06 \times 2.506 = 3.612 \text{ meq.}$$

	HA	+	NaOH	$\longrightarrow$	NaA	+	H_2O
Initial	2.506		2.506		0		0
At equivalence point	0		0		2.506		2.506

Now 1.253 meq. of HCl are added so,

NaA	+	HCl	$\longrightarrow$	NaCl	+	HA	
2.506		1.253		0		0	(Before)
1.253		0		1.253		1.253	(After)

Now mixture contains HA and NaA so it will be Acidic buffer,

$$pH = pK_a + \log \frac{[Salt]}{[Acid]} = pK_a + \log\left(\frac{1.253}{1.253}\right)$$

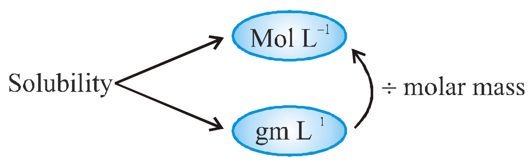
or $\quad pH = pK_a$

or $\quad K_a = \text{antilog}(-4.92)$

or $\quad K_a = 1.2 \times 10^{-5}$

Solubility (s) and Solubility Product (Ksp)

Solubility : "Moles of a substance dissolved per unit volume of a solution."



Classification of Salts :

If $S > 0.1$ M $\Rightarrow$ Soluble Salts

If $0.01 \text{ M} < S < 0.1$ M $\Rightarrow$ Partial Soluble salts

If $S < 0.01$ M $\Rightarrow$ Sparingly soluble salts

Note : All salts of alkali metals and NH_4^+ ion are generally water soluble.

Examples of sparingly soluble salts are AgCl, $PbCl_2$, Hg_2Cl_2, $PbSO_4$, Ag_2CO_3, $CaSO_4$, AgCN, etc.

Process of Dissolution of Sparingly Soluble Salts

Let AB $\longrightarrow$ Sparingly Soluble Salt

$$AB(s) \underset{\text{Precipitation}}{\overset{\text{dissolution}}{\underset{H_2O(\ell)}{\rightleftharpoons}}} \overset{\oplus}{A}(aq) + \overset{\ominus}{B}(aq)$$

Initially,

rate of dissociation $>$ rate of ppt.

$\therefore$ more salt can be dissolved and solution is unsaturated.

But, when

Saturated solution

rate of dissolution = rate of ppt ion

In a saturated solution, whatever salt is dissolved will be present in the form of its ions and therefore, concentration of ions in a saturated solution will represent solubility of the salt.

This is generally used for sparingly soluble salts. We will be dealing with the solubilities in the following type of solution

Solubility Product (K_{sp})

For a saturated solution,

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

$$K_{eq.} = \frac{[A^+][B^-]}{[AB]} \quad [\because \text{concentration of solid is constant}]$$

$$\therefore \underbrace{Keq. [AB]}_{\downarrow} = [A^+] [B^-]$$

$$\boxed{K_{sp} = [A^+] [B^-]}$$

Solubility product (K_{sp}) is a type of equilibrium constant, so will be dependent only on temperature for a particular salt.

Here different methods for writing K_{sp} for different types of salts are following :

(a) AB Type Salt

$$AB(s) \rightleftharpoons \underset{s}{A^+(aq)} + \underset{s}{B^-(aq)}$$

$$K_{sp} = [A^+] [B^-] = s^2$$

$$\boxed{s = \sqrt{K_{sp}}}$$

(b) A_2B Type Salt

$$A_2B(s) \rightleftharpoons \underset{2s}{2A^+(aq)} + \underset{s}{B^-(aq)}$$

$$K_{sp} = [A^+]^2[B^-] = [2s]^2[s] = 4s^3$$

$$\boxed{K_{sp} = 4s^3}$$

(c) AB_3 Type Salt

$$AB_3(s) \rightleftharpoons \underset{s}{A^{3+}(aq)} + \underset{3s}{3B^-(aq)}$$

$$\boxed{K_{sp} = [s][3s]^3 = 27s^4}$$

(d) A_2B_3 Type Salt

$$A_2B_3(s) \rightleftharpoons \underset{2s}{2A^{3+}(aq)} + \underset{3s}{3B^{2-}(aq)}$$

$$K_{sp} = [2s]^2[3s]^3$$

$$\boxed{K_{sp} = 108\ s^5}$$

(e) AxBy Type Salt

$$AxBy \rightleftharpoons xA^{y+} + yB^{x-}$$
$$\quad xs \qquad ys$$
$$K_{sp} = (xs)^x (ys)^y$$
$$\boxed{K_{sp} = x^x.y^y.s^{x+y}}$$

Following examples will illustrate the different type of solubilities and the effects of different factors or situation on solubility of a salt.

Simple Solubility

Let the salt is $A_x B_y$, in solution in water, let the solubility in H_2O = 's' M, then

$$A_xB_y \rightleftharpoons xA^{y+} + yB^{-x}$$
$$- \qquad xs \qquad ys \qquad\qquad \therefore\ k_{sp} = (xs)^x (ys)^y = x^x, y^y. (s)^{x+y}$$

Ex. Calculate k_{sp} of $Li_3Na_3[AlF_6]_2$

Sol. $k_{sp} = 3^3.3^3.2^2.(s)^8 = 3^6.4\,(s)^8 = 2916\,s^8$

Self Practice Problem

Ex. Calculate k_{sp} of $Mg_3(PO_4)_2$

Sol. $108\,s^5$

Solubility in Different Solutions

Solubility in Presence of Common - Ion

Because of the presence of common ion the solubility of the salt decreases

Ex. Calculate solubility of silver oxalate in 10^{-2}M Potassium oxalate solution given that k_{sp} of silver oxalate $= 10^{-10}$

Sol. [oxalate] = 10^{-2} + x, where x is the solubility of silver oxalate, this can be neglected in comparison to 10^{-2}. so

$$k_{sp} = 10^{-10} = 10^{-2} \times (2x)^2 \Rightarrow \frac{10^{-8}}{2\times 2} = x^2 \Rightarrow x = 5\times 10^{-5}$$

Self Practice Problem

Ex. Calculate the solubility of $BaCl_2$ in presence of 'c' mol/litre NaCl in terms of $K_{sp}(BaCl_2)$.

Sol. K_{sp}/c^2

- **Calculation of Simultaneous Solubility**
- When two sparingly soluble salts are added in water simultaneously, there will be two simultaneous equilibria in the solution.

  Let simultaneous solubility of AB be x mol L^{-1}

$$AB(s) \rightleftharpoons A^+(aq) + B^-(aq)$$
$$x+y \qquad x$$
$$K_{sp1} = x(x+y)$$

  Simultaneously solubility of AC be y mol L^{-1}

$$AC(s) \rightleftharpoons A^+(aq) + C^-(aq)$$
$$x+y \qquad y$$
$$K_{sp2} = y(x+y)$$

  Solving

$$x + y = \sqrt{K_{sp1} + K_{sp2}} \qquad \text{and}$$

$$\frac{x}{y} = \frac{K_{sp1}}{K_{sp2}}$$

Self Practice Problem

Ex. Calculate solubility of $BaSO_4$ when $BaSO_4$ and $CaSO_4$ are dissolved in water simultaneously $K_{sp}CaSO_4 = p$, $K_{sp}BaSO_4 = q$ and solubility of $CaSO_4$ is 'b' mol/litre.

Sol. bq/p

Ex. Calculate simultaneous solubility of silverthiocyanate and sliver bromide in water given that k_{sp} of silver thiocyanate $= 10^{-12}$ and k_{sp} of silver bromide $= 5 \times 10^{-13}$ respectively.

Sol. Let the solubility of AgSCN be x and that of AgBr is y, then

$$AgSCN \rightleftharpoons \underset{x+y}{Ag^+} + \underset{x}{SCN^-} \qquad AgBr \rightleftharpoons \underset{x+y}{Ag^+} + \underset{y}{Br^-}$$

$10^{-12} = x(x + y)$ ...... (i)

$5 \times 10^{-13} = y(x + y)$ ...... (ii)

On solving we get, $x = 2y$

So $y = 4.08 \times 10^{-7}$ and $x = 8.16 \times 10^{-7}$

Ex. 50 mL of 0.02 M solution of $Ca(NO_3)_2$ is added to 150 mL of 0.08 M solution of $(NH_4)_2SO_4$. Predict whether $CaSO_4$ will be precipitated or not, $K_{sp}(CaSO_4) = 4 \times 10^{-5}$.

Sol. Calculation of Ca^{2+} concentration, $M_1V_1 = M_2V_2$

$0.02 \times 50 = M_2 \times 200$

$\therefore [Ca(NO_3)_2]$ after mixing $= 5 \times 10^{-3}$ mol L^{-1}

Since $Ca(NO_3)_2$ is completely ionized, $[Ca^{2+}] = [Ca(NO_3)_2] = 5 \times 10^{-3}$ mol L^{-1}

Calculation of SO_4^{2-} ion concentration

Applying $M_1'V_1' = M_2'V_2'$

$\therefore 0.08 \times 150 = M_2' \times 200$

$$\therefore M_2' = \frac{0.08 \times 150}{200} = 6 \times 10^{-2}\ M$$

$\therefore [(NH_4)_2SO_4]$ is completely ionized, $[SO_4^{2-}] = [(NH_4)_2SO_4) = 6 \times 10^{-2}$ mol/L

Ionic product $= [Ca^{2+}][SO_4^{2-}] = [5 \times 10^{-3}][6 \times 10^{-2}] = 3 \times 10^{-4}$

Since Ionic product (3×10^{-4}) is greater than solubility product of $CaSO_4$ (4×10^{-5}), hence precipitate of $CaSO_4$ will be formed.

Ex. What is the maximum volume of water required to dissolve 1 g of calcium sulphate at 25°C. For calcium sulphate, $K_{sp} = 9.0 \times 10^{-6}$.

Sol. $CaSO_4(aq) \rightleftharpoons Ca^{2+}(aq) + SO_4^{2-}(aq)$

If S is the solubility of $CaSO_4$ in moles L^{-1}

$K_{sp} = [Ca^{2+}] \times [SO_4^{2-}] = S^2$

$$\therefore S = \sqrt{K_{sp}} = \sqrt{9.0 \times 10^{-6}}$$

$= 3 \times 10^{-3}$ mol L^{-1}

$= 3 \times 10^{-3} \times 136$ g $L^{-1} = 0.408$ gL^{-1}

For dissolving 0.408 g of $CaSO_4$ water required = 1 L

$\therefore$ For dissolving 1g $CaSO_4$ water required $= \frac{1}{0.408}$ L $= 2.45$ L

Ex. A weak acid HA after treatment with 12mL of 0.1M strong base BOH has a pH of 3. At the end point, the volume of same base required is 26.6 mL. Calculate K_a of acid.

Sol. For neutralization :

Total Meq. of acid = Meq. of base = 26.6 × 0.1 = 2.66

Now for partial neutralization of acid

	HA	+	BOH	→	BA	+	H_2O
Meq. before reaction	2.66		1.2		0		0
Meq. after reaction	1.46		0		1.2		1.2

The resultant mixture acts as a buffer and [HA] and [BA] may be placed in terms of Meq. since volume of mixture is constant.

$\therefore \quad pH = -\log K_a + \log \frac{[Salt]}{[Acid]} \quad$ or $\quad 3 = -\log K_a + \log \frac{[1.2]}{[1.46]}$

$\therefore \quad K_a = 8.219 \times 10^{-4}$

Ex. Calculate simultaneous solubility of AgCNS and AgBr in a solution of water. K_{sp} of AgBr = 25×10^{-13} and K_{sp} of AgCNS = 5×10^{-12}.

Sol. Let solubility of AgCNS and AgBr in a solution be a and b mol $litre^{-1}$ respectively.

$$AgCNS\ (s) \rightleftharpoons \underset{a}{Ag^+} + \underset{a}{CNS^-}$$

$$AgBr\ (s) \rightleftharpoons \underset{b}{Ag^+} + \underset{b}{Br^-}$$

$\therefore$ For AgCNS $\quad K_{sp_{AgCNS}} = [Ag^+][CNS^-]$

$5 \times 10^{-12} = (a + b)(a)$ ....(1)

For AgBr $\quad K_{sp_{AgBr}} = [Ag^+][Br^-]$

$25 \times 10^{-13} = (a + b)(b)$ ....(2)

By Eqs. (1) and (2),

$\therefore \quad \frac{a}{b} = \frac{5 \times 10^{-12}}{25 \times 10^{-13}} = 2 \quad$ or $\quad a = 2b$

$\therefore \quad$ By Eq. (1), $(2b + b)(2b) = 1 \times 10^{-12}$

$6b^2 = 5 \times 10^{-12}$

$b = 0.912 \times 10^{-6}$ mol $litre^{-1} = 9.12 \times 10^{-5}$ M

By Eq. (1), $(a + a/2)(a) = 5 \times 10^{-12}$

$$a = 1.82 \times 10^{-6} \text{ mol litre}^{-1}$$

Ex. Equal volumes of 0.04 M $CaCl_2$ and 0.0008 M Na_2SO_4 are mixed. Will a precipitate form? K_{sp} for $CaSO_4 = 2.4 \times 10^{-5}$

Sol.

	$CaCl_2$ +	Na_2SO_4 →	$CaSO_4$ +	2NaCl
Millimole added	0.04 V	0.0008×V	0	0

Suppose V mL of both are mixed

$$\therefore \quad [Ca^{2+}] = \frac{0.04\,V}{2V}$$

$$[SO_4^{2-}] = \frac{0.0008\,V}{2V}$$

$$\therefore \quad [Ca^{2+}][SO_4^{2-}] = \frac{0.04\,V}{2V} \times \frac{0.0008\,V}{2V} = 8 \times 10^{-6}$$

Thus, $[Ca^{2+}][SO_4^{2-}]$ in solution < K_{sp}

$8 \times 10^{-6} < 2.4 \times 10^{-5}$

$\therefore$ $CaSO_4$ will not precipitate.

Ex. Calculate the $[OH^-]$ of a solution after 50 mL of 0.2 M $MgCl_2$ is added to 500 mL of 0.4 M NaOH. K_{sp} of $Mg(OH)_2$ is 1.2×10^{-11}.

Sol.

	$MgCl_2$ +	2NaOH →	$Mg(OH)_2$ +	2NaCl
m mole before reaction	10	20	0	0
	0	0	10	20

Thus, 10 m mole of $Mg(OH)_2$ are formed. The product of $[Mg^{2+}][OH^-]^2$ is therefore $\left[\frac{10}{100}\right] \times \left[\frac{20}{100}\right]^2 = 4 \times 10^{-3}$ which is more than K_{sp} of $Mg(OH)_2$. Now solubility (S) of $Mg(OH)_2$ can be derived by

$K_{sp} = 4S^3$

$$\therefore \quad S = \sqrt[3]{K_{sp}} = \sqrt[3]{1.2 \times 10^{-11}} = 1.4 \times 10^{-4} \text{ M}$$

$$\therefore \quad [OH^-] = 2S = 2.8 \times 10^{-4} \text{ M}$$

Ex. Will a precipitate of $Mg(OH)_2$ be formed in a 0.002 M solution of $Mg(NO_3)_2$, if the pH of solution is adjusted to 9 ? K_{sp} of $Mg(OH)_2 = 8.9 \times 10^{-12}$.

Sol. pH = 9

$\therefore$ $[H^+] = 10^{-9}$ M

or $[OH^-] = 10^{-5}$ M

Now if $Mg(NO_3)_2$ is present in a solution of $[OH^-] = 10^{-5}$ M, then,

Product of ionic conc. $= [Mg^{+2}][OH^-]^2 = [0.002][[10^{-5}]^2$

$= 2 \times 10^{-13}$ lesser than K_{sp} of $Mg(OH)_2$ i.e, 8.9×10^{-12}

$\therefore$ $Mg(OH)_2$ will not precipitate.

- **Condition of Precipitation**
- For precipitation ionic product [IP] should be greater than solubility product k_{sp}

Ex. You are given 10^{-5} M NaCl solution and 10^{-8} M $AgNO_3$ solution, they are mixed in 1 : 1 volume ratio, predict whether AgCl will be precipitated or not, if solubility product of AgCl in 10^{-2} M $AgNO_3$ is = 10^{-10} mole per litre.

Sol. Ionic product = $\frac{10^{-5}}{2} \times \frac{10^{-8}}{2} = 25 \times 10^{-15} < k_{sp}$

Hence no precipitation will take place.

- **Solubility in Appropriate Buffer Solutions**

Appropriate buffer means that the components of buffer should not interfere with the salt or only H^+ or OH^- ions should be interacting with the ions of the salt.

For example in AgCN since, a buffer solution resist change in its pH, H^+ ion concentration remains same and hence, solubility of AgCN in buffer solution can be calculated as $\frac{K_{sp}}{K_a} = \frac{s^2}{[H^+]_{buffer}}$.

- **Selective Precipitation:** When the k_{sp} values differ then one of the salt can be selectively precipitated.

Ex. What $[H^+]$ must be maintained in saturated H_2S(0.1 M) to precipitate CdS but not ZnS, if $[Cd^{2+}] = [Zn^{2+}] = 0.1$ initially ?

$K_{sp} = (ZnS) = 1 \times 10^{-21}$

$K_a = (H_2S) = 1.1 \times 10^{-21}$

Sol. In order to prevent precipitation of ZnS

$[Zn^{2+}]\,[S^{2-}] < K_{sp}(ZnS) = 1 \times 10^{-21}$

(ionic product)

or $(0.1)\,[S^{2-}] < 1 \times 10^{-21}$

or $[S^{2-}] < 1 \times 10^{-20}$

This is the maximum value of $[S^{2-}]$ before ZnS will precipitate. Let $[H^+]$ to maintain this $[S^{2-}]$ be x. Thus for

$$H_2S \rightleftharpoons 2H^+ + S^{2-}$$

$$K_a = \frac{[H^+]^2[S^{2-}]}{[H_2S]} = \frac{x^2\,(1\times10^{-20})}{0.1}$$

$= 1.1 \times 10^{-21}$

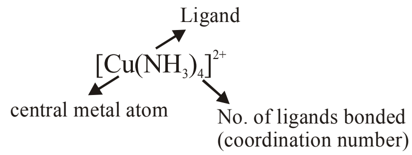
or $x = [H^+] = 0.1$ M

$\therefore$ No ZnS will precipitate at a concentration of H^+ greater than 0.1 M

- **Effect on Solubility Because of Complex Formation**

Taking AgCN as an example we can explain the solubility AgCN in different mediums as follows :

Acidic medium > water > basic



Formation of $[Ag(NH_3)_2]^+$

$$Ag^+(aq) + NH_3(aq) \overset{K_1}{\rightleftharpoons} Ag(NH_3)^+(aq) \qquad K_1 = \frac{[Ag(NH_3)^+]}{[Ag^+][NH_3]}$$

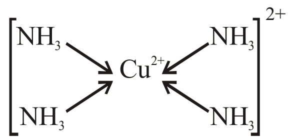
$$Ag(NH_3)^+ + NH_3(aq) \overset{K_2}{\rightleftharpoons} [Ag(NH_3)_2]^+(aq) \qquad K_2 = \frac{[Ag(NH_3)_2{}^+]}{[Ag(NH_3)^+][NH_3]}$$

$$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+$$

$K_{stab} / K_f \longrightarrow$ formation constant / stability constant

$\therefore \quad K_f = K_1 \times K_2$

$[Cu(NH_3)_4]^{2+}$



Ex.

$$Cu^{2+}(aq) + 4NH_3(aq) \overset{K_f}{\rightleftharpoons} [Cu(NH_3)_4]^{2+}$$

$$K_{stab} / K_f = \frac{[Cu(NH_3)_4{}^{2+}]}{[Cu^{2+}][NH_3]^4}$$

Higher is the value of K_f/K_{stab}, more stable will be the complex and vice-versa.

$$[Cu(NH_3)_4]^{2+} \overset{K_{instant}}{\rightleftharpoons} Cu^{2+} + 4NH_3$$

$$\therefore \quad K_{stab} / K_f = \frac{1}{K_{instant}}$$

The ion which undergo complex formation will be more stable in aqueous solution as compared to that of parent ion. Therefore, the salts whose ions (both cation or anion) undergo complex formation will have more solubility as compared to solubility in pure water.

Ex. $S_1 \Rightarrow$ AgCl in H_2O

$S_2 \Rightarrow$ AgCl in NaCl $\Rightarrow$ common ion effect

$S_3 \Rightarrow$ AgCl in aq. NH_3 or NH_4OH $\Rightarrow$ complex formed

$$\boxed{S_3 > S_1 > S_2}$$

Ex. What must be the concentration of aq. NH_3(eq.) which must be added to a solution containing 4×10^{-3} M Ag^+ and 0.001 M NaCl, to prevent the precipitation of AgCl. Given that $K_{sp}(AgCl) = 1.8 \times 10^{-10}$ and the formation constant of $[Ag(NH_3)_2]^+$ is $K_{formation} = \frac{10^8}{6}$.

Sol. Calculate silver ion concentration which can be allowed to remain in the solution,

$1.8 \times 10^{-10} = [Ag^+][Cl^-]$

$[Ag^+] = \dfrac{1.8\times10^{-10}}{0.001} = 1.8 \times 10^{-7} M,$

This quantity is so small that almost all the Ag^+ ion will be consumed.

$$Ag^+ \quad + \quad 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+ \qquad K = \frac{10^8}{6}$$

4×10^{-3} b   0

1.8×10^{-7} $(b - 8 \times 10^{-3})$ 4×10^{-3} $K = \dfrac{10^8}{6} = \dfrac{4\times10^{-3}}{1.8\times10^{-7}\times(b-8\times10^{-3})^2} \Rightarrow b = 0.0445$

Ex. The solubility of $Mg(OH)_2$ is increased by addition of NH_4^+ ion. Find

(i) K_c for the reaction

$$Mg(OH)_2 + 2NH_4^+ \rightleftharpoons 2NH_3 + 2H_2O + Mg^{2+}$$

(ii) Calculate solubility of $Mg(OH)_2$ in a solution containing 0.5 M NH_4Cl

$(K_{sp[Mg(OH)_2]} = 1.0 \times 10^{-11}, K_{b\,(NH_3)} = 1.8 \times 10^{-5})$

Sol. (i) For the reaction

$$Mg(OH)_2 + 2NH_4^+ \rightleftharpoons 2NH_3 + 2H_2O + Mg^{2+}$$

$$K_c = \frac{[NH_3]^2[Mg^{2+}]}{[NH_4^+]^2} \qquad \text{..........(1)}$$

Also for the reaction

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

$$K_{b_{(NH_3)}} = \frac{[NH_4^+][OH^-]}{[NH_3]} \qquad \text{..........(2)}$$

[As water is in large excess in both the cases]

Now, $$K_c \times K_b^2 = \frac{[NH_3]^2[Mg^{2+}]}{[NH_4^+]^2} \times \frac{[NH_4^+]^2[OH^-]^2}{[NH_3]^2}$$

$$= [Mg^{+2}]\,[OH^-]^2 = K_{sp[Mg(OH)]_2}$$

$$\therefore \quad K_c = \frac{K_{sp}}{K_b^2} = \frac{10^{-11}}{(1.8\times10^{-5})^2} = 3.08 \times 10^{-2}$$

(ii) Now, let us, assume that 'a' moles of $Mg(OH)_2$ be dissolved in presence of 0.5 M NH_4Cl.

	$Mg(OH)_2$	+	$2NH_4^+$	$\rightleftharpoons$	$2NH_3$	+	$2H_2O$	+	Mg^{2+}
Initial	—		0.5		0		—		0
Eqm.	—		(0.5–2a)		2a		—		a

$$\therefore \quad K_c = \frac{a \times (2a)^2}{(0.5-2a)^2} \approx \frac{4a^3}{0.25} = 3.08 \times 10^{-2}$$

or $a = 0.124$ M

Ex. 0.10 mol sample of $AgNO_3$ is dissolved in one litre of 2.00 M NH_3. Is it possible AgCl(s) form the solution by adding 0.010 mol of NaCl ? ($K_{sp(AgCl)} = 1.8 \times 10^{-10}$, $K_{f[Ag(NH_3)_2^+]} = 1.6 \times 10^7$)

Sol. $Ag^+ \quad + \quad 2NH_3 \rightleftharpoons [Ag(NH_3)_2^+]$

0.10 M 2.00 0

0.10–0.10 (2–0.20 M) 0.10 M

= 0 = 1.80 M

It is assumed that all Ag^+ ions have been complexed and only x amount is left

$$K_f = \frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2} \Rightarrow 1.6 \times 10^7 = \frac{0.10}{x(1.80)^2}$$

$\therefore$ $x = 1.93 \times 10^{-9}$ M = $[Ag^+]$ undisolved

$[Cl^-] = 1.0 \times 10^{-2}$ M

$\therefore$ $[Ag^+][Cl^-] = 1.93 \times 10^{-9} \times 1.0 \times 10^{-2} = 1.93 \times 10^{-11} < 1.8 \times 10^{-10} [K_{sp(AgCl)}]$

Hence, AgCl (s) will not precipitate.

Ex. How many grams of CaC_2O_4 will dissolve in distilled water to make one litre of saturated solution ($K_{sp} = 6.25 \times 10^{-10}$ and its molecular mass is 128) :

(A) 0.0064 g **(B)** 0.0128 g **(C)** 0.0032 g **(D)** 0.0640 g

Sol. **(C)**

$[Ca^{2+}][C_2O_4^{2-}] = 6.25 \times 10^{-10}$ so solubility = 2.5×10^{-5} mol/L = $2.5 \times 128 \times 10^{-5} = 3.2 \times 10^{-3}$ g/L

Ex Select the sulphides which has maximum solubility in water ?

(A) CdS ($K_{sp} = 36 \times 10^{-30}$) **(B)** FeS ($K_{sp} = 11 \times 10^{-20}$)

(C) HgS ($K_{sp} = 32 \times 10^{-54}$) **(D)** ZnS ($K_{sp} = 11 \times 10^{-22}$)

Sol. **(B)**

All salt are AB type so solubility will be $\sqrt{K_{sp}}$. Higher the value of K_{sp}, the maximum will be solubility.

Ex. If equal volumes of the following solutions are added, precipitation of AgCl ($K_{sp} = 1.8 \times 10^{-10}$) will occur only with.

(A) 10^{-4} M (Ag^+) and 10^{-4} M (Cl^-) **(B)** 10^{-5} M (Ag^+) and 10^{-5} M (Cl^-)

(C) 10^{-6} M (Ag^+) and 10^{-6} M (Cl^-) **(D)** 10^{-10} M (Ag^+) and 10^{-10} M (Cl^-)

Sol. **(A)**

One can calculate ionic product from given data and for precipitation Ionic product > K_{sp}.

Ex. If hydrolysis of any one of the ions will occur, after the dissolution of a sparingly soluble salt, then -

(A) solubility of salt decreases. **(B)** solubility of salt increases

(C) there will be no effect on solubility **(D)** question is absurd

Sol. **(B)**

Dissolution equilibria shift towards right side due to hydrolysis of cation or anion.

Ex. What is the concentration of Ag^+ ions in 0.01 M $AgNO_3$ that is also 1.0 M NH_3 ? Will AgCl precipitate from a solution that is 0.01 M $AgNO_3$, 0.01 M NaCl and 1 M NH_3?

$K_d(Ag[NH_3]_2^+) = 5.88 \times 10^{-8}$;

$K_{sp}(AgCl) = 1.8 \times 10^{-10}$.

Sol. Let us first assume that 0.01 M $AgNO_3$ shall combine with 0.02 NH_3 to form 0.01 M $Ag(NH_3)_2^+$ and the consider its dissociation.

$AgNO_3$	+	$2NH_3$	$\longrightarrow$	$Ag(NH_3)_2^+$	...Initial conc.
0.01 M		1 M		0	
0		(1–0.02)=0.98M		0.01 M	...at eq. conc.

$$Ag(NH_3)_2^+ \rightleftharpoons Ag^+ + 2NH_3$$

$Ag(NH_3)_2^+$	Ag^+	$2NH_3$
$(0.01 - x)$	x	$(0.98 + 2x)$
$= 0.01$ M		≈ 0.98 M
		....Equib. conc.

Since x <<< 1

$$K_d = \frac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2^+]} = 5.88 \times 10^{-8}$$

$$\therefore [Ag^+] = \frac{5.88 \times 10^{-8} \times 0.01}{(0.98)^2} = 6.12 \times 10^{-10}\ M$$

Further, ionic product of AgCl = $[Ag^+][Cl^-] = (6.12 \times 10^{-10})(0.01) = 6.12 \times 10^{-12}$

Because the ionic product is smaller than $K_{sp} = 1.8 \times 10^{-10}$, no precipitate should form.

INDICATORS

An indicator is a substance which changes its colour at the end point or neutral point of the acid-base titration i.e. the substance which is used to indicate neutral point of acid-base titration are called indicators.

At End Point $N_1V_1 = N_2V_2$

Indicators are of two types

(i) Acidic (ii) Basic

(i) Phenolphthalein (HPh) :- HPh is acid indicator. It ionises in water to give colourless H^+ ions and pink coloured anions.

$$HPh \rightleftharpoons \underset{\text{Colourless}}{H^+} + \underset{\text{Pink}}{Ph^-}$$

If $[Hph] > [Ph^-] \longrightarrow$ Colourless

$[Hph] < [Ph^-] \longrightarrow$ Pink

- In acidic medium the dissociation of HPh is almost nil so it gives no colour because acid suppress the ionisation of HPh due to the presence of common ion H^+ and the solution remains colourless.

  $HPh \rightleftharpoons H^+ + Ph^-$

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

- In alkaline medium, the OH^- ions combine with H^+ ions of the indicator to form water.

  $HPh \rightleftharpoons H^+ + Ph^-$

  $NaOH \longrightarrow Na^+ + OH^-$

  Thus Ph^- ions gives pink colour in alkaline medium.

(ii) Methyl Orange (MeOH) :- It is a weak base and dissociates as :-

$MeOH \rightleftharpoons Me^+ + OH^-$

Yellow Red Colourless

If $[MeOH] > [Me^+] \longrightarrow$ Yellow

$[MeOH] < [Me^+] \longrightarrow$ Red

MeOH is not dissociated in alkaline medium due to the presence of common ions OH^- and the solution remains yellow.

$MeOH \rightleftharpoons Me^+ + OH^-$

$NaOH \longrightarrow Na^+ + OH^-$

In acidic medium OH^- combine with H^+ thus increase the ionisation of MeOH. Hence yellow colour of solution change to red colour.

$MeOH \rightleftharpoons Me^+ + OH^-$

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

Modern Quinonoid Theory

According to this theory,

(i) An acid-base indicator is a dynamic equilibrium mixture of two alternative tautometric forms ; ordinarily one form is benzenoid while the other is quinonoid.

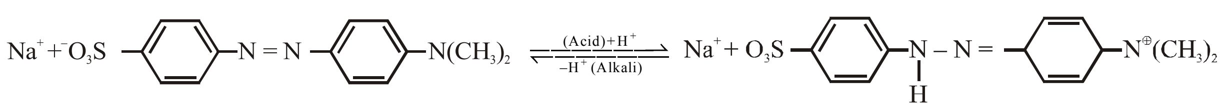
(ii) The two forms have different colours.

(iii) Out of these one form exist in acidic solution, while the other in alkaline solution.

(iv) The change in pH cause the transition of benzenoid form to quinonoid form and vice-versa and consequently change in colour.

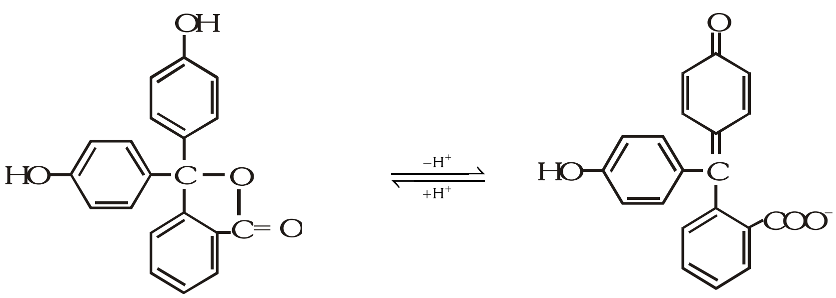
Ex.

(a) For methyl orange



Yellow benzenoid form (in bases) Red quinonoid form (in acids)

(b) For Phenolphthalein



Colourless benzenoid form (in Acid) Red quinonoid form (in Alkali)

THEORIES OF INDICATORS

(a) Ostwald Theory :- According to this theory

(i) Indicators are organic, aromatic weak acids or weak bases.

(ii) The colour change is due to ionisation of the acid - base indicator. The unionised form has different colour than the ionised form.

(iii) Every indicator shows colour changes in opposite medium due to the conversion of unionized part into ionized part.

For example phenolpthalein shows pink colour in basic medium and methyl orange shows red colour in acidic medium.

Note : For oxidation reduction (Redox) reactions indicators are not used because these reactions are very fast. Indicators are not used in coloured solution also.

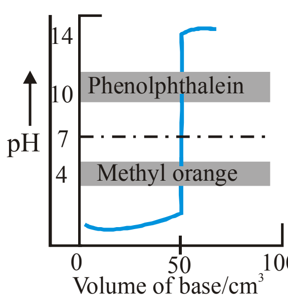
TITRATION OF STRONG ACID AGAINST STRONG ALKALI

The graph (A) shows how pH changes during the titration of 50 cm^3 of 0.1 M HCl with 0.1 M NaOH.

$$NaOH\,(aq) + HCl\,(aq) \longrightarrow NaCl\,(aq) + H_2O\,(\ell)$$

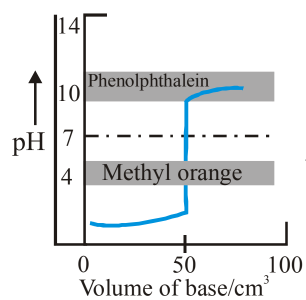
The pH of 0.1 M solution of HCl in the beginning would be 1. As alkali is added, the pH changes slowly in the beginning. However, at the equivalence point pH changes rapidly from about 3.5 to 10. It can be shown by simple calculations that pH of the solution is 3.7 when 49.8 cm^3 of 0.1 M NaOH solution have been added. The pH suddenly changes to 10 after addition of 50.1 cm^3 of the NaOH solution. Thus, any indicator having pH range between 3.5 to 10 will identify the equivalence point. This means that any one of phenolphthalein, methyl orange or bromothylmol blue could be used as an indicator.

(A)



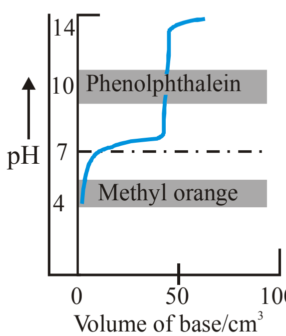
Strong acid v/s strong base

(B)



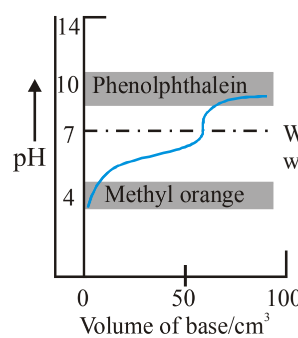
Strong acid v/s weak base

(C)



Weak acid v/s strong base

(D)



Weak acid v/s weak base

TITRATION OF STRONG ACID AGAINST WEAK ALKALI

The graph (B) shows how pH changes during titration of 50 cm^3 of 0.1 M HCl with 0.1 M NH_3.

$HCl\,(aq) + NH_4OH\,(aq) \longrightarrow NH_4Cl\,(aq) + H_2O\,(\ell)$

In this case, the pH changes rapidly from 3.5 to 7.0 at the equivalence point. Methyl orange, methyl red and bromocresol green are suitable indicators for this type of titration. Phenolphthalein is unsuitable because its pH range lies outside the vertical portion of the curve.

TITRATION OF WEAK ACID AGAINST STRONG BASE

The graph (C) shows how pH changes during titration of 50 cm^3 of 0.1 M CH_3COOH with 0.1 M NaOH.

$CH_3COOH\,(aq) + NaOH\,(aq) \longrightarrow CH_3COONa\,(aq) + H_2O\,(\ell)$

The vertical portion of this titration curve lies between pH range 7 to 10.6. Phenolphthalein is suitable indicator for this titration. Methyl orange is not suitable for this titration because its pH range lies on the flat portion of the curve.

TITRATION OF WEAK ACID AGAINST WEAK BASE

The graph (D) represents the titration curve obtained for titration of 50 cm^3 of 0.1 M CH_3COOH with 0.1 M NH_3.

$CH_3COOH\,(aq) + NH_4OH\,(aq) \longrightarrow CH_3COONH_4\,(aq) + H_2O\,(\ell)$

For this type of titration there is no sharp increase in pH at the equivalence point. No indicator is suitable for this type of titration.

Methyl orange	3.2 – 4.5	Pink to yellow	3.7
Methyl red	4.4 – 6.5	Red to yellow	5.1
Litmus	5.5 – 7.5	Red to blue	7.0
Phenol red	6.8 – 8.4	Yellow to red	7.8
Phenolpthalein	8.3 – 10.5	Colourless to pink	9.6

Ex. Bromophenol blue is an indicator with a value of $K_a = 6.84 \times 10^{-6}$. At what pH it will work as an indicator? Also report the % of this indicator in its basic form at a pH of 5.84.

Sol. $HBPh \rightleftharpoons H^+ + BPh^-$

$K_a = \dfrac{[H^+][BPh^-]}{[HBPh]}$, when $BPh^- = HBPh$, indicator will work. Thus

$[H^+] = 6.84 \times 10^{-6}$

$\therefore$ pH = 5.165

Also if pH = 5.84

tips

1. A strong electrolyte is defined as a substance which dissociates almost completely into ions in aqueous solution and hence is a very good conductor of electricity **Ex.**, NaOH, KOH, HCl, H_2SO_4, NaCl, KNO_3 etc.

2. A weak electrolyte is defined as a substance which dissociates to a small extent in aqueous solution and hence conducts electricity also to a small extent e.g. NH_4OH, CH_3COOH etc.

3. Degree of dissociation :- The fraction of the total amount of an electrolyte which dissociates into ions is called the degree of dissociation (α),

i.e. $$\alpha = \frac{\text{Number of moles dissociated}}{\text{Number of moles taken}}$$

4. According to Arrhenius concept of acids and bases, an acid is a substance which gives H^+ ions in the aqueous solution whereas a base is a substance which gives OH^- ions in the aqueous solution.

5. According to Bronsted-Lowry concept of acids and bases, an acid is a substance which can give a proton and a base is a substance which accepts a proton.

6. According to Lewis concept of acids and bases, an acid is a substance which can accept a lone pair of electrons whereas a base is a substance which can donate a lone pair of electrons.

Types of Lewis Bases

(i) Neutral molecules containing a lone pair of electrons on the central atom like : NH_3, $R\ddot{\underset{\cdot\cdot}{O}}H$, $H_2\ddot{O}:$ etc. (ii) All negative ions like F^-, Cl^-, Br^-, I^-, OH^- etc.

Types of Lewis Acids

(i) Molecules having central atom with incomplete octet e.g. BF_3, $AlCl_3$ etc.

(ii) Simple cations e.g. Ag^+, Cu^{2+}, Fe^{3+} etc.

(iii) Molecules having central atom with empty d-orbitals e.g. $SnCl_4$, SiF_4, PF_5 etc.

(iv) Molecules containing multiple bonds between different atoms e.g. O = C = O.

7. According to Ostwald's dilution law, for the solution of a weak electrolyte with concentration C, mol L^{-1} and α as the degree of dissociation,

$$K_a = \frac{C\alpha^2}{1-\alpha} \approx C\alpha^2 \quad \text{or} \quad \alpha = \sqrt{K_a / C} = \sqrt{K_a V}$$

8. Relative strength of two weak acids is given by $\frac{\text{Strength of acid } HA_1}{\text{Strength of acid } HA_2} = \sqrt{\frac{K_{a_1}}{K_{a_2}}}$

9. Ionic product of water, $K_w = [H^+]\,[OH^-]$ or $[H_3O^+]\,[OH^-]$. Its value at 25°C = 10^{-14}

10. pH = $-\log [H_3O^+]$, pOH = $-\log [OH^-]$, $pK_a = -\log K_a$, $pK_b = -\log K_b$

11. As $K_w = [H^+]\,[OH^-] = 10^{-14}$ therefore pK_w = pH + pOH = 14.

12. Solubility product of a sparingly soluble salt $A_x B_y$ is given by

$$K_{sp} = [A^{y+}]^x \times [B^{x-}]^y$$

Ex. for AgCl, $K_{sp} = [Ag^+][Cl^-]$, for $Ca_3(PO_4)_2$, $K_{sp} = [Ca^{2+}]^3 [PO_4^{3-}]^2$ etc.

13. If two solutions are mixed in which ions can combine to form a precipitate, concentration of ions in the solution after mixing are calculated. Then ionic product is calculated using the same expression as for K_{sp}. If ionic product > solubility product, a precipitate is formed.

14. To calculate the solubility of a salt like AgCl in the presence of a strong electrolyte like NaCl, total $[Cl^-]$ is calculated (Cl^- ions from AgCl being negligible). Knowing K_{sp}, $[Ag^+]$ can be calculated.

15. pH of an acidic buffer is given by Henderson equation viz

$$pH = pK_a + \log \frac{[Salt]}{[Acid]}$$

16. pH of a basic buffer is given by

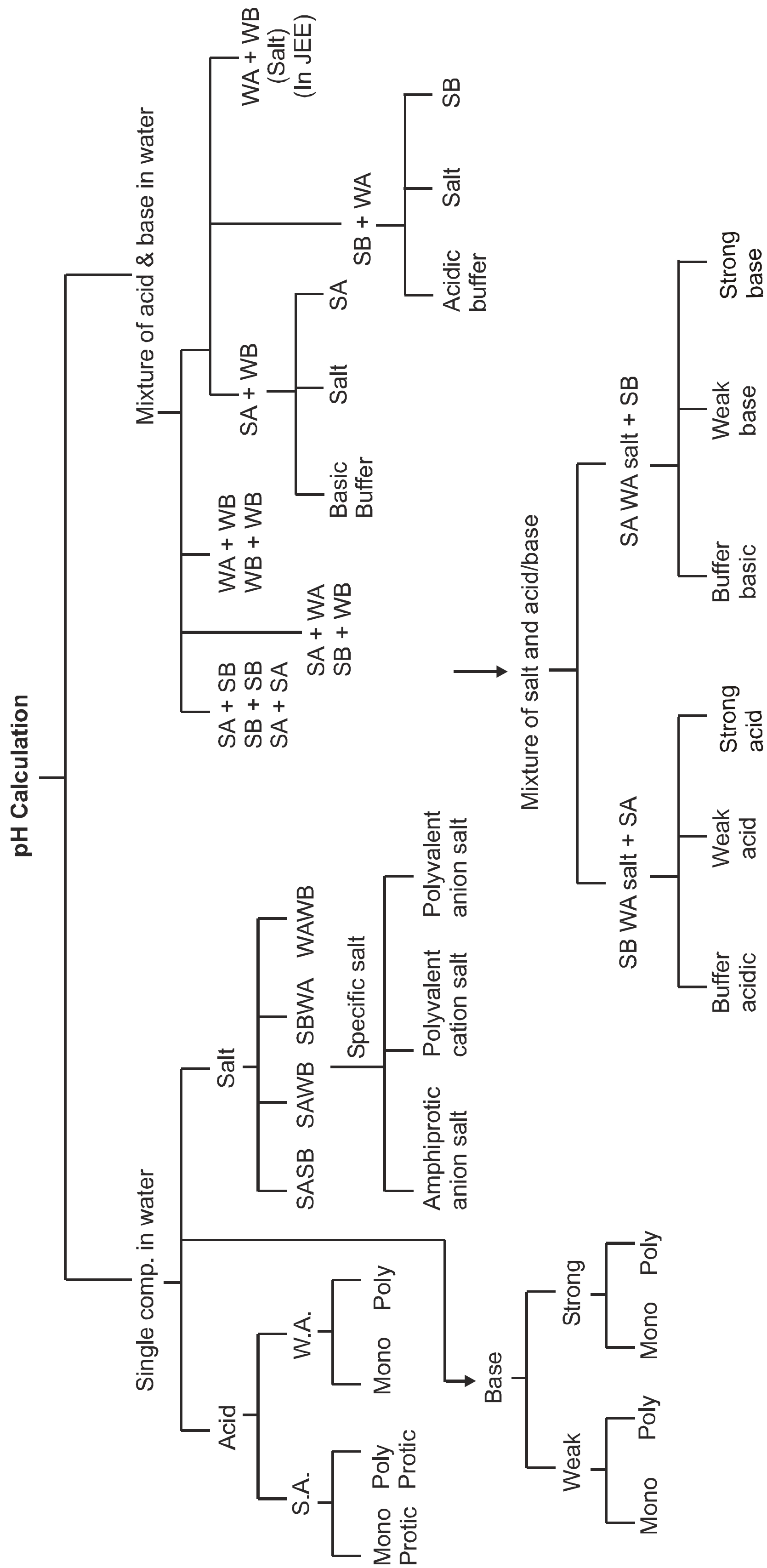
$$pOH = pK_b + \log \frac{[Salt]}{[Base]} \text{ and then } pH = 14 - pOH$$

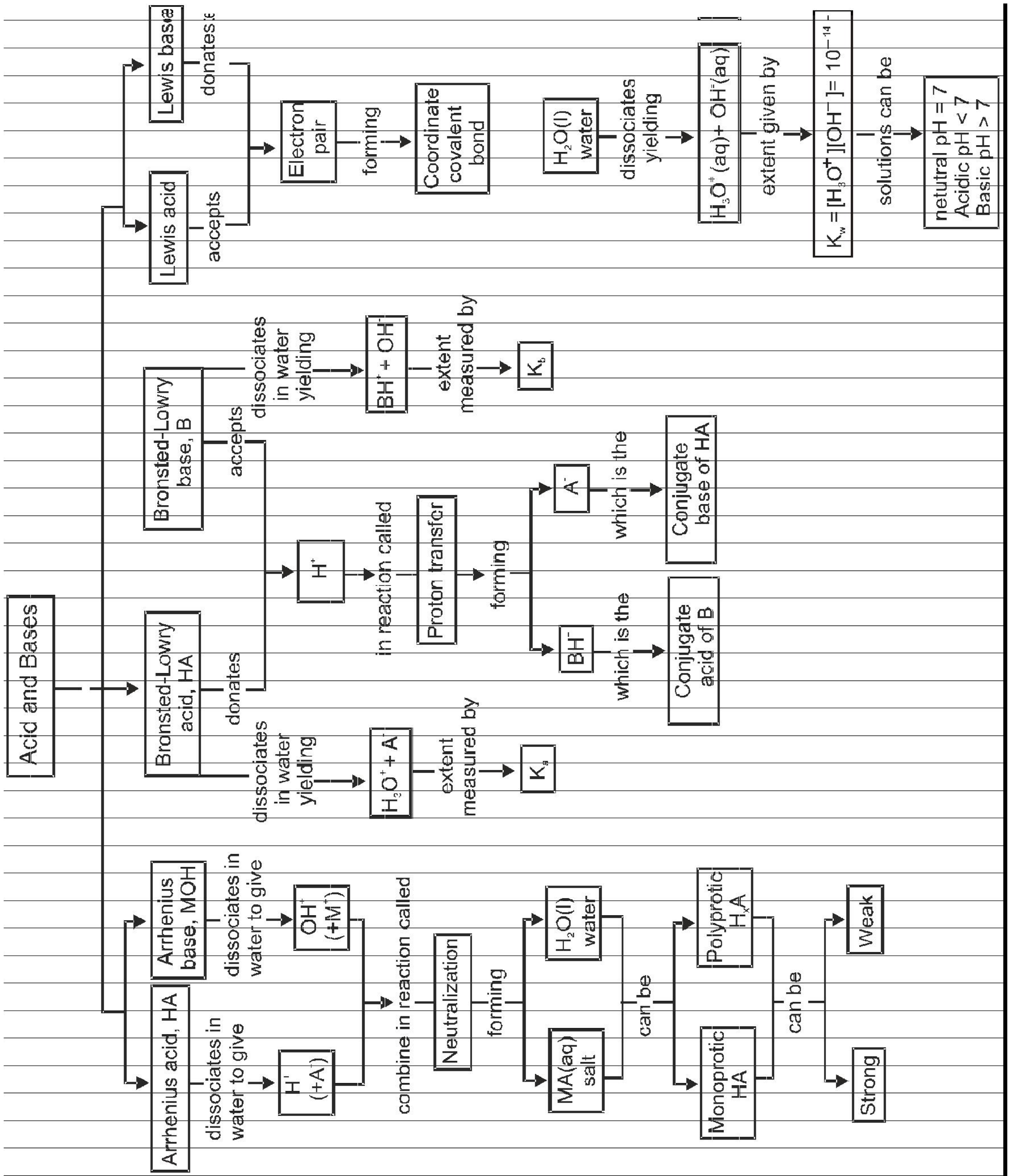
17. $\text{Buffer capacity} = \dfrac{\text{No. of moles of the acid or base added to 1 litre of buffer}}{\text{Change in pH}} = \dfrac{n}{\Delta pH}$

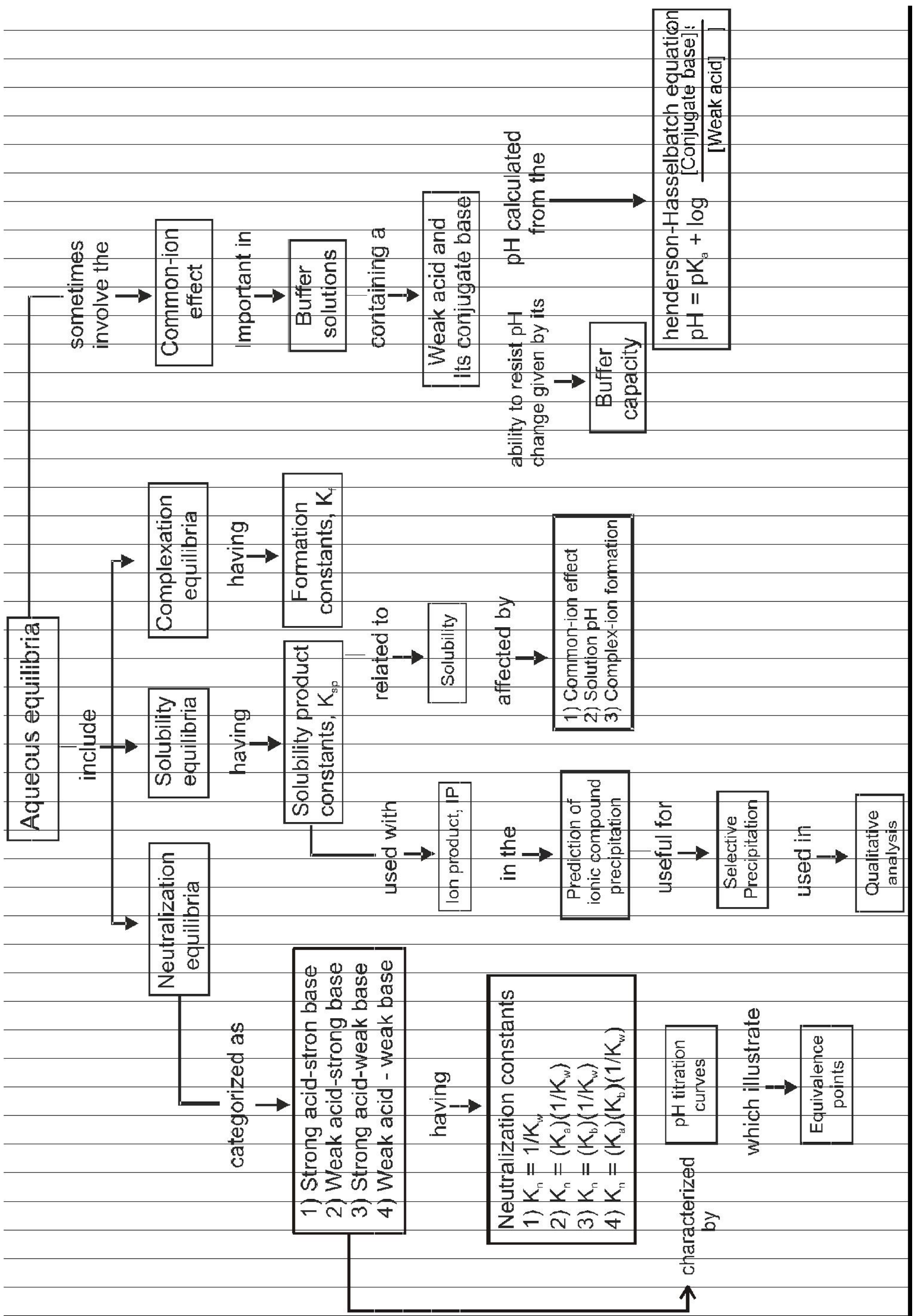
18. pH of boiling water is 6.5625. It does not mean that boiling water is not neutral. It is due to greater dissociation of H_2O into H^+ and OH^-.

19. pH can be zero in 1 N HCl solution or it can be negative for more concentrated solution like 2N, 3N, 10 N etc.

20. The buffer system present in blood is $H_2CO_3 + NaHCO_3$.


pH Calculation
Single comp. in water
Mixture of acid & base in water
Acid
S.A.
Mono Protic
Poly Protic
W.A.
Mono
Poly
Base
Weak
Mono
Poly
Strong
Mono
Poly
Salt
SASB
SAWB
SBWA
WAWB
Specific salt
Amphiprotic anion salt
Polyvalent cation salt
Polyvalent anion salt
SA + SB
SB + SB
SA + SA
SA + WA
SB + WB
WA + WB
WB + WB
SA + WB
Basic Buffer
Salt
SA
SB + WA
Acidic buffer
Salt
SB
WA + WB
(Salt)
(In JEE)
Mixture of salt and acid/base
SB WA salt + SA
Buffer acidic
Weak acid
Strong acid
SA WA salt + SB
Buffer basic
Weak base
Strong base


Acid and Bases
Arrhenius acid, HA
dissociates in water to give
H+ (+A-)
Arrhenius base, MOH
dissociates in water to give
OH- (+M+)
combine in reaction called
Neutralization
forming
MA(aq) salt
H2O(l) water
can be
Monoprotic HA
Polyprotic HxA
can be
Strong
Weak
Bronsted-Lowry acid, HA
donates
dissociates in water yielding
H3O+ + A-
extent measured by
Ka
Bronsted-Lowry base, B
accepts
dissociates in water yielding
BH+ + OH-
extent measured by
Kb
H+
in reaction called
Proton transfer
forming
BH+
which is the
Conjugate acid of B
A-
which is the
Conjugate base of HA
Lewis acid
accepts
Lewis base
donates
Electron pair
forming
Coordinate covalent bond
H2O(l) water
dissociates yielding
H3O+(aq) + OH-(aq)
extent given by
Kw = [H3O+][OH-] = 10-14
solutions can be
netutral pH = 7
Acidic pH < 7
Basic pH > 7


Aqueous equilibria
include
Neutralization equilibria
Solubility equilibria
Complexation equilibria
sometimes involve the
Common-ion effect
Important in
Buffer solutions
containing a
Weak acid and its conjugate base
pH calculated from the
henderson-Hasselbatch equation
pH = pKa + log [Conjugate base] / [Weak acid]
ability to resist pH change given by its
Buffer capacity
having
Formation constants, Kf
having
Solubility product constants, Ksp
related to
Solubility
affected by
1) Common-ion effect
2) Solution pH
3) Complex-ion formation
used with
Ion product, IP
in the
Prediction of ionic compound precipitation
useful for
Selective Precipitation
used in
Qualitative analysis
categorized as
1) Strong acid-stron base
2) Weak acid-strong base
3) Strong acid-weak base
4) Weak acid - weak base
having
Neutralization constants
1) Kn = 1/Kw
2) Kn = (Ka)(1/Kw)
3) Kn = (Kb)(1/Kw)
4) Kn = (Ka)(Kb)(1/Kw)
characterized by
pH titration curves
which illustrate
Equivalence points