# **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<sub>2</sub>) towards oppositely charged electrodes

# **DEGREE OF DISSOCIATION**

- When an electrolyte is dissolved in a solvent (H<sub>2</sub>O), it spontaneously dissociates into ions.
- It may dissociate partially ( $\alpha \leq 1$ ) or sometimes completely ( $\alpha \approx 1$ ) •

Ex.

 $NaCl + aq \longrightarrow Na^{+}(aq) + Cl^{-}(aq)$ 

CH<sub>2</sub>COOH  $\ddagger \uparrow \uparrow \uparrow$  CH<sub>2</sub>COO<sup>-</sup>(aq)+H<sup>+</sup>(aq)

The degree of dissociation ( $\alpha$ ) 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<sup>+</sup>Cl<sup>-</sup>, K<sup>+</sup>Cl<sup>-</sup>, etc.

For strong electrolyte ionisation is 100%.

 $\alpha = 1$ i.e.

Ex.

- (a) Strong acid  $\rightarrow$  H<sub>2</sub>SO<sub>4</sub>, HCl, HNO<sub>3</sub> HClO<sub>4</sub>, H<sub>2</sub>SO<sub>5</sub>, HBr, HI
- (b) Strong base  $\rightarrow$  KOH, NaOH, Ba(OH), CsOH, RbOH
- (c) All water soluble salts  $\rightarrow$  NaCl, KCl, CuSO<sub>4</sub>.....



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

### Ex.

(a) Weak acid  $\rightarrow$  HCN, CH<sub>3</sub>COOH, HCOOH, H<sub>2</sub>CO<sub>3</sub>, H<sub>3</sub>PO<sub>3</sub>, H<sub>3</sub>PO<sub>2</sub>, B(OH)<sub>3</sub>,

H,BO,

(boric acid)

- (b) Weak base  $\rightarrow$  NH<sub>4</sub>OH, Cu(OH)<sub>2</sub>, Zn(OH)<sub>2</sub>, Fe(OH)<sub>3</sub>, Al(OH)<sub>3</sub>
- (c) All sparingly soluble salts like AgCl, AgBr,  $PbSO_4$ , etc.

### FACTORSAFFECTING THE VALUE OF DEGREE OF DISSOCIATION

- (1) Temperature  $\rightarrow$  On increasing temperature ionization increases so,  $\alpha$  increases
- (2) Nature of electrolyte

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

(3) Nature of solvent

If Dielectric constant  $\mu$  of solvent increases, then the value of  $\alpha$  increases.

 $\begin{aligned} H_2O &\rightarrow \mu = 81 \\ D_2O &\rightarrow \mu = 79 \\ C_6H_6 &\rightarrow \mu = 2.5 \\ CCl_4 &\rightarrow \mu = 0 \end{aligned}$ 

- **Ex.** Which one is greater  $\alpha_1$  or  $\alpha_2$  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  $\alpha_1$  or  $\alpha_2$  for the following equations :

(B)  $\alpha_2 > \alpha_1$ 

(i)  $HCN + CCl_4 \rightarrow \alpha_1$ 

 $\rightarrow$   $\mu(CCl_{4}) = 0$  and  $\mu(C_{6}H_{6}) = 2.5$ 

Sol.

So,  $\alpha_2 > \alpha_1$ 

(A)  $\alpha_1 > \alpha_2$ 

# 5. Mixing of Ions

Common Ion Effect	Odd Ion Effect
$NH_4OH \square NH_4^+ + OH^-$	$NH_4OH \square NH_4^+ + OH^-$
On mixing NH <sub>4</sub> Cl	On mixing HCl
$\rm NH_4Cl \rightarrow \rm NH_4^+ + Cl^-$	$\text{HCl} \rightarrow \text{H}^+ + \text{Cl}^-$
Due to mixing of common ion concentration	Due to mixing of odd ions concentration
of ammonium ion will increase therefore	of OH <sup>¯</sup> will decrease ∴ Equilibrium will
equilibrium will shift in backward direction	shift in forward direction i.e. rate of
i.e. rate of backward reaction increases	forward reaction increases, means a
means $\alpha$ decreases.	increases

(ii) HCN +  $C_6H_6 \rightarrow \alpha_2$ 

(D) None

Ans. (B)

(C)  $\alpha_1 = \alpha_2$ 

**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<sub>3</sub>COOH, the following equilibria exists :

$$CH_{3}COOH(aq.) f CH_{3}COO^{-}(aq.) + H^{+}(aq.) \dots (1)$$

$$C - C\alpha C\alpha (C_{1} + C\alpha)$$

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

$$C_{1} C_{1} C_{1} \dots (2)$$

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

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,COOH will decrease

- Ex. Calculate concentration of each species at equilibrium containing
  - (i)  $0.1 \text{ M NH}_4 \text{OH only}$
  - (ii) 5.35 g/L NH<sub>4</sub>Cl along with 0.1 M NH<sub>4</sub>OH ( $k_b = 1.8 \times 10^{-5}$ )

Sol. (i) 
$$NH_4OH(aq) f NH_4^+(aq) + OH^-(aq)$$
  
0.1-0.1 $\alpha$  0.1 $\alpha$  0.1 $\alpha$ 

$$k_{b} = \frac{0.1\alpha^{2}}{(1-\alpha)} \implies \alpha = \sqrt{\frac{k_{b}}{C}} = \sqrt{\frac{1.8 \times 10^{-5}}{0.1}} = \sqrt{1.8 \times 10^{-4}} = 1.34 \times 10^{-2}$$

 $\therefore \alpha = 0.0134$ [NH.<sup>+</sup>] = [OH<sup>-</sup>] = c\alpha

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

(ii)  $\operatorname{NH}_4\operatorname{OH} f \operatorname{NH}_4^+ + \operatorname{OH}^-$ 

$$0.1 - 0.1 \alpha$$
 ( $0.1 \alpha + 0.1$ )  $0.1 \alpha$ 

$$NH_4Cl \longrightarrow NH_4^+ + Cl^-$$

$$0.1 M \qquad 0.1 \qquad 0.1$$

$$5.35 g/L$$

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

$$\zeta_{b} = \frac{0.1(1+\alpha).1\alpha}{(1-\alpha)}$$
$$a << 1$$

 $\alpha = 0.00018$ 

+  $\alpha \approx 1$  and  $1 - \alpha \approx 1$ 



- Ex. The solubility product of  $Mg(OH)_2$  is  $1.2 \times 10^{-11}$ . What minimum OH<sup>-</sup> 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  $1.1 \times 10^{-10}$  M?
- **Sol.** K<sub>sp</sub> expression:

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

We set  $[Mg^{2+}] = 1.1 \times 10^{-10}$  and  $[OH^{-}] = x$ . Substituting into the K<sub>sn</sub> expression:

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

x = 0.33 M

Any sodium hydroxide solution greater than 0.33 M will reduce the  $[Mg^{2+}]$  to less than 1.1 x 10<sup>-10</sup> 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+:

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

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

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

Since there is a 2:1 ratio between the moles of aqueous silver ion and the moles of silver chromate that dissolved,  $1.5 \times 10^{-5}$  M is the molar solubility of Ag<sub>2</sub>CrO<sub>4</sub> in 0.010 M K<sub>2</sub>CrO<sub>4</sub> solution.

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

1.5 x 10<sup>-5</sup> 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  $A^{\dagger}B^{-}$  dissolved in water, if  $\alpha$  is the degree of dissociation then

	AB ‡^^*	$\mathbf{A}^{+}$	+ B <sup>-</sup>
initial conc.	С	0	0
conc-at eq.	$C(1-\alpha)$	Сα	Cα

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

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



- as concentration increases  $\Rightarrow \alpha$  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<sub>3</sub>, HClO<sub>4</sub>, HCl, HI, HBr, H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub> etc.

- H<sub>3</sub>BO<sub>3</sub> 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  $H^+(H_3O)_n$
- The structure of solid HClO<sub>4</sub> is studied by X-ray, It is found to be consisting of  $H_3O^+$  and  $ClO_4^-$

 $HClO_4 + H_2O_{\ddagger}^{\uparrow} \uparrow H_3O^{+} + ClO_4^{-}$  (better representation)

Arrhenius Base : Any substance which releases OH<sup>-</sup> (hydroxyl) ion in water (OH<sup>-</sup> ion donor)

- OH<sup>-</sup> ion is present also in hydrated form of  $H_3O_2, H_2O_4, H_5O_3$  general form OH<sup>-</sup>  $(H_2O)_n$
- 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.

 $H_2O$   $\hat{\ddagger} \hat{\uparrow} \hat{\uparrow} H^+ + OH^-$ 

 $H^+ + H_2O_{\uparrow}^{\uparrow} H_3O^+$ 

 $H_2O + H_2O \ddagger \uparrow H_3O^+ + OH^-$ 

Above reaction is called Autoionisation or selfionisation of water.

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

 $[H_{3}O^{+}] = [OH^{-}]$ 

(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)

$$SO_2 + H_2O \longrightarrow H_2SO_3 \stackrel{\circ}{\ddagger} \stackrel{\wedge H_2O}{} \ddagger H_3O^+ + HSO_3^-$$
  
Acid

$$NH_3 + H_2O \longrightarrow NH_4OH \stackrel{2}{\ddagger} ^{\Lambda H_2O} \uparrow NH_4^+ + OH^-$$
  
Base



# **Basicity or Protocity of an Acid**



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<sub>3</sub>, CH<sub>3</sub>COOH, HCN etc.
- (ii) Dibasic or Diprotic acids like, H<sub>2</sub>SO<sub>4</sub>, H<sub>2</sub>CO<sub>3</sub>, H<sub>2</sub>SO<sub>3</sub>, H<sub>2</sub>S etc.
- (iii) Tribasic or Triprotic acids like H<sub>3</sub>PO<sub>4</sub>,H<sub>3</sub>AsO<sub>4</sub> etc.

# Acidity or Hydroxity of a Base



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

- (i) Mono acidic or Monohydroxic like NaOH, NH<sub>4</sub>OH, AgOH etc.
- (ii) Diacidic or dihydroxic like Ba(OH)<sub>2</sub>, Mg(OH)<sub>2</sub>, Ca(OH)<sub>2</sub>, Sr(OH)<sub>2</sub> etc.
- (iii) Triacidic or trihydroxic like Fe(OH)<sub>3</sub>, Al(OH)<sub>3</sub> etc.

# Strength of Acid or Base

(i) Strength of Acid or Base depends on the extent of its ionisation. Hence equilibrium constant K<sub>a</sub> or K<sub>b</sub> respectively of the following equilibria give a quantitative measurement of the strength of the acid or base.

(ii) 
$$HA + H_2O \stackrel{*}{\downarrow} \stackrel{*}{} \stackrel{*}{\uparrow} H_3O^+ + A^-;$$
  
 $K_a = \frac{[H_3O^+][A^-]}{[HA]}$   
(iii) Similarly  
 $B + H_2O \stackrel{*}{\downarrow} \stackrel{*}{} \stackrel{*}{\uparrow} BH^+ + OH^-;$   
 $K_b = \frac{[BH^+][OH^-]}{[B]}$  here  $H_2O$  is szolvent.





acid

# IONIC EQUILIBRIUM

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

$$HX + B \stackrel{2}{f} \stackrel{2}{} \stackrel{2}{} \stackrel{2}{} \stackrel{2}{} \stackrel{1}{} X^{-} + HB^{+}$$



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

	Acid		Base		Conjuga Acid	te	Conjugate Base
•	HCl	+	H <sub>2</sub> O	<u>}</u> ^ ^ <b>†</b>	$H_{3}O^{+}$	+	Cl⁻
•	$\mathrm{HSO}_4^-$	+	NH <sub>3</sub>	<u>}</u> ^ ^†	$\mathrm{NH}_4^+$	+	$\mathrm{SO}_4^{-2}$
•	$[Fe(H_2O)_6]$	<sup>3+</sup> +	$H_2O$	<u>}</u> ^^+	$H_{3}O^{+}$	+	$[Fe(H_2O)_5(OH)]^{2+}$

- 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	<b>Conjugate base</b>	Base	Conjugate acid
Ex:	HCl	Cl	NH <sub>3</sub>	$\mathrm{NH}^+_{\!\scriptscriptstyle A}$
	H <sub>2</sub> SO <sub>4</sub>	HSO	H,O	$H_3O^+$
	HSO	$SO_4^{2-7}$	RNH <sub>2</sub>	$RNH_3^+$
	HO	OH⁻	2	5

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

$$HCl + H_2O \ddagger \uparrow \uparrow H_3O^+ + Cl^-$$
  
base  
$$NH_3 + H_2O \ddagger \uparrow \uparrow NH_4^+ + OH^-$$

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.

$$H_2O + S^{2-} \ddagger \hat{} \uparrow \forall OH^- + HS^-$$

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

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

(a) 
$$CH_3COOH + NH_3 \ddagger \uparrow \uparrow H_4 + CH_3COO$$

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

(c)  $[Fe(H_2O)_6]^{3+} + H_2O_{\ddagger}^{2+} \land \uparrow H_3O^{+} + [Fe(H_2O)_5(OH)]^{2+}$ 



# **CHEMISTRY FOR JEE MAIN & ADVANCED**

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

 $\hat{\mathbf{T}} \hat{\mathbf{T}} = \mathbf{H}_{\mathbf{A}} \mathbf{O}^{+} + \mathbf{A}^{-}$ HA H<sub>2</sub>O +

Strong acid Strong base Weak acid Weak base

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) 
$$C_2H_5OH + H_2SO_4$$
  $\ddagger \uparrow \uparrow C_2H_5OH_2 + HSO$   
Ethanol (Oxonium ion)

(Oxonium ion)

(b) 
$$(C_2H_5)_2O:+HCl \hat{\ddagger}^{\uparrow} (C_2H_5)_2O:H+Cl$$

Ethylether Oxonium ion

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

$$H_2O + H_2O \rightarrow H_3O^+ + OH$$

acid base

$$NH_3 + NH_3 \rightarrow NH_4^+ + NH_2^-$$

acid base

$$H_2SO_4 + H_2SO_4 \rightarrow H_3SO_4^+ + HSO4^-$$

acid base

- 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.
  - $HClO_4 + HF \stackrel{2}{t} \stackrel{2}{} \stackrel{2}{} \stackrel{2}{} H_2F^+ + ClO_4^-$ (a)  $(\text{HClO}_4 \text{ acts as a acid in HF})$ 
    - Acid Base Acid Base
  - HNO<sub>3</sub> behaves as base in HClO<sub>4</sub> and HF (b)  $HNO_3 + 4HF \ddagger \uparrow \uparrow H_3O^+ + NO_2^+ + 2HF_2^-$ (base) (acid)

(c) Urea is weak acidic in liquid 
$$NH_3$$

$$\begin{array}{rcl} \text{NH}_2\text{CONH}_2 + \text{NH}_3 \longrightarrow \text{NH}_4^+ + \text{NH}_2\text{CONH}^-\\ \\ \text{Acid} & \text{Base} & \text{Acid} & \text{Base} \end{array}$$

**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



Туре	Acid	Base
Molecular	HCl, HNO3, HClO4,	NH3, N2H4, Amines,
	$H_2SO_4, H_3PO_4,$	H <sub>2</sub> O, Alcohol, Ethers etc.
	H <sub>2</sub> O etc.	
Cationic	NH4 <sup>+</sup> , N2H5 <sup>+</sup> , PH4 <sup>+</sup> ,	$[Fe(H_2O)_5OH]^{2+}$
	Na <sup>+</sup> , Ba <sup>2+</sup> (All cations)	$[Al(H_2O)_5OH]^{2+}$ etc.
	$[Fe(H_2O)_6]^{3+}$ , $[Al(H_2O)_6]^{3+}$ etc.	
Anionic	HS <sup>-</sup> , HSO <sub>3</sub> <sup>-</sup> , H <sub>2</sub> PO <sub>4</sub> <sup>-</sup> ,HSO <sub>4</sub> <sup>-</sup>	Cl <sup>-</sup> , Br <sup>-</sup> , OH <sup>-</sup> , HSO4 <sup>-</sup> , CN <sup>-</sup> ,
	$\text{HCO}_3^-, \text{HPO}_4^{2-}$ etc.	CO <sub>3</sub> <sup>2-</sup> ,SO <sub>4</sub> <sup>2-</sup> , NH <sub>2</sub> <sup>-</sup> , CH <sub>3</sub> COO <sup>-</sup> etc.
	all amphiprotic anions	all anions.

# Table - 1

# **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<sub>2</sub> 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)  $H_2O + H_2O_{\frac{1}{2}} \wedge 2^{+} H_3O^{+} + OH^{-}$ 
  - (b)  $NH_3 + NH_3 \stackrel{2}{+} \stackrel{2}{-} \stackrel{2}{+} NH_4^+ + NH_2^-$
  - (c)  $3HX_{\frac{1}{2}}^{+} \stackrel{\sim}{+} H_2X + HX_2^{-}$
  - (d)  $2H_2SO_4 \stackrel{2}{\ddagger} \stackrel{2}{\uparrow} \stackrel{2}{\uparrow} H_3SO_4^+ + HSO_4^-$
- (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<sub>3</sub>CN, DMF, DMSO (dimethyl sulfoxide), THF and SO<sub>2</sub>.



- (c) Highly polar, autoionising solvents.
  - **Ex.** Inter halogen compounds ( $BrF_3$ ,  $IF_5$  and trichloro phosphine)
  - (a)  $2 \operatorname{BrF}_{3} \stackrel{2}{\ddagger} \stackrel{2}{} \stackrel{2}{} \operatorname{BrF}_{2}^{+} + \operatorname{BrF}_{4}^{-}$
  - (b)  $2 IF_5$   $\ddagger \hat{\uparrow} \hat{\uparrow} IF_4^+ + IF_6^-$
  - (c)  $2Cl_3PO \stackrel{2}{\pm} \stackrel{2}{\phantom{a}} \stackrel{2}{\phantom{a}} Cl_2PO^+ + Cl_4PO^-$

### **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<sub>3</sub>COOH 
$$\ddagger \uparrow \uparrow \downarrow Cl^-$$
 + CH<sub>3</sub>COOH<sub>2</sub><sup>+</sup>  
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<sub>3</sub> < HCl < H<sub>2</sub>SO<sub>4</sub> < HBr < HClO<sub>4</sub>

(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<sub>2</sub>O) is an oxide ion (O<sup>2-</sup>) donor and an acid (like SiO<sub>2</sub>, CO<sub>2</sub> or P<sub>4</sub>O<sub>10</sub>) is an oxide ion (O<sup>2-</sup>) acceptor.
- Ex. Base Acid
- (a) CaO + SiO<sub>2</sub>  $\longrightarrow$  CaSiO<sub>3</sub>
- (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.**  $ZnO, Al_2O_3, BeO, Ga_2O_3$



# IONIC EQUILIBRIUM

			ЕТО	OS KEY POINTS	-	
	(i) (ii)	The concept is pa operations or du The approach ca	articularly applicable to uring the manufacture of an be extended to includ	reactions which take place at hig f ceramics and glass. e other negative ion systems (lik	th temperature i.e. in meta	allurgical rbanion).
	Exam	ple based on :	Bronsted - Lowery	Concept		
Ex.	Select	the aprotic solvent	from the following is :			
Sel	$(\mathbf{A}) \Pi_2 \mathbf{C}$	,	( <b>b</b> ) $C_6 \Pi_6$		$(\mathbf{D})$ $\mathbf{NH}_3$	
501. E	( <b>b</b> ) acc		hear is			
EX.	$(\Lambda) C^{-}$	ongest conjugate		$(C) SO^{2-}$	$(\mathbf{D})$ NO $$	
Sel		COOLLis weekest	( <b>b</b> ) CH <sub>3</sub> COO	C) SO <sub>4</sub>	$(\mathbf{D}) \mathbf{NO}_2$	
501. E-		$_{3}$ COOH is weakest	actualmong $\Pi CI, C\Pi_3 CO$	SOH, $HSO_4$ and $HNO_2$ .		
EX.		s the strongest Br	$(\mathbf{P}) C [\mathbf{O}^-]$	Swing amons : $(C) ClO^{-}$	(D) C10=	
Sal		) ClO is weakest asid				
501. E-			among HCIO, HCIO <sub>2</sub> , H			
EX.	NIL CC		$MUI^+ + MUCONU^-$	e.		
501.	NH <sub>2</sub> CC	$\operatorname{NH}_2 + \operatorname{NH}_3 \longrightarrow$	$h_4 + h_2 CONH$			
			Acid base			
I.	In Iiqui	a NH <sub>3</sub> solution ure	ea can snow weak acidic	c nature.		
EX.	Ammo	110m 10n 1s-				
6.1	(A)AL	ewis acid	(B) Lewis base	(C) Bronsted acid	(D) Bronsted base	Ans. (C)
501.	Correct	t answer is (C)				
	Self P	ractice Problen	n			
1.	(a)	Write conjugate ad	cids of			
		$\mathrm{SO}_4^{2-}, \mathrm{RNH}_2, \mathrm{NH}_2^-,$	F <sup>-</sup>			
	(b)	Write conjugate ba	ase of			
	(c)	Write conjugate as	<sub>3</sub> , HCIO <sub>4</sub> .	of amphoteric species		
	(0)	HS <sup>-</sup> , NH <sub>2</sub> , H <sub>2</sub> O, HS				
2.	Which	of the following is	s the strongest base-			
	(A) NH	2	(B) CH <sub>3</sub> COO <sup>-</sup>	$(\mathbf{C}) \mathbf{C}_2 \mathbf{H}_5 \mathbf{O}^-$	<b>(D)</b> OH <sup>-</sup>	Ans. (A)
	Lewis	Concept (Elec	tronic Concept)			
	•	An acid is a molec	cule/ion which can acce	ot an electron pair with the form	ation of a coordinate bo	nd.
		Acid $\rightarrow e^{-}$ pair acc	ceptor	I I		
	Ex.	Electron deficient	molecules : $BF_3$ , $AlCl_3$			
		Cations	$: H^{+}, Fe^{2+}, Na$	$a^+$		
		Molecules with va	cant orbitals : $SF_4$ , $PF_3$			
	•	A base is any mole $P_{asa} \rightarrow (O_{asa})$	ecule/10n which has a lo	one pair of electrons which can	be donated.	
		$Dasc \rightarrow (One electron)$	Luon pair donate)			
	Ex.	Molecules with lor	he pairs : $NH_3$ , $PH_3$ , $H_2C$	), CH <sub>3</sub> OH		

# **CHEMISTRY FOR JEE MAIN & ADVANCED**

Ex. In which of the following reaction does NH<sub>3</sub> act as an acid ? **(B)**  $NH_3 + Na \longrightarrow NaNH_2 + \frac{1}{2}H_2$ (A)  $NH_3 + H^+ \longrightarrow NH_4^+$ (C)  $NH_3 + HCl \longrightarrow NH_4Cl$ (D) none of these Sol. **(B)** In the following reaction, NH<sub>3</sub> changes of NaNH<sub>2</sub> which contains NH<sub>2</sub> ion. This means that NH<sub>3</sub> has donated a proton to Na and hence acts as an acid. Sulphanilic acid is a/an Ex. (A) Arrhenius acid (B) Lewis base (C) Neither (A) or (B) (D) Both (A) and (B) SO<sub>3</sub>H (D) Sulphanilic acid is Sol. NH2 The SO<sub>2</sub>H group is capable of donating H<sup>+</sup> and hence it acts as arrhenius acid while nitrogen in the NH<sub>2</sub> group

### **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 = No. of moles/litre =  $\frac{1000 \text{ g} / \text{ litre}}{18 \text{ g} / \text{ mole}}$  = 55.55 mole/litre = 55.55 M (density = 1 g/cc)

contains lone pair of electrons and hence can act as lewis base by donating it.

### **Ionic Product of Water**

According to arrhenius concept

H<sub>2</sub>O  $\ddagger \uparrow \uparrow H^+ + OH^-$  so, ionic product of water,  $k_w = [H^+][OH^-] = 10^{-14} \text{ at } 25^\circ (\text{exp.})$ 

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

K<sub>w</sub> 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

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

$$=\frac{10^{-7}}{55.55}=18\times10^{-10} \text{ or } 1.8\times10^{-7}\%$$

Absolute Dissociation Constant of Water

$$H_{2}O_{a}^{+} \uparrow \uparrow H^{+} + OH^{-} \qquad K_{a} = K_{b} = \frac{[H^{+}][OH^{-}]}{[H_{2}O]} = \frac{10^{-7} \times 10^{-7}}{55.55} = 1.8 \times 10^{-16}$$
  
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<sub>3</sub>O<sup>+</sup> or H<sup>+</sup> ions in water.
   So greater then tendency to give H<sup>+</sup>, more will be the acidic strength of the substance.
- Basic strength means the tendency of a base to give OH<sup>-</sup> ions in water.
   So greater the tendency to give OH<sup>-</sup> ions, more will be basic strength of the substance.
- The concentration of H<sup>+</sup> ions is written in a simplified form introduced by Sorenson known as pH scale. pH is defined as negative logarithm of activity of H<sup>+</sup> ions.

activity (a) = 
$$\gamma \cdot \frac{C}{C_o}$$

 $C \rightarrow$  unitless,  $C_{o} \rightarrow$  standard concentration



:.  $pH = -\log a_{H^+}$  (where  $a_{H^+}$  is the activity of H<sup>+</sup>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

### Strong acid Solution

- (i) If concentration is greater than 10<sup>-6</sup> M.
   In this case H<sup>+</sup> ions coming from water can be neglected, so [H<sup>+</sup>] = normality of strong acid solution
- (ii) If concentration is less than 10<sup>-6</sup> M
   In this case H<sup>+</sup> ions coming from water cannot be neglected.
  - So  $[H^+]$  = normality of strong acid +  $H^+$  ions coming from water in presence of this strong acid



**(a)** 

- Solved Examples Ex. Calculate pH of  $10^{-8}$  M HCl solution. Sol.  $H_2O = \frac{2}{7} + \frac{3}{7} + H^+ + OH^ 10^{-8} + x = x$   $k_w = [H^+][OH]$   $10^{-14} = x(x + 10^{-8})$   $\Rightarrow x^2 + x \times 10^{-8} - 10^{-14} = 0$   $x = \frac{-10^{-8} \pm \sqrt{10^{-16} + 4 \times 10^{-14}}}{2} = \frac{-10^{-8} + 10^{-7}\sqrt{4 + \frac{1}{100}}}{2} = \frac{(\sqrt{401} - 1)10^{-8}}{2} = 0.95 \times 10^{-7}$   $[H^+] = 10.5 \times 10^{-8} = 1.05 \times 10^{-7}$   $pH = -log [H^+]$   $pH = 7 - log 1.05 \approx 6.98$   $10^{-9}$  M HCl  $pH \approx 7$  $10^{-16}$  M HCl  $pH \approx 7$
- (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<sup>-7</sup> M (due to common ion effect)

$$\begin{array}{rll} H_2O & \hat{\ddagger} & \hat{\uparrow} & OH^- & + & H^+ \\ & - & (x+10^{-7}) & x \\ K_w = [H^+] [OH^-] = 10^{-14} = x \, (x+10^{-7}) \\ x^2 + 10^{-7} x - 10^{-14} = 0 \end{array}$$

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

 $[OH^{-}] = 10^{-7} + 0.618 \times 10^{-7} = 1.618 \times 10^{-7}$ pOH = 7 - log(1.618) = 6.79 pH = 14 - 6.79 = 7.21

# **Self Practice Problem**

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



1.

(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 =  $N_1 V_1$ 

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]

$$[\mathrm{H}^{+}] = \mathrm{N} = \frac{\mathrm{N}_{1}\mathrm{V}_{1} + \mathrm{N}_{2}\mathrm{V}_{2}}{\mathrm{V}_{1} + \mathrm{V}_{2}}$$

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

similar to above calculation

$$[OH^{-}] = N = \frac{N_1 V_1 + N_2 V_2}{V_1 + V_2} \qquad [H^{+}] = \frac{10^{-14}}{[OH^{-}]}$$

Ex. Calculate pH of mixture of (400 mL, 
$$\frac{1}{200}$$
 M H<sub>2</sub>SO<sub>4</sub>) + (400 mL,  $\frac{1}{100}$  M HCl) + (200 mL of water)

### Sol. Normality Method

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

$$N_1V_1 + N_2V_2 = 8 \times 10^{-3}$$
 [H<sup>+</sup>] =  $\frac{8 \times 10^{-3}}{1} = 8 \times 10^{-3}$ 

pH = 3 - log 8 = 2.1

**Molarity Method :** 

 $\begin{array}{cccc} H_2SO_4 & \longrightarrow & 2H^+ & + & SO_4 \\ 2m \operatorname{mole} & & 4m \operatorname{mole} \\ HCl & \longrightarrow & H^+ & + & Cl^- \\ 4m \operatorname{mole} & & 4m \operatorname{mole} \end{array}$ 

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

 $pH = -log [H^+] = -log [8 \times 10^{-3}] = 2.1$  Ans.

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

Sol. 
$$[OH^{-}] = \frac{500 \times 10^{-5} + 500 \times 2 \times 2.5 \times 10^{-5}}{1000}$$
  
=  $3 \times 10^{-5} M$   
 $M_1 = 3 \times 10^{-5} M$   
 $V_2 + V_1 = 1 L$ 

1



# **CHEMISTRY FOR JEE MAIN & ADVANCED**

 $V_1 = 100 L$ no. of moles of [OH<sup>-</sup>] initially = no. of moles of [OH<sup>-</sup>]  $3 \times 10^{-5} = M \times 100$ 

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

$$H_2O \stackrel{2}{\ddagger} \stackrel{2}{\uparrow} \stackrel{2}{\uparrow} H^+ + OH^-$$

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

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

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

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

$$\left[\mathrm{OH}^{-1}\right]_{\mathrm{Net}} = \left[3 + \frac{\sqrt{13} - 3}{2}\right] \times 10^{-7} = \left[\frac{3 + \sqrt{13}}{2}\right] \times 10^{-7} = 3.302 \times 10^{-7}$$

# **Self Practice Problem**

- 1. Calculate the pH for-
  - (a)  $50 \text{ mL of } 0.1 \text{ M HCl}, 25 \text{ mL of } 0.1 \text{ M H}_2\text{SO}_4, 25 \text{ mL of } 0.2 \text{ M HNO}_3 + 100 \text{ mL of } \text{H}_2\text{O}_4$
  - (b) 50 mL of 0.2 M NaOH + 100 mL of 0.1 M RbOH the resulting solution is diluted by  $350 \text{ mL H}_2\text{O}$ .

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

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

- 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 N2, then

Number of  $H^+$  ions from I-solution =  $N_1 V_1$ 

Number of OH<sup>-</sup>ions from II-solution =  $N_2 V_2$ Г

$$If N_{1}V_{1} > N_{2}V_{2}$$

$$If N_{2}V_{2} > N_{1}V_{1}$$

$$[H^{+}] = N = \frac{N_{1}V_{1} - N_{2}V_{2}}{V_{1} + V_{2}}$$

$$[OH^{-}] = N = \frac{N_{1}V_{1} - N_{2}V_{2}}{V_{1} + V_{2}}$$

$$Solution will$$
be acidic in nature
$$[H^{+}] = \frac{10^{-14}}{[OH^{-}]}$$
Ex. Calculate pH of mixture of (400 mL,  $\frac{1}{200}$  M Ba(OH)<sub>2</sub>) + (400 mL,  $\frac{1}{50}$  M HCl) + (200 mL of water)  

$$[H^{+}] = \frac{400 \times \frac{1}{50} - 400 \times \frac{1}{200} \times 2}{1000} = 4 \times 10^{-3}$$
, 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 Ex. aqueous solution of NaOH (pH = 12.0)? Sol. pH of HCl = 2 $\therefore$  [HCl] = 10<sup>-2</sup> M pH of NaOH = 12, pOH = 2 :  $[NaOH] = 10^{-2} M$ HC1 + NaOH  $\longrightarrow$  NaCl H,O  $150 \times 10^{-2}$  $350 \times 10^{-2}$ Meq. initial 0 0 = 1.5=3.50 0.2 Meq. final 1.5 1.5 : [OH<sup>-</sup>] from NaOH =  $\frac{2}{500} = 4 \times 10^{-3} \text{ M}$  $pOH = -\log[OH^{-}] = -\log(4 \times 10^{-3})$ : pOH=2.3979  $\therefore$  pH = 14 - pOH = 14 - 2.3979 = 11.6021 Self Practice Problem Calculate pH of mixture 200 mL of  $0.2 \text{ MH}_2\text{SO}_4 + 300 \text{ mL of } 0.2 \text{ MNaOH} + 200 \text{ mL of } 0.1 \text{ MKOH}.$ 1. Calculate the pH when 200 mL of 0.25 M H<sub>2</sub>SO<sub>4</sub> is mixed with 200 mL of 0.2 M Ba(OH)<sub>2</sub> 2. 1. 7 Ans. 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<sub>a</sub> dissociation constant of the acid. We have to use Ostwald's Dilution law (as have been derived earlier) HA  $\frac{1}{2}$   $\hat{}$   $\hat{}$  H<sup>+</sup> + A<sup>+</sup> С t = 0 $C(1-\alpha)$   $C\alpha$   $C\alpha$   $K_a = \frac{[H^+][A^-]}{[HA]} = \frac{C\alpha^2}{1-\alpha}$ t<sub>eq</sub> If  $\alpha \ll 1 \Rightarrow (1-\alpha) \approx 1 \Rightarrow K_a \approx C\alpha^2 \Rightarrow \alpha = \sqrt{\frac{K_a}{C}}$  (is valid if  $\alpha < 0.1$  or 10%)  $[H^+] = C\alpha = C\sqrt{\frac{K_a}{C}} = \sqrt{K_a \times C} \text{ So } pH = \frac{1}{2}(pK_a - \log C) \text{ valid only if } \alpha <<<1.$ on increasing the dilution  $\Rightarrow C \downarrow = \alpha \uparrow$  and  $[H^+] \downarrow \Rightarrow pH \uparrow$ **(b)**  $10^{-3}$  M CH<sub>3</sub>COOH **(c)**  $10^{-6}$  M CH<sub>3</sub>COOH Calculate pH of (a)  $10^{-1}$  M CH<sub>3</sub>COOH Ex. Take K =  $2 \times 10^{-5}$ (a) CH<sub>3</sub>COOH  $\ddagger \uparrow \uparrow \uparrow$  CH<sub>3</sub>COO<sup>-</sup> + H<sup>+</sup> C 0 0 C(1-\alpha) C\alpha C\alpha Sol.  $C(1-\alpha)$  $K_{a} = \frac{C\alpha^{2}}{1-\alpha} \Rightarrow \alpha = \sqrt{\frac{K_{a}}{C}} = \sqrt{\frac{2 \times 10^{-5}}{10^{-1}}} = \sqrt{2 \times 10^{-4}} \quad (\alpha << 0.1)$ So,  $[H^+] = 10^{-1} \times \sqrt{2} \times 10^{-2} \implies pH = 3 - \frac{1}{2} \log 2 = 2.85$ 



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

So we have to do the exact calculations

$$K_{a} = \frac{C\alpha^{2}}{1-\alpha} \Longrightarrow 2 \times 10^{-5} = \frac{10^{-3} \times \alpha^{2}}{1-\alpha} \implies \alpha = 13.14\%$$

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

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

so we have to do the exact calculation,  $2 \times 10^{-5} = 10^{-6} \frac{\alpha^2}{1-\alpha} \Rightarrow \alpha \approx 0.95$  or 95%  $[\text{H}^+] = 0.95 \times 10^{-6} = 9.5 \times 10^{-7} \Rightarrow \text{ pH} = 7 - \log(9.5) = 6.022$ 

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

 $(pH) of 10^{-6} M HCl; pH of 10^{-6} M CH_3 COOH; 6)$ 

### (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<sup>+</sup>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 
$$\frac{1}{2}$$
  $\hat{}$   $\hat{}$  H<sup>+</sup> + A  
C<sub>2</sub> 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<sub>3</sub>COOH

 $CH_3COOH \stackrel{*}{\ddagger} \stackrel{^{\frown}}{} \stackrel{^{\bullet}}{} CH_3COO^- + H^+$ С 0 0  $C(1-\alpha)$ Сα Cα  $K_a = \frac{C\alpha.C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)} \implies K_a = C\alpha^2$ (if α << 1) Similarly, for weak base, i.e. NH<sub>4</sub>OH  $NH_4OH$   $\frac{1}{4}$   $^{\uparrow}$   $^{\uparrow}$   $NH_4^+ + OH^-$ С 0 0  $C(1-\alpha)$ Сα Cα

$$K_{L} = C\alpha^{2}$$

 $K_a$  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,  $\frac{\text{Strength of base (I)}}{\text{Strength of base (II)}} = \sqrt{\frac{K_{b_1}.c_1}{K_{b_2}.c_2}}$ 

The modern method is to convert K<sub>a</sub> 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<sub>a</sub> 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,  $pK_{h} = -\log K_{h}$ 

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

$$[\mathrm{H}^{+}] = \sqrt{\mathrm{K}_{\mathrm{a}_{1}}\mathrm{c}_{1} + \mathrm{K}_{\mathrm{a}_{2}}\mathrm{c}_{2}}$$

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<sub>1</sub> & HA<sub>2</sub> and their final concentrations are C<sub>1</sub> & C<sub>2</sub> respectively, then

$$\begin{aligned} HA_{1} \stackrel{2}{+} \stackrel{2}{} \stackrel{2}{+} \stackrel{2}{+} H^{+} &+ A_{1}^{-} & HA_{2} \stackrel{2}{+} \stackrel{2}{+} \stackrel{2}{+} H^{+} &+ A_{2}^{-} \\ t = 0 \quad C_{1} & 0 \quad 0 & C_{2} & 0 \quad 0 \\ At eq. \quad C_{1}(1-\alpha_{1}) \quad C_{1}\alpha_{1} + C_{2}\alpha_{2} \quad C_{1}\alpha_{1} & C_{2}(1-\alpha_{2}) \quad C_{2}\alpha_{2} + C_{1}\alpha_{1} \quad C_{2}\alpha_{2} \\ K_{a_{1}} = \frac{C_{1}\alpha_{1} (C_{1}\alpha_{1} + C_{2}\alpha_{2})}{C_{1}(1-\alpha_{1})} & K_{a_{2}} = \frac{(C_{2}\alpha_{2} + C_{1}\alpha_{1})C_{2}\alpha_{2}}{C_{2}(1-\alpha_{2})} \end{aligned}$$

(Since  $\alpha_1, \alpha_2$  both are small in comparison to unity)



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

$$[\mathrm{H}^{+}] = \mathrm{C}_{1}\alpha_{1} + \mathrm{C}_{2}\alpha_{2} = \frac{\mathrm{C}_{1}\mathrm{K}_{\mathrm{a}_{1}}}{\sqrt{\mathrm{C}_{1}\mathrm{K}_{\mathrm{a}_{1}} + \mathrm{C}_{2}\mathrm{K}_{\mathrm{a}_{2}}}} + \frac{\mathrm{C}_{2}\mathrm{K}_{\mathrm{a}_{2}}}{\sqrt{\mathrm{C}_{1}\mathrm{K}_{\mathrm{a}_{1}} + \mathrm{C}_{2}\mathrm{K}_{\mathrm{a}_{2}}}} \implies [\mathrm{H}^{+}] = \sqrt{\mathrm{C}_{1}\mathrm{K}_{\mathrm{a}_{1}} + \mathrm{C}_{2}\mathrm{K}_{\mathrm{a}_{2}}}$$

• 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  $2.5 \times 10^{-8}$  calculate for its decimolar solution at 25°C.
  - (i) % dissociation
  - (ii) pH
  - (iii)  $OH^-$  ion concentration

Sol. HA 
$$\frac{1}{2}$$
  $\hat{}$   $\hat{}$   $H^+ + A^-$ 

$$C = 0 = 0$$

$$K_{a} = \frac{[H^{+}][A^{-}]}{[HA]} \Longrightarrow K_{a} = \frac{C\alpha C\alpha}{C(1-\alpha)} = \frac{C\alpha^{2}}{(1-\alpha)} \approx C\alpha$$

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

$$=5 \times 10^{+} = 0.05\%$$

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

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

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

**Ex.** Determine the degree of dissociation of  $0.05 \text{ M NH}_3$  at 25°C in a solution of pH = 10.

Sol. 
$$\operatorname{NH}_{4}\operatorname{OH} \stackrel{\circ}{\ddagger} \stackrel{\circ}{} \stackrel{\circ}{} \stackrel{\circ}{} \operatorname{NH}_{4}^{+} + \operatorname{OH}^{-}$$
  
 $C \qquad 0 \qquad 0$   
 $\operatorname{Given, pH} = 10$   
 $[\operatorname{H}^{+}] = 10^{-10}$   
 $[\operatorname{H}^{+}] [\operatorname{OH}^{-}] = 1 \times 10^{-14}$   
 $\therefore [\operatorname{OH}^{-}] = \frac{1 \times 10^{-14}}{10^{-10}} = 10^{-4} = C\alpha$   
 $\therefore \alpha = \frac{[\operatorname{OH}^{-}]}{C} = \frac{10^{-4}}{0.05} = 2 \times 10^{-3} \text{ or } 0.2 \%$ 



- Ex. Two weak monobasic organic acids HA and HB have dissociation constants as  $1.6 \times 10^{-5}$  and  $0.4 \times 10^{-5}$  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 → H<sup>+</sup> + A<sup>-</sup> HB → H<sup>+</sup> + B<sup>-</sup> Let, x = [H<sup>+</sup>] from HA and y = [H<sup>+</sup>] from HB ⇒ [H<sup>+</sup>]<sub>final</sub> = x + y K<sub>HA</sub> =  $\frac{(x + y)x}{c}$  and K<sub>HB</sub> =  $\frac{(x + y)y}{c}$   $\frac{[H<sup>+</sup>]_{HA}}{[H<sup>+</sup>]_{HB}} = \frac{x}{y} = \sqrt{\frac{k_{HA} \times C}{k_{HB} \times C}}$   $\frac{x}{y} = \sqrt{\frac{1.6 \times 10^{-5}}{0.4 \times 10^{-5}}} = 2$ x = 2y ⇒ y =  $\frac{x}{2}$ Substitute for y =  $\frac{x}{2}$  in K<sub>HA</sub> =  $\frac{x^2 + xy}{c}$ 

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

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

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

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

$$p\text{H} = -\log_{10} (3.45 \times 10^{-3})$$
  

$$p\text{H} = 2.462$$

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

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

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

HSaC 
$$\hat{\ddagger}^{\uparrow} \hat{\#}^{+}$$
 H<sup>+</sup> + SaC<sup>-</sup>  
Conc. Before dissociation  $2 \times 10^{-3}$   $10^{-3}$  0

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

$$\Rightarrow K_{a} = \frac{[H^{+}][SaC^{-}]}{[HSaC]}$$
∴ 2×10<sup>-12</sup> =  $\frac{[10^{-3}][SaC^{-1}]}{2 \times 10^{-3}}$   
∴ [SaC<sup>-</sup>] = 4×10<sup>-12</sup> M



# **CHEMISTRY FOR JEE MAIN & ADVANCED**

Ex. A solution contains 0.08 M HCl, 0.08 M CHCl<sub>2</sub>COOH and 0.1 M CH<sub>3</sub>COOH. The pH of this solution is 1. If K<sub>a</sub> for acetic acid is  $10^{-5}$ , calculate K<sub>a</sub> for CHCl<sub>2</sub>COOH.

 $H^+$ 

0.08

(0.08 + x)

(from HCl)

**Sol.** pH will be decided by  $[H^+]$  furnished by HCl and CHCl,COOH.

CHCl,COOH <sup>‡</sup><sup>^</sup><sup>+</sup> CHCl,COO<sup>−</sup> + Initial conc. 0.08 0 Final conc. (0.08 - x)х  $\therefore [H^+] = 0.08 + x;$ but pH = 1,  $\therefore$  [H<sup>+</sup>] = 10<sup>-1</sup> = 0.1  $\therefore 0.08 + x = 0.1 \text{ M}$  $\therefore x = 0.02$ K<sub>a</sub> for CHCl<sub>2</sub>COOH can be given as  $0.1 \times 0.02$ -2

$$K_{a} = \frac{[H_{a}][CHCl_{2}COOH]}{[CHCl_{2}COOH]} = \frac{0.1 \times 0.02}{(0.08 - 0.02)} = 3.33 \times 10^{-10}$$

# **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, and HA, acids, then [H<sup>+</sup>] of both acids should be equal i.e.

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

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  $1.8 \times 10^{-9}$ . Find K<sub>w</sub> and K<sub>d</sub> at 25°C.

(A)  $3.24 \times 10^{-18}$ ;  $5.83 \times 10^{-20}$ (B)  $1 \times 10^{-14}$ ;  $1.8 \times 10^{-16}$ (C)  $1.8 \times 10^{-16}$ ;  $1 \times 10^{-14}$ (D)  $1 \times 10^{-14}$ ;  $1 \times 10^{-14}$ 

**Sol.** (**B**)

Since  $\alpha = 1.8 \times 10^{-9}$ and for water  $c = \frac{1000}{18} = 55.56$  $[H^+] = [OH^-] = c\alpha = 55.56 \times 1.8 \times 10^{-9} = 1 \times 10^{-7} M$  $K_w = [H^+] \times [OH^-] = (1 \times 10^{-7})^2 = 10^{-14}$ 

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<sup>+</sup>] and [OH<sup>-</sup>] of the 10<sup>-1</sup> M aqueous solution of 2% ionised weak acid is : (A)  $2 \times 10^{-3}$  M and  $5 \times 10^{-12}$  M (B)  $1 \times 10^{-3}$  M and  $3 \times 10^{-11}$  M (C)  $2 \times 10^{-4}$  M and  $5 \times 10^{-11}$  M (D)  $3 \times 10^{-2}$  M and  $4 \times 10^{-13}$  M Sol. (A) [H<sup>+</sup>] = C $\alpha$  =  $2 \times 10^{-3}$  M or [OH<sup>-</sup>] =  $\frac{10^{-14}}{[H^+]}$  =  $5 \times 10^{-12}$  M



**(D)** 0.010

When a 0.1 N solution of an acid at 25°C has a degree of ionisation of 4%, the concentration of OH<sup>-</sup> present is : Ex. (A)  $2.5 \times 10^{-3}$ **(B)**  $2.5 \times 10^{-11}$ (C)  $2.5 \times 10^{-12}$ (D)  $2.5 \times 10^{-13}$ 

(C)  $0.057 \times 10^{-2}$ 

Sol. **(C)** 

 $[H^+] = C\alpha = 0.1 \times 4 \times 10^{-2} = 4 \times 10^{-3} M$ or  $[OH^{-}] = \frac{10^{-14}}{[H^{+}]} = 2.5 \times 10^{-12} N$ 

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

**(B)**  $1.0 \times 10^{-6}$ 

(A)  $1.0 \times 10^{-3}$ 

Sol. **(C)** 

$$K_{a} = \frac{[H^{+}][OAc^{-}]}{[HOAc]}$$
  
or  $1.8 \times 10^{-5} = \frac{(10^{-4})^{2}}{[HOAc]}$   
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 **(B)** 

- Sol.
- How much water must be added to 200 mL of 0.2 M solution of CH, COOH for the degree of dissociation of the acid Ex. to double ? K<sub>a</sub> for the acetic acid =  $1.8 \times 10^{-5}$ :

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

so 
$$M_1 = 0.2 \text{ M}; M_2 = \frac{1}{4} \text{ M}$$
  
 $V_1 = 200 \text{ mL}, V_2 = ?$   
 $M_1 V_1 = M_2 V_2$   
or  $V_2 = \frac{M_1 V_1}{M_2} = \frac{0.2 \times 200 \times 4}{0.2} = 800 \text{ mL}$ 

o 
$$800 - 200 = 600$$
 mL water should be added.

The degree of dissociation of acetic acid in a 0.1 M solution is  $1.32 \times 10^{-2}$ . Calculate dissociation constant of acid and Ex. its pK<sub>a</sub> value :

	CH₃COOH ‡ˆî†	$CH_3COO^-$	$+$ $H^+$
Initially	0.1	0	0
at equilibrium	0.1(1-0.0132)	$0.1 \times 0.0132$	$0.1 \times 0.0132$
$K_{a} = \frac{[CH_{3}COO^{-}][H^{+}]}{[CH_{3}COOH]}$	$=\frac{0.1\times0.0132\times0.1\times0}{0.1(1-0.0132)}$	$\frac{0.0132}{0} = 1.76 \times 10^{-10}$	0 <sup>-5</sup>
$pK_a = -\log K_a = -\log(1)$	$.76 \times 10^{-5}) = 4.75$		



s

Sol.

# **CHEMISTRY FOR JEE MAIN & ADVANCED**

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

Sol. 
$$pH=13 \text{ so } [H^{-}] = 10^{-13} \text{ M}$$
  
moles of H<sup>-</sup> in one mL  $= \frac{10^{-13}}{10^3} = 10^{-16} \text{ mol.}$   
 $\therefore$  No. of H<sup>+</sup> 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 HOCI & 0.2 M CH<sub>2</sub>COOH solution given that  
K<sub>a<sub>1</sub></sub> (HOCI)  $= 2 \times 10^{-5}$   
also calculate OH, OCT, CH<sub>2</sub>COO<sup>-</sup>  
Sol. Final solution volume become double  
 $C_1 = 0.01, C_2 = 0.1$   
 $[H^{-}] = \sqrt{K_{a_1}C_1 + K_{a_2}C_2}$   
 $= \sqrt{2 \times 10^{-4} \times 0.01 + 2 \times 10^{-5} \times 0.1} = \sqrt{2 \times 10^{-6} + 2 \times 10^{-6}} = 2 \times 10^{-3}$   
 $pH = 3 - log = 3 - 0.3010 = 2.69$   
 $\alpha_1 = \frac{2 \times 10^{-4}}{2 \times 10^{-3}} = 10^{-1} \alpha_2 = \frac{2 \times 10^{-5}}{2 \times 10^{-3}} = 10^{-2}$   
HOCI  $\frac{3}{4} \times \frac{3}{7}$  H<sup>+</sup> + OCI<sup>-</sup> CH<sub>2</sub>COOH  $\frac{3}{4} \div \frac{3}{7}$  H<sup>-</sup> + CH<sub>2</sub>COO<sup>-</sup>  
 $C_1(1 - \alpha_1)$   $C_1\alpha_1 + C_2\alpha_2$   $C_1\alpha_1$   
 $= 0.1 \times 10^{-3}$   
 $= 0.1 \times 10^{-3}$   
 $[OH] = \frac{K_{m}}{(H^{-})} = \frac{10^{-14}}{2 \times 10^{-3}} = 0.5 \times 10^{-11}$   
 $= 5 \times 10^{-12}$  M  
[HOCI]  $= 10^{-1}(1 - 0.1) = 9 \times 10^{-3}$  M  
[CH<sub>2</sub>COOH]  $= 10^{-1}(1 - 0.01) \approx 10^{-1}$ 

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

**(i)** 

- $\alpha_1$  = degree of ionization of H<sub>2</sub>A in presence of HA<sup>-</sup>
- $\alpha_2$  = degree of ionisation of HA<sup>-</sup> in presence of H<sub>2</sub>A
- $K_{a_1}$  = first ionisation constant of  $H_2A$
- $K_{a_2}$  = second ionisation constant of  $H_2A$



$$\begin{array}{rcl} H_{2}A + H_{2}O \ddagger \uparrow \uparrow \uparrow HA^{-} & + H_{3}O^{+} & HA^{-} + H_{2}O \ddagger \uparrow \uparrow \uparrow A^{2-} & + H_{3}O^{+} \\ \text{at eq. } C - x & x - y & x + y & \text{at eq. } x - y & y & x + y \\ (K_{eq})_{1}[H_{2}O] = \frac{[H_{3}O^{+}][HA^{-}]}{[H_{2}A]} = K_{a_{1}} & (K_{eq})_{2}[H_{2}O] = \frac{[H_{3}O^{+}][A^{2-}]}{[HA^{-}]} = K_{a_{2}} \\ \therefore & K_{a_{1}} = \frac{(x - y)(x + y)}{(C - x)} & K_{a_{2}} = \frac{(y)(x + y)}{(x - y)} \end{array}$$

### **Approximation**

For diprotic acids,  $K_{a_2} \ll K_{a_1}$  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  $K_{a_1} = \frac{x^2}{C - x}$ ,  $K_{a_2} = y$ 

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

- Hence, for a diprotic acid (or a polyprotic acid) the [H<sub>3</sub>O<sup>+</sup>] can be calculated from its first equilibrium constant expression alone provided  $K_{a_2} \ll K_{a_1}$
- Calculate pH of [HS<sup>-</sup>], [S<sup>2-</sup>], [Cl<sup>-</sup>] in a solution which is 0.1 M HCl & 0.1 M H<sub>2</sub>S given that  $K_{a_1}(H_2S) = 10^{-7}$ , Ex.  $Ka_2(H_2S) = 10^{-14}$  also calculate  $\alpha_1 \& \alpha_2$ .

Sol.

0.1 0.1  $C_1 = C_2 = 0.1$ 

 $HC1 + H_2S$ 

 $\therefore$  pH = 1 (most of [H<sup>+</sup>] comes from HCl]

$$H_{2}S \quad f \quad H^{+} \quad HS^{-}$$
  

$$0.1(1-\alpha_{1}) \qquad 10^{-1} \qquad C\alpha_{1} = 0.1 \text{ or}$$
  

$$Ka_{1} = \frac{C\alpha_{1} \times 10^{-1}}{C(1-\alpha_{1})} = \frac{10^{-7}}{10^{-1}} = \alpha_{1}$$

 $10^{-1}$ 

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

ĵ ^ ~\*  $HS^{-}$  $S^{2-}$  $H^{\dagger}$  $\begin{array}{l} C\alpha_{1}(1-\alpha_{2}) \\ 10^{-14} \!=\! 0.1 \times \alpha_{2} \end{array}$  $C\alpha_1\alpha_2$ 0.1  $\Rightarrow \alpha_2 = 10^{-13}$ 

$$[\tilde{S}^{2^{-}}] = C\alpha_1 \alpha_2$$
  
=  $10^{-6} \times 10^{-1} \times 10^{-13} = 10^{-20} M$ 

**(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<sub>a</sub> and K<sub>b</sub> for Conjugate Acid Base Pair

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

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

 $pK_{a} + pK_{b} = 14 \text{ at } 25^{\circ}\text{C}$ 

Weak acids, generically abbreviated as HA, donate H<sup>+</sup> (or proton) to water to form the conjugate base A<sup>-</sup> and H<sub>3</sub>O<sup>+</sup> :

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

acid base acid base

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

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

base acid acid base

For a weak acid or base, the equilibrium constant for the ionization 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 :

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

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  $K_a$ :

$$K_{a} = \frac{[H_{3}O^{+}][A^{-}]}{[HA]}$$

### Finding Kb for A- Reacting as a Base

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

 $A^{-}(aq) + H_2O(l) f HA(aq) + OH^{-}(aq)$ 

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<sup>-</sup>, that gives :

$$K_{a} \cdot K_{b} = \left(\frac{[H_{3}O^{+}][A^{-}]}{[HA]}\right) \left(\frac{[HA][OH^{-}]}{[A^{-}]}\right)$$
$$= [H3O^{+}][OH^{-}]$$
$$= K_{w}$$



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

$$K_a \cdot K_b = K_w$$

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

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

 $pK_{a} + pK_{b} = 14 \text{ at } 25^{\circ}\text{C}$  (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<sup>+</sup> ions)

Ex. NaCl, NaNO<sub>3</sub>, K<sub>2</sub>SO<sub>4</sub>, Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, Na<sub>3</sub>BO<sub>3</sub>, Na<sub>2</sub>HPO<sub>3</sub>, NaH<sub>2</sub>PO<sub>2</sub> etc.

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

**Ex.** NaHCO<sub>3</sub>, NaHSO<sub>4</sub>, NaH<sub>2</sub>PO<sub>4</sub>, Na<sub>2</sub>HPO<sub>4</sub> 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), Cl, Bi(OH), Cl 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<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>. 6H<sub>2</sub>O (Ferrous ammonium sulphate), K<sub>2</sub>SO<sub>4</sub>Al<sub>2</sub> (SO<sub>4</sub>)<sub>3</sub>.24H<sub>2</sub>O (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.

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#### 1.3 **Complex Salts**

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

#### Ex. $K_4$ Fe(CN)<sub>6</sub>, Co(NH<sub>3</sub>)<sub>6</sub> SO<sub>4</sub> etc.

(ii) 
$$\operatorname{FeSQ}_{4^{4}2^{+}} \overset{4}{}_{4^{4}S} \overset{4}{}_{5^{4}} \overset{4}{}_$$

(iii)  $\text{CoSO}_4$  + 6NH<sub>3</sub>  $\longrightarrow$  Co(NH<sub>3</sub>)<sub>6</sub>SO<sub>4</sub>

Simple Molecular complex

salt compound salt

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

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

$$\mathsf{K}_{4}$$
Fe(CN)<sub>6</sub>  $\ddagger \hat{\uparrow}^{H_{2}O_{4}} \uparrow 4K^{+} + [Fe(CN)_{6}]^{4}$ 

complex ion

(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.

$$\begin{bmatrix} Ca \swarrow OCI \\ Cl \end{bmatrix}, \begin{bmatrix} Na \\ K \searrow SO_4 \end{bmatrix}, \begin{bmatrix} Na \\ NH_4 \searrow PO_4 \\ H \end{bmatrix}$$

### **Hydrolysis of Salt**

### Salt Hydrolysis

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

Water + Salt  $\ddagger \hat{\uparrow} \hat{\uparrow} Acid + Base$ 

 $\Delta H = +ve$ 

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

Hydrolysis constant  $K_{h} = \frac{[Acid][Base]}{[Salt]}$ 

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 -

$$CaSO_{4}, NH_{4}Cl, (NH_{4})_{2}SO_{4}, Ca(NO_{3})_{2}, ZnCl_{2}, CuCl_{2}, CaCl_{2}$$
$$NH_{4}Cl + H_{2}O \stackrel{+}{\ddagger} \stackrel{\wedge}{} \stackrel{\wedge}{} MH_{4}OH + HCl$$
$$NH_{4}^{+}+Cl^{-} + H_{2}O \stackrel{+}{\ddagger} \stackrel{\wedge}{} \stackrel{\wedge}{} MH_{4}OH + H^{+} + Cl^{-}$$
$$NH_{4}^{-} + H_{4}O \stackrel{+}{\ddagger} \stackrel{\wedge}{} \stackrel{\wedge}{} MH_{4}OH + H^{+}$$



Ex.

.....(1)

.....(2)

.....(3)

- (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  $K_h$ ,  $K_W \& K_b$

$$NH_4^+ + H_2O^{\ddagger} \uparrow \uparrow H_4OH + H^+$$

Hydrolysis constant K<sub>h</sub>

$$\boldsymbol{K}_{h} = \frac{\left[\boldsymbol{N}\boldsymbol{H}_{4}\boldsymbol{O}\boldsymbol{H}\right]\left[\boldsymbol{H}^{+}\right]}{\left[\boldsymbol{N}\boldsymbol{H}_{4}^{+}\right]}$$

For weak Base

 $NH_4OH \ddagger \hat{\uparrow} \hat{\uparrow} NH_4^+ + OH^-$ 

$$\mathbf{K}_{\mathbf{b}} = \frac{\left\lfloor \mathbf{NH}_{4}^{+} \right\rfloor \left\lfloor \mathbf{OH}^{-} \right\rfloor}{\left[ \mathbf{NH}_{4} \mathbf{OH} \right]}$$

For water

 $H_{2}O_{\pm}^{\pm} \widehat{}^{+}H^{+}+OH^{-}$  $K_{w}=[OH^{-}][H^{+}]$ 

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

$$\frac{\left[\mathrm{NH}_{4}\mathrm{OH}\right]\left[\mathrm{H}^{+}\right]}{\left[\mathrm{NH}_{4}^{+}\right]} \times \frac{\left[\mathrm{NH}_{4}^{+}\right]\left[\mathrm{OH}^{-}\right]}{\left[\mathrm{NH}_{4}\mathrm{OH}\right]} = [\mathrm{H}^{+}][\mathrm{OH}^{-}]$$

i.e.

$$K_{h} = \frac{K_{w}}{K_{b}}$$

 $K_h \times K_b = K_w$ 

(b) Degree of hydrolysis – Represented by h

 $NH_{4}^{+} + H_{2}O^{\ddagger}$  $\rm NH_4OH + H^+$ С 0 0 C - xх Х  $nx = a\alpha$ 1x = Chx = ChC - ChCh Ch  ${\rm K_{h}} = \frac{\left[{\rm NH_{4}OH}\right]\left[{\rm H^{+}}\right]}{\left\lceil {\rm NH_{4}^{+}}\right\rceil} =$  $\frac{Ch \times Ch}{C-Ch}$  $\frac{\mathrm{C}^{2}\mathrm{h}^{2}}{\mathrm{C}(1-\mathrm{h})} = \frac{\mathrm{C}\mathrm{h}^{2}}{(1-\mathrm{h})}$ Since h <<<<1 then  $(1-h) \approx 1$  $\therefore K_h = Ch^2$ 

(initial concentration at equilibrium)



$$h^{2} = \frac{K_{h}}{C} \implies h = \sqrt{\frac{K_{h}}{C}}$$
  
 $\therefore K_{h} = \frac{K_{w}}{K_{b}} \implies h = \sqrt{\frac{K_{w}}{K_{b}}} \implies h = \sqrt{\frac{K_{w}}{K_{b} \times C}}$ 

(c) pH of the solution :

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

$$[H^{+}] = Ch = C \sqrt{\frac{K_{w}}{K_{b} \times C}} \implies [H^{+}] = \sqrt{\frac{K_{w} \times C}{K_{b}}}$$
On taking – log on both sides
$$-\log [H^{+}] = -\log \sqrt{\frac{K_{w} \times C}{K_{b}}} \implies pH = -\log \left(\frac{K_{w} \times C}{K_{b}}\right)^{\frac{1}{2}}$$

$$pH = -\frac{1}{2} [\log K_{w} + \log C - \log K_{b}]$$

$$pH = -\frac{1}{2} \log K_{w} - \frac{1}{2} \log C - \frac{1}{2} (-\log K_{b})$$

$$pH = \frac{1}{2} pK_{w} - \frac{1}{2} \log C - \frac{1}{2} pK_{b}$$

$$pH = 7 - \frac{1}{2} pK_{b} - \frac{1}{2} \log C$$
**ETOOS 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  $[10^{-2} \text{ N}]$ 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<sub>h</sub> at 363 K (90°C) of a salt of [Strong Acid – Weak Base] if the value of K<sub>b</sub> is  $10^{-5}$  [At 90°C K<sub>w</sub> =  $10^{-12}$ ]

**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  $1.8 \times 10^{-5}$ .
- **Sol.**  $NH_4Cl$  is a salt of strong acid and weak base for solutions of such salts.

pH = 
$$\frac{1}{2}$$
 [pK<sub>w</sub> - log C - pK<sub>b</sub>]  
⇒ 10.26 = 14 - log C - 4.74  
⇒ log C = 9.26 - 10.26 = -1.0  
∴ C = 10<sup>-1</sup> M  
[NH<sub>4</sub>Cl] = 10<sup>-1</sup> M  
W<sub>NH<sub>4</sub>NO<sub>3</sub></sub> = 10<sup>-1</sup> × 53.5 gL<sup>-1</sup> = 5.35 gL<sup>-1</sup>

- **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 + 
$$H_2O$$
  $\ddagger$   $\uparrow$   $\uparrow$  NaOH + HCN  
C 0 0  
C(1-h) Ch Ch

$$\therefore [OH^{-}] = Ch = C\sqrt{\frac{K_{h}}{C}} = \sqrt{K_{h}C} = \sqrt{\frac{K_{w}C}{K_{a}}}$$

pOH = 
$$\frac{1}{2}$$
 (pK<sub>w</sub> - pK<sub>a</sub> - log C) =  $\frac{1}{2}$  [14 - 9.30 - log (0.4)] = 2.548  
∴ pH = 14 - 2.5 = 11.45

**Ex.** The acid ionization constant for

$$Zn^{2+} + H_2O_{\frac{1}{2}}^{2+} T = Zn(OH)^+ + H^+$$

is  $1.0 \times 10^{-9}$ . Calculate the pH of 0.10 M solution of ZnCl<sub>2</sub>. Also calculate basic dissociation constant of Zn(OH)<sup>+</sup>.

**Sol.** 
$$Zn^{2+} + H_2O_{\pm}^{\pm} \uparrow Zn(OH)^+ + H^+$$

$$\therefore [H^{+}] = C.h = C\sqrt{\frac{K_{h}}{C}} = \sqrt{K_{h}C}$$

$$= \sqrt{\frac{K_{w}C}{K_{b}}} \qquad \qquad \left[ \begin{array}{c} \text{where } K_{b} \text{ is basic dissociation constant of } Zn(OH)^{+} \\ \text{i.e. } Zn(OH)^{+} \frac{2}{T} \stackrel{\wedge}{\to} Zn^{2+} + OH^{-} \end{array} \right]$$



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

$$\therefore \qquad \mathbf{K}_{\mathrm{a}} \times \mathbf{K}_{\mathrm{b}} = 10^{-14}$$

or 
$$K_{\rm b} = \frac{10^{-14}}{10^{-9}} = 10^{-5}$$

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

pH = 3

(2) Hydrolysis of [WA-SB] Type Salt –

Ex. KCN, NaCN, K<sub>2</sub>CO<sub>3</sub>, BaCO<sub>3</sub>, K<sub>3</sub>PO<sub>4</sub>

$$NaCN + H_2O_{1}^{2} ^{2} ^{2}$$
  $NaOH + HCN$ 

$$Na^{+}+CN^{-}+H_{2}O_{+}^{+} ^{\uparrow} Na^{+}+OH^{-}+HCN$$

 $CN^- + H_2O_{\ddagger}^{\uparrow} \uparrow HCN + OH^-$ 

- (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.

K<sub>h</sub> :

- (3) pH of the solution is greater than 7.
- (a) Relation between  $K_h, K_w, K_a$

$$CN^{-}+H_{2}O^{+} \uparrow^{+} HCN+OH^{-}$$

For weak acid

HCN  $\frac{1}{2}$   $\hat{}$   $\hat{}$   $\hat{}$  CN<sup>-</sup> + H<sup>+</sup>

$$K_{a} = \frac{\begin{bmatrix} CN^{-} \\ H^{+} \end{bmatrix}}{\begin{bmatrix} HCN \end{bmatrix}} \qquad \dots (2)$$

.....(1)

For water

$$H_{2}O_{\frac{1}{2}}^{+} \stackrel{\wedge}{} H^{+} + OH^{-}$$
$$K_{w} = [OH^{-}][H^{+}] \qquad \dots (3)$$

 $eq. (1) \times eq. (2) = eq. (3)$ 

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

$$K_{h} \times K_{a} = K_{w}$$

$$K_{h} = \frac{K_{w}}{K_{a}}$$



 $CN^- + H_2O$   $\uparrow \uparrow HCN + OH^-$ 0 С 0 Initial concentration at equlibrium  $\mathbf{C} - \mathbf{x}$ х х  $nx = a\alpha$ 1x = Chx = ChC - ChCh Ch  $K_{h} = \frac{[HCN][OH^{-}]}{[CN^{-}]} = \frac{Ch \times Ch}{C - Ch} = \frac{C^{2}h^{2}}{C(1-h)}$  $K_{h} = \frac{Ch^{2}}{(1-h)}$ Since h <<<<1 therefore  $(1-h) \approx 1$  $K_h = Ch^2$  $h^2 = \frac{K_h}{C} \implies h = \sqrt{\frac{K_h}{C}}$  $h = \sqrt{\frac{K_{w}}{K_{a} \times C}}$ (c) pH of the solution  $[OH^{-}] = Ch$  $[OH^{-}] = C \times \sqrt{\frac{K_{w}}{K_{a} \times C}}$  $\left[OH^{-}\right] = \sqrt{\frac{K_{w} \times C}{K_{a}}}$  $K_w = [OH^-][H^+]$  $\left[\mathbf{H}^{+}\right] = \frac{\mathbf{K}_{\mathbf{W}}}{\left[\mathbf{OH}^{-}\right]}$  $\left[\mathbf{H}^{+}\right] = \frac{\mathbf{K}_{\mathbf{w}}}{\sqrt{\frac{\mathbf{K}_{\mathbf{w}} \times \mathbf{C}}{\mathbf{K}_{\mathbf{a}}}}}$  $\left[\mathrm{H}^{+}\right] = \sqrt{\frac{\mathrm{K}_{\mathrm{W}} \times \mathrm{K}_{\mathrm{a}}}{\mathrm{C}}}$ 



On taking – log on both sides

$$-\log [H^{+}] = -\log \sqrt{\frac{K_{w} \times K_{a}}{C}}$$

$$pH = -\log \left(\frac{K_{w} \times K_{a}}{C}\right)^{\frac{1}{2}}$$

$$pH = -\frac{1}{2} \left[\log K_{w} + \log K_{a} - \log C\right]$$

$$pH = -\frac{1}{2} \log K_{w} - \frac{1}{2} \log K_{a} + \frac{1}{2} \log C$$

$$pH = \frac{1}{2} pK_{w} + \frac{1}{2} pK_{a} + \frac{1}{2} \log C$$

$$pH = 7 + \frac{1}{2} pK_{a} + \frac{1}{2} \log C$$

r] ogC

# ETOOS KEY POINTS



Ex. Find out pH, h and [OH<sup>-</sup>] 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)  $h = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{K_w}{K_a \times C}} = \sqrt{\frac{10^{-14}}{10^{-7} \times 10^{-3}}} = \sqrt{10^{-14} \times 10^{10}} = \sqrt{10^{-4}} = 10^{-4}$   
(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  $6.2 \times 10^{-12}$ .
- Sol. NaCN is a salt of strong base NaOH and weak acid HCN. K<sup>+</sup> does not react with water whereas CN<sup>-</sup> reacts with water as here under

$$CN^- + H_2O^{+} ^{+} MCN + OH^-$$

$$K_{h} = \frac{[HCN][OH^{-}]}{[CN^{-}]} = \frac{K_{w}}{K_{a}} = \frac{10^{-14}}{6.2 \times 10^{-12}} = 1.6 \times 10^{-3}$$

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

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

 $[OH^{-}] = x$ 

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

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

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

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

$$[\mathrm{H}_{3}\mathrm{O}^{+}] = \frac{\mathrm{K}_{\mathrm{W}}}{[\mathrm{OH}^{-}]} = \frac{10^{-14}}{4 \times 10^{-3}} = 0.25 \times 10^{-11}$$

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

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<sub>3</sub>COOH =  $1.9 \times 10^{-5}$ .

Sol. For CH<sub>3</sub>COONa + H<sub>o</sub>O CH,COOH NaOH +С 0 0 Initial Ch After C(1-h) 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 × 2.29 × 10<sup>-4</sup> = 2.29 × 10<sup>-6</sup> M pOH = 5.64  $\therefore$  pH = 14 - 5.64 = 8.36



# **CHEMISTRY FOR JEE MAIN & ADVANCED**

## 3. Hydrolysis of (WA-WB) Type Salt

- **Ex.**  $NH_4CN, CaCO_3, (NH_4)_2CO_3, ZnHPO_3$  $NH_4CN + H_2O_{1}^{+} ^{-} ^{+} NH_4OH + HCN$  $NH_4^{+} + CN^{-} + H_2O_{1}^{+} ^{-} ^{-} NH_4OH + HCN$
- (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 
$$K_{y_{1}}K_{w_{2}}K_{w_{3}}K_{w_{4}}K_{w_{5}}$$
  
 $NH_{4}^{+}+CN^{-}+H_{2}O^{\frac{1}{2},^{+}M^{+}} NH_{4}OH+HCN$   
 $K_{h} = \frac{[NH_{4}OH][HCN]}{[NH_{4}^{+}][CN^{-}]}$  ....(1)  
For weak base  $NH_{4}OH^{\frac{1}{2},^{+}M^{+}} NH_{4}^{+}+OH$   
 $K_{h} = \frac{[NH_{4}^{+}][OH^{-}]}{[NH_{4}OH]}$  ....(2)  
For weak acid  $HCN^{\frac{1}{2},^{+}M^{+}} H^{+}+CN^{-}$   
 $K_{a} = [H^{+}][CN^{-}]$  .....(3)  
For water  $H_{2}O^{\frac{1}{2},^{+}M^{+}} H^{+}+OH$   
 $K_{a} = [OH^{-}][H^{-}]$  .....(4)  
Multiply Eq. (1) × Eq. (2) × Eq. (3) = Eq. (4)  
 $\frac{[NH_{4}OH][HCN]}{[NH_{4}^{+}][CN^{-}]} \times \frac{[M^{+}][CN^{-}]}{[HCN]} = [H^{-}][OH^{-}]$   
 $K_{a} \times K_{b} \times K_{a} - K_{a}$   
 $K_{b} = \frac{K_{w}}{K_{a} \times K_{b}}$   
Degree of Hydrolysis -  
 $NH_{4}^{+} + CN^{+} H_{2}O^{\frac{1}{2},^{+}M^{+}} NH_{4}OH^{+} + HCN$   
 $C - C C 0 0 0$  Initial concentration  
 $at equilibrium$   
 $\Theta nx = a\alpha$   
 $\therefore x = Ch$   
 $C - Ch C - Ch Ch Ch Ch Ch
 $K_{h} = \frac{[NH_{4}OH][HCN]}{[NH_{4}^{+}][CN^{-}]} = \frac{Ch \times Ch}{(C - Ch)(C - Ch)} = \frac{C^{2}h^{2}}{C(1 - h) \times C(1 - h)} = \frac{h^{2}}{(1 - h)^{2}}$   
Since  $h < \ll 1$   
Then  $(1 - h) \approx 1$   
 $\therefore [K_{h} = h^{2}]$$ 



(2)

.....(5)

or

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

$$h = \sqrt{\frac{K_{\rm W}}{K_{\rm a} \times K_{\rm b}}}$$

(b) pH of the solution

From eq. (3)

$$K_{a} = \frac{\left[H^{+}\right]\left[CN^{-}\right]}{\left[HCN\right]}$$
$$\left[H^{+}\right] = \frac{K_{a} \times [HCN]}{\left[CN^{-}\right]}$$
$$\left[x_{a} + z_{a} +$$

$$\left[H^{+}\right] = \frac{K_{a} \times Ch}{C - Ch} = \frac{K_{a} \times h}{1 - h}$$

Since h <<<<1

$$(1-h) \approx 1$$

$$[H^{+}] = K_{a} \times h \qquad [Now put the value of h from eq. (5)]$$

$$= K_{a} \times \sqrt{\frac{K_{w}}{K_{a} \times K_{b}}}$$

$$[H^{+}] = \sqrt{\frac{K_{w} \times K_{a}}{K_{b}}}$$

On taking – log on both sides

$$-\log [H^{+}] = -\log \left(\frac{K_{w} \times K_{a}}{K_{b}}\right)^{\frac{1}{2}}$$

$$pH = -\frac{1}{2} \left[\log (K_{w} \times K_{a}) - \log K_{b}\right]$$

$$pH = -\frac{1}{2} \left[\log K_{w} + \log K_{a} - \log K_{b}\right]$$

$$pH = -\frac{1}{2} \left[\log K_{w}\right] - \frac{1}{2} \left[\log K_{a}\right] - \frac{1}{2} \left[-\log K_{b}\right]$$

$$pH = +\frac{1}{2} pK_{w} + \frac{1}{2} pK_{a} - \frac{1}{2} pK_{b}$$

$$pH = 7 + \frac{1}{2} pK_{a} - \frac{1}{2} pK_{b}$$







**Ex.** Calculate the degree of hydrolysis of a mixture containing 0.1N NH<sub>4</sub>OH 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.

$$NaCl + H_2O$$
  $\ddagger \uparrow \uparrow \uparrow NaOH + HCl$ 

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

 $H_2O$   $\ddagger$   $\uparrow$   $H^+ + OH^-$  (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 dissociation always takes place in steps, so for example for  $H_3PO_4$

$$H_{3}PO_{4} \ddagger \uparrow \uparrow + H_{2}PO_{4}^{-} \qquad K_{a_{1}} = \frac{[H^{+}][H_{2}PO_{4}^{-}]}{[H_{3}PO_{4}]} \qquad \dots (1)$$

$$H_{2}PO_{4}^{-} \ddagger \uparrow \uparrow + H^{+} + HPO_{4}^{-2} \qquad K_{a_{2}} = \frac{[H^{+}][HPO_{4}^{2-}]}{[H_{2}PO_{4}^{-}]} \qquad \dots (2)$$

$$HPO_{4}^{2-} \ddagger \uparrow \uparrow \uparrow + PO_{4}^{-3} \qquad K_{a_{3}} = \frac{[H^{+}][PO_{4}^{3-}]}{[HPO_{4}^{2-}]} \qquad \dots (3)$$

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

pH of the solution can be calculated from Ist step only because [H<sup>+</sup>] from II<sup>nd</sup> & III<sup>rd</sup> step can be neglected as

- (a)  $K_{a_1} >> K_{a_2} >> K_{a_3}$
- (b)  $[H^+]$  from I<sup>st</sup> dissociation will suppress the dissociation of II<sup>nd</sup> & III<sup>rd</sup> step. Now for the hydrolysis of polyvalent ions of salts (like K<sub>3</sub>PO<sub>4</sub>, Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, ZnSO<sub>4</sub>, FeCl<sub>3</sub>, (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub> or ions like PO<sub>4</sub><sup>3-</sup>, C<sub>2</sub>O<sub>4</sub><sup>2-</sup>, Zn<sup>2+</sup>, Fe<sup>3+</sup> etc).

Consider the hydrolysis in step



$$K_{a_2} \times K_{h_2} = K_w$$
$$K_{a_2} \times K_{h_1} = K_w$$

Genarally pH is calculated only using the first step hydrolysis

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

$$h = \sqrt{\frac{K_{h_{1}}}{C}} \implies [OH^{-}] = Ch = \sqrt{K_{h_{1}} \times C} \implies [H^{+}] = \frac{K_{w}}{[OH^{-}]} = K_{w}\sqrt{\frac{K_{a_{3}}}{K_{w}C}} = \sqrt{\frac{k_{w} \times K_{a_{3}}}{C}}$$

So 
$$pH = \frac{1}{2} [pK_w + pK_{a_3} + logC]$$

**Ex.** What is the pH of  $1.0 \text{ M Na}_{3}\text{PO}_{4}$  in aqueous solution ?

$$PO_4^{3-} + H_2O_{\ddagger}^{3-} \uparrow HPO_4^{2-} + OH^-; K_b = 2.4 \times 10^{-2}$$

Sol. 
$$K_a(HPO_4^{2-}) = \frac{10^{-14}}{2.4 \times 10^{-2}} = 4.17 \times 10^{-13}$$
  
 $pK_a = -\log K_a = 12.38$   
or  $pH = 7 + \frac{1}{2} pK_a + \frac{1}{2} \log C = 7 + \frac{1}{2} (12.38) + \frac{1}{2} \log(1) = 13.19$ 

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) 
$$HCO_3^- + H_2O_{12}^+ \stackrel{\text{anisation}}{\longrightarrow} CO_3^{2-} + H_3O^+ (acid)$$
  
(ii)  $HCO_3^- + H_2O_{12}^+ \stackrel{\text{anisation}}{\longrightarrow} H_2CO_3^+ OH^- (base)$   
 $pH(HCO_3^-) = \left(\frac{pK_{a_1} + pK_{a_2}}{2}\right)$ 



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

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

# 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)

 $HCO_3^- + H_2O_{1}^+ \land \uparrow H_2CO_3^- + OH^-$ 

(Hydrolysis of cation)

$$NH_4^+ + H_2O_{\ddagger}^+ \uparrow NH_4OH + H^+$$

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 p	H > 7.		
Ex.	If one equivalent of a stro	ng acid is added to one equ	ivalent of a weak base, the re	sulting solution will be.	
	(A) neutral	(B) acidic	(C) alkaline	(D) none of these	
Sol.	(B), since after neutralisat	ion salt of (SA + WB) will fo	orm and its pH < 7.		
Ex.	Which is the correct optic	on fo <mark>r hydrol</mark> ysis constant of	f NH <sub>4</sub> CN ?		
	(A) $\sqrt{\frac{K_w}{K_a}}$	<b>(B)</b> $\frac{K_{w}}{K_{a} \times K_{b}}$	(C) $\sqrt{\frac{K_b}{K_c}}$	<b>(D)</b> $\frac{K_a}{K_b}$	
Sol.	<b>(B)</b> , Since NH <sub>4</sub> CN is a salt	of (WA+WB).			
	Equilibrium constant of h	ydrolysis of WA + WB is $\frac{1}{K}$	$\frac{K_{w}}{K_{a} \times K_{b}}$		
Ex.	Increasing order of pH of	0.1 M solution of the follow	ving salts is :		
	(A) NaCl <nh<sub>4Cl<nacn< th=""><th></th><th><b>(B)</b> <math>NH_4Cl &lt; NaCl &lt; NaCN</math></th><th></th></nacn<></nh<sub>		<b>(B)</b> $NH_4Cl < NaCl < NaCN$		
	(C) NaCN < NH <sub>4</sub> Cl < NaCl		(D) NaCl < NaCN < NH <sub>4</sub> Cl		
Sol.	<ul> <li>(B), Since NH<sub>4</sub>Cl is the salt of (WB + SA) so pH &lt; 7, NaCl is salt of (SA + SB) so pH = 7 and NaCN is salt of (WA + SB) so pH &lt; 7.</li> </ul>				
Ex.	When a solution of 0.01 M CH <sub>3</sub> COOH is titrated with a solution of 0.01 M NaOH. Calculate the pH at the equivalence point. ( $pK_a$ of CH <sub>3</sub> COOH is 4.74)				
Sol.	CH,COOH+NaOH <sup>‡</sup> <sup>^</sup> <sup>†</sup> CH,COONa+H,O				
	Let acid be = $V mL$				
	VmL of 0.01 M CH COOF	I will require V mL of 0.01 M	NaOH But CH COONa form	ed will make solution alkaline due	

V mL of 0.01 M CH<sub>3</sub>COOH will require V mL of 0.01 M NaOH. But  $CH_3COONa$  formed will make solution alkaline due to hydrolysis



CH<sub>3</sub>COONa + H<sub>2</sub>O  $\ddagger \uparrow \uparrow \downarrow$  CH<sub>3</sub>COOH + NaOH [CH<sub>3</sub>COONa] =  $\frac{0.01}{2}$  = 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  $0.5 \text{ M Na}_3\text{PO}_4$  in aqueous solution ?

$$PO_4^{3-} + H_2O_{1}^{3-} + HPO_4^{2-} + OH^-; K_b(PO_4^{-3}) = 2.4 \times 10^{-2}$$

**Sol.** HPO<sub>4</sub><sup>2-</sup> and PO<sub>4</sub><sup>-3</sup> 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<sub>a</sub> +  $\frac{1}{2}$  log C
pH = 13.04

- Ex. What is degree of hydrolysis,  $K_{h}$  and pH of 1 M urea hydrochloride solution in water.  $K_{h}$  (urea) =  $1.5 \times 10^{-14}$ .
- **Sol.** NH,CONHCl is a salt of (SA + WB)

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<sub>b</sub> -  $\frac{1}{2}$  log C  
= 7 -  $\frac{1}{2}$  (13.82) -  $\frac{1}{2}$  log(1) 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.

 $CH_{3}COONH_{4} \longrightarrow CH_{3}COO^{-} + NH_{4}^{+}$ 

If a strong acid such as HCl is added then

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

The  $\text{H}^+$  ions from the added acid (HCl) combine with  $\text{CH}_3\text{COO}^-$  ions to form  $\text{CH}_3\text{COOH}$ , which is a weak acid so will not further ionized.

Thus there is no rise in  $\boldsymbol{H}^{\scriptscriptstyle +}$  ion concentration and the pH remains constant.

 $CH_3COO^- + H^+ = CH_3COOH$  (Weak acid)

If a strong base is added as NaOH

$$NaOH \longrightarrow Na^{+} + OH$$

 $NH_{4}^{+}+OH^{-} \longrightarrow NH_{4}(OH)$  (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 :-

$$pH=7+\frac{1}{2}pk_{a}-\frac{1}{2}pk_{b}$$

### (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<sub>3</sub>COONa). Other example :

 $HCN + KCN, (H_2CO_3 + NaHCO_3) \longrightarrow blood$ 

 $CH_3COOH \Longrightarrow CH_3COO^- + H^+$  (Weakly ionised)

 $CH_3COONa \longrightarrow CH_3COO^- + Na^+$  (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<sup>-</sup> of the added base reacts with acetic acid to form unionise water and acetate ions.

 $CH_3COOH + OH^- \implies H_2O + CH_3COO^-$ . Thus there is no increase in OH<sup>-</sup> 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<sub>3</sub>COO, A<sup>-</sup> = CH<sub>3</sub>COO<sup>-</sup>

$$HA \Longrightarrow H^{+} + A^{-}$$
$$NaA \longrightarrow Na^{+} + A^{-}$$

Applying law of mass action to dissociation equilibrium of HA

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

taking log

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



$$-\log [\mathrm{H}^{+}] = -\log \mathrm{K}_{\mathrm{a}} - \log \frac{[\mathrm{HA}]}{[\mathrm{A}^{-}]}$$

$$pH = pK_a + log \frac{[A^-]}{[HA]}$$

 $[A^-]$  = 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.)

EDUBULL KEY POINTSA solution can act as buffer only if ratio of concentration of salt to acid is between 0.1 to 10.
$$CH_3COOH$$
: $CH_3COONa$ 110 $pH = pK_a + 1$ 101 $pH = pK_a - 1$ Thus pH range of an acidic buffer solution is  $pK_a + 1$  to  $pK_a - 1$  $pH$  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.

 $pH = pK_a + log1/1 \implies pH = pK_a$ 

- 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<sub>3</sub>COOH. (Given  $pK_a$  for CH<sub>3</sub>COOH=4.74)
- Sol. If 80 mL of 0.1 N NaOH is added to 100 mL of 0.1 N CH<sub>3</sub>COOH, 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<sub>a</sub> + 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 to 100 mL of 0.1 N CH<sub>3</sub>COOH, complete neutralization takes place and the

concentration of H<sub>3</sub>CCOONa = 
$$\frac{0.1}{2}$$
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<sub>a</sub> 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<sub>3</sub>COONa in solution  $\frac{100 \times 0.2}{1000} = 0.02$   
Let, volume of 0.2 acetic acid added = V mL  
 $\therefore$  Moles of acetic acid =  $\frac{V \times 0.2}{1000}$   
 $\therefore \frac{0.02}{V \times \frac{0.2}{1000}} = 18.2$   
 $\therefore V = 5.49$  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 ?  
Given K<sub>a</sub> for acetic acid is  $1.8 \times 10^{-5}$ .  
Sol. (a) Initially [Acetic acid] = 1 M  
[Acetate] = 1 M

Now 0.2 moles of HCl are added to it. HCl +  $CH_3COO^- \rightarrow CH_3COOH$ Mole before reaction 0.2 1 1 Mole after reaction 0 0.8 1.2

$$pH = pk_a + log \frac{[conjugate]}{[acid]}$$

:. 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<sub>3</sub>COO<sup>-</sup>  $\rightarrow$  CH<sub>3</sub>COOH + Cl<sup>-</sup>

		5	5	
Mole before reaction	0.2	0.1	0.1	0
Mole after reaction	0.1	0	0.2	0.1
$\therefore$ [H <sup>+</sup> ] from free HCl = 0.	$1 = 10^{-1}M$			
$\therefore pH = 1$				



 $Cl^{-}$ 

0

0.2

- **Note :** CH<sub>3</sub>COOH no doubt gives H<sup>+</sup> but being weak acid as well as in presence of HCl does not dissociate appreciably and thus, H<sup>+</sup> from CH<sub>3</sub>COOH 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<sub>3</sub>COONa and 1 mole HCl are present.

$$CH_{3}COONa + HCl \rightarrow CH_{3}COOH + NaCl$$
Before reaction 1 1 0 0  
After reaction 0 0 1 1 1  

$$\therefore [CH_{3}COO] = 1 M$$

$$\therefore [H^{+}] = C.\alpha = C\sqrt{\left(\frac{K_{a}}{C}\right)} = \sqrt{(K_{a}.C)} = \sqrt{(K_{a})} \Rightarrow C = 1$$

$$\therefore pH_{1} = -\frac{1}{2}\log K_{a}$$
Case II : pH when 1 mole CH.COONa and 1 mole of CH.COOH : a buffer solution

 $\therefore \quad pH_2 = -\log K_a + \log \frac{[salt]}{[acid]} \quad \Rightarrow [Salt] = 1M$   $pH_2 = -\log K_a \quad \Rightarrow [Acid] = 1M$   $\therefore \quad \frac{pH_1}{pH_2} = \frac{1}{2}$ 

### (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  $NH_4Cl$ .

 $NH_4OH \longrightarrow NH_4^+ + OH^-$  (Weakly ionised)

 $NH_4Cl \rightarrow NH_4^+ + Cl^-$  (Highly ionised)

When a few drops of a base (NaOH) are added, the OH<sup>-</sup> 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.

 $\mathrm{NH}_4^+ + \mathrm{OH}^- \rightarrow \mathrm{NH}_4\mathrm{OH}$ 

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.

$$\rm NH_4OH + H^+ \rightarrow \rm NH_4^+ + H_2O$$

Thus the addition of acid does not increase the H<sup>+</sup> 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<sup>-1</sup>. (pK<sub>b</sub> for  $NH_3 = 4.7$ , log 2 = 0.30)
- **Sol.**  $pOH = -\log K_b + \log \frac{[salt]}{[Base]}$

$$5 = 4.7 + \log \frac{a}{b} \Longrightarrow \frac{a}{b} = 2$$
$$a = 2b$$



# IONIC EQUILIBRIUM

Given a+b=0.32b+b=0.3

3b = 0.3

or b = 0.1 mole/L

Amount of base =  $0.1 \times 17 = 1.7$  g/L

 $\therefore$  a=0.2 mole/L

Amount of salt =  $0.2 \times 53.5 = 10.7$  g/L

Thus, [Salt] = 0.2 M and [Base] = 0.1 M

### • pH of Basic Buffer Solution

 $\begin{array}{c} \mathrm{NH_4OH} & \longrightarrow \mathrm{NH_4^+} + \mathrm{OH^-} \\ \mathrm{NH_4Cl} & \rightarrow \mathrm{NH_4^+} + \mathrm{Cl^-} \end{array}$ 

$$\mathbf{K}_{b} = \frac{\left[\mathbf{N}\mathbf{H}_{4}^{+}\right]\left[\mathbf{O}\mathbf{H}^{-}\right]}{\left[\mathbf{N}\mathbf{H}_{4}\mathbf{O}\mathbf{H}\right]}$$

$$\left[OH^{-}\right] = \frac{K_{b}\left[NH_{4}OH\right]}{\left[NH_{4}^{+}\right]} = \frac{K_{b}\left[Base\right]}{\left[Salt\right]}$$

 $(NH_4^+ mainly comes from salt)$ 

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.

 NH4OH
 :
 NH4Cl

 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

 $[NH_4OH] : [NH_4Cl] \quad i.e. [Salt] = [Base]$   $1 \qquad 1$   $pOH = pK_b + log \frac{1}{1}$   $pOH = pK_b \quad and \quad pH = 14 - pK_b$ 

Maximum buffer action because pH remains constant.



# **CHEMISTRY FOR JEE MAIN & ADVANCED**

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.



Ex. An organic base B has  $K_b$  value equal to  $1 \times 10^{-8}$ . 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.** 
$$B + H_2O_{\ddagger}^{\uparrow} \uparrow BH^+ + OH^-$$

$$K_{b} = \frac{[XH^{+}][OH^{-}]}{[B]} = 1 \times 10^{-8}$$

$$pOH = pK_{b} + \log \frac{[BH^{+}]}{[B]}$$

$$\Rightarrow 7 = -\log (10^{-8}) + \log \frac{[BH^{+}]}{[B]} \Rightarrow 7 = 8 + \log \frac{[BH^{+}]}{[B]}$$

$$\log \frac{[BH^{+}]}{[B]} = -1$$

$$\therefore \frac{[BH^{+}]}{[B]} = 10^{-1} = 0.1$$
Let, volume of HCl taken = xL
$$\therefore$$
 Volume of Base taken = (1 - x) L
After the reaction, millimole of BH^{+} formed = 0.01 \times (x)
Millimoles of base left = 0.01 (1 - 2x)

$$\frac{[BH^{+}]}{[B]} = \frac{x}{[1-2x]} = 0.1$$

 $\therefore x = 0.083 L = Volume of HCl$ 

 $\therefore$  Volume of base = 0.0917 L



(D)  $10 - \log 2$ 

# **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.

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 NH₄OH (mol L <sup>-1</sup> )		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  $NH_4OH = 0$ .

pOH will be maximum and so pH will be minimum.

- Ex. pH of a mixture containing 0.2 M X<sup>-</sup> (base) and 0.4 M HX with  $pK_b(X^-) = 4$  is :
- (A)  $4 + \log 2$  (B)  $4 \log 2$  (C)  $10 + \log 2$
- Sol. (D). HX  $\hat{\ddagger} \hat{\uparrow} \hat{\uparrow} H^+ + X^-, K_a = \frac{10^{-14}}{K_b} = 10^{-10}$

$$[\mathrm{H}^{+}] = \mathrm{K}_{\mathrm{a}} \frac{[\mathrm{HX}]}{[\mathrm{X}^{-}]} = \frac{10^{-10} \times 0.4}{0.2}$$

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  $0.3 = \log \left[\frac{(150 - x)}{x}\right]$  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  $25^{\circ}$ C is  $1.34 \times 10^{-5}$ .
- Sol. Using Henderson's expression

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

We get  $4.74 = -\log(1.34 \times 10^{-5}) + \log\frac{[\text{Salt}]}{0.02}$ 

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 
$$\frac{(0.01482 - 0.01) \text{molL}^{-1}}{(0.02 + 0.01) \text{molL}^{-1}}$$

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<sub>a</sub> of the acid.
- **Sol.** For complete neutralisation, meq. of acid = meq. of NaOH

					$= 25.06 \times$	2.506 = 3	3.612 meq	•
			HA	+ Na	a <mark>OH —</mark>	NaA +	H <sub>2</sub> O	
Initial			2.506	5 2.5	506	0	0	
At equi	ivalence	point	0	0		2.506	2.506	
Now 1.	253 meq.	of HCl ar	e added	l so,				
	NaA +	HCl –	→ 1	VaCl	+ HA			
	2.506	1.253		0	0	(Be	efore)	
	1.253	0	1	.253	1.253	(At	fter)	
Now m	Now mixture contains HA and NaA so it will be Acidic buffer,							
$\mathbf{pH} = \mathbf{pK} + \log \frac{[Salt]}{[Salt]} = \mathbf{pK} + \log \left(\frac{1.253}{[Salt]}\right)$								

$$pH = pK_a + \log \frac{[Sall]}{[Acid]} = pK_a + \log \left(\frac{1.253}{1.253}\right)$$
$$pH = pK_a$$
$$K_a = antilog (-4.92)$$
$$K_a = 1.2 \times 10^{-5}$$

or or or

# 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 M $\leq$ S $\leq$ 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<sub>2</sub>, Hg<sub>2</sub>Cl<sub>2</sub>, PbSO<sub>4</sub>, Ag<sub>2</sub>CO<sub>3</sub>, CaSO<sub>4</sub>, AgCN, etc.

### **Process of Dissolution of Sparingly Soluble Salts**

Let  $AB \longrightarrow Sparingly Soluble Salt$ 

$$AB(s) \xrightarrow[Precipitation]{\text{dissolution}} A^{\oplus}(aq) + B^{\Theta}(aq)$$

Initially,

rate of dissociation > rate of ppt.

... 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<sub>sn</sub>)

For a saturated solution,

$$AB f A^{\oplus} + B^{\ominus}$$

 $r_{eq.} = \frac{[A^+][B^-]}{[AB]}$  [Q concentration of solid is constant]

1

$$\therefore \underbrace{\text{Keq. [AB]}}_{\Psi} = [A^+] [B$$

$$\underbrace{\text{Ksp}}_{\Psi} = [A^+] [B^-]$$



Solubility product (K<sub>sp</sub>) 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

$$AB(s) f A^{+}(aq) + B^{-}(aq)$$

$$s s$$

$$K_{sp} = [A^{+}] [B^{-}] = s^{2}$$

$$s = \sqrt{K_{sp}}$$

(b) A<sub>2</sub>B Type Salt

$$A_2B(s) f = 2A^+(aq) + B^-(aq)$$
  
 $2s = s$   
 $K_{sp} = [A^+]^2[B^-] = [2s]^2[s] = 4s^3$   
 $K_{sp} = 4s^3$ 

(c) AB<sub>3</sub> Type Salt

$$AB_{3}(s) f A^{3+}(aq) + 3B^{-}(aq)$$
  
s 3s  
 $K_{sp} = [s][3s]^{3} = 27s^{4}$ 

(d) A,B, Type Salt

$$A_{2}B_{3}(s) f 2A^{3+}(aq) + 3B^{2-}(aq)$$

$$2s 3s$$

$$K_{sp} = [2s]^{2}[3s]^{3}$$

$$K_{sp} = 108 s^{5}$$

(e) AxBy Type Salt

AxBy 
$$f = xA^{y^+} + yB^{x^-}$$
  
xs ys  
 $K_{sp} = (xs)^x (ys)^y$   
 $K_{sp} = x^x \cdot y^y \cdot s^{x^+y}$ 

Following examples will illustrate the different type of solubilities and the effects of different factors or situation on solubility of a salt.

 $\therefore$  k<sub>sp</sub> = (xs)<sup>x</sup> (ys)<sup>y</sup> = x<sup>x</sup>, y<sup>y</sup>.(s)<sup>x+y</sup>

**Simple Solubility** 

Let the salt is  $A_x B_y$ , in solution in water, let the solubility in  $H_2O =$ 's' M, then

$$A_{x}B_{y} \stackrel{2}{+} \stackrel{2}{} xA^{y+} + yB^{-x}$$

xs ys

**Ex.** Calculate  $k_{sp}$  of Li<sub>3</sub>Na<sub>3</sub>[AlF<sub>6</sub>]<sub>2</sub>

**Sol.**  $k_{sp} = 3^3 \cdot 3^3 \cdot 2^2 \cdot (s)^8 = 3^6 \cdot 4 \cdot (s)^8 = 2916 \cdot s^8$ 

**Self Practice Problem** 

Ex. Calculate  $k_{sp}$  of Mg<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> Sol. 108 s<sup>5</sup>



# **Solubility in Different Solutions**

### Solubility in Presence of Common - Ion

Because of the presence of common ion the solubility of the salt decreases

- Calculate solubility of silver oxalate in 10<sup>-2</sup>M Potassium oxalate solution given that k<sub>s</sub> of silver oxalate Ex.  $= 10^{-10}$
- $[oxalate] = 10^{-2} + x$ , where x is the solubility of silver oxalate, this can be neglected in comparison to Sol.  $10^{-2}$ . so

$$k_{sp} = 10^{-10} = 10^{-2} \times (2x)^2 \implies \frac{10^{-8}}{2 \times 2} = x^2 \implies x = 5 \times 10^{-5}$$

### **Self Practice Problem**

Calculate the solubility of BaCl<sub>2</sub> in presence of 'c' mol/litre NaCl in terms of K<sub>sp</sub>(BaCl<sub>2</sub>). Ex.  $K_{sn}/c^2$ 

Sol.

### **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<sup>-1</sup>

$$AB(s) f A^{+}(aq) + B^{-}(aq)$$
$$x + y x$$

$$K_{sn1} = x(x+y)$$

Simultaneously solubility of AC be y mol  $L^{-1}$ Δ

$$AC(s) f A^+(aq) + C^-(aq)$$

y

 $K_{sp2} = y(x+y)$ 

Solving

$$x + y = \sqrt{K_{sp1} + K_{sp2}}$$
 and  
$$\frac{x}{y} = \frac{K_{sp1}}{K_{sp2}}$$

# **Self Practice Problem**

- Calculate solubility of BaSO<sub>4</sub> when BaSO<sub>4</sub> and CaSO<sub>4</sub> are dissolved in water simultaneously Ex.  $K_{sp}CaSO_4 = p, K_{sp}BaSO_4 = q$  and solubility of  $CaSO_4$  is 'b' mol/litre.
- Sol. bq/p
- Calculate simultaneous solubility of silverthiocyanate and sliver bromide in water given that k<sub>sp</sub> of silver thiocyanate Ex. =  $10^{-12}$  and k<sub>sp</sub> of silver bromide =  $5 \times 10^{-13}$  respectively.
- Let the solubility of AgSCN be x and that of AgBr is y, then Sol.

 $AgSCN \ddagger \uparrow \uparrow Ag^+ + SCN^ AgBr \ddagger \hat{\uparrow} Ag^+ + Br$ x + y = yx + y = x $10^{-12} = x(x+y)$ .....(i)  $5 \times 10^{-13} = y(x + y)$ ..... (ii) On solving we get, x = 2ySo  $y = 4.08 \times 10^{-7}$  and  $x = 8.16 \times 10^{-7}$ 



# **CHEMISTRY FOR JEE MAIN & ADVANCED**

- Ex. 50 mL of 0.02 M solution of Ca(NO<sub>3</sub>)<sub>2</sub> is added to 150 mL of 0.08 M solution of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>. Predict whether CaSO<sub>4</sub> will be precipitated or not,  $K_{sp}$ (CaSO<sub>4</sub>) = 4 × 10<sup>-5</sup>.
- 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 =  $5 \times 10^{-3} \text{ mol } L^{-1}$ Since  $Ca(NO_3)_2$  is completely ionized,  $[Ca^{2^+}] = [Ca(NO_3)_2] = 5 \times 10^{-3} \text{ mol } L^{-1}$ Calculation of  $SO_4^{2^-}$  ion concentration Applying  $M'_1V'_1 = M'_2V'_2$  $\therefore 0.08 \times 150 = M'_2 \times 200$

$$\therefore M_2' = \frac{0.08 \times 150}{200} = 6 \times 10^{-2} \,\mathrm{M}$$

 $\therefore [(NH_4)_2SO_4] \text{ is completely ionized, } [SO_4^{2-}] = [(NH_4)_2SO_4] = 6 \times 10^{-2} \text{ mol/L}$ Ionic product =  $[Ca^{2+}] [SO_4^{2-}] = [5 \times 10^{-3}] [6 \times 10^{-2}] = 3 \times 10^{-4}$ Since Ionic product  $(3 \times 10^{-4})$  is greater than solubility product of  $CaSO_4 (4 \times 10^{-5})$ , 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.**  $\operatorname{CaSO}_4(\operatorname{aq}) \stackrel{\circ}{\ddagger} \stackrel{\wedge}{\uparrow} \operatorname{Ca}^{2+}(\operatorname{aq}) + \operatorname{SO}_4^{2-}(\operatorname{aq})$

If S is the solubility of CaSO<sub>4</sub> in moles L<sup>-1</sup>  

$$K_{sp} = [Ca^{2+}] \times [SO_4^{2-}] = S^2$$
  
 $\therefore S = \sqrt{K_{sp}} = \sqrt{9.0 \times 10^{-6}}$   
 $= 3 \times 10^{-3} \text{ mol } L^{-1}$   
 $= 3 \times 10^{-3} \times 136 \text{ g } L^{-1} = 0.408 \text{ g} L^{-1}$   
For dissolving 0.408 g of CaSO<sub>4</sub> water required = 1 L

:. For dissolving 1g CaSO<sub>4</sub> 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 =  $26.6 \times 0.1 = 2.66$ 

Now for partial neutralization of acid

	HA +	BOH	$\rightarrow$ 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.

pH =  $-\log K_a + \log \frac{[Salt]}{[Acid]}$  or  $3 = -\log K_a + \log \frac{[1.2]}{[1.46]}$  $K_a = 8.219 \times 10^{-4}$ 



- Ex. Calculate simultaneous solubility of AgCNS and AgBr in a solution of water.  $K_{sp}$  of AgBr =  $25 \times 10^{-13}$  and  $K_{sp}$  of AgCNS =  $5 \times 10^{-12}$ .
- **Sol.** Let solubility of AgCNS and AgBr in a solution be a and b mol litre<sup>-1</sup> respectively.



Ex.

Sol.

# **CHEMISTRY FOR JEE MAIN & ADVANCED**

Ex. Calculate the  $[OH^-]$  of a solution after 50 mL of 0.2 M MgCl<sub>2</sub> is added to 500 mL of 0.4 M NaOH. K<sub>sp</sub> of Mg(OH)<sub>2</sub> is  $1.2 \times 10^{-11}$ .

Sol.		MgCl <sub>2</sub>	+ 2NaOH	$\rightarrow$ Mg(OH) <sub>2</sub> +	2NaCl
	m mole before reaction	10	20	0	0
		0	0	10	20

Thus, 10 m mole of Mg(OH)<sub>2</sub> 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)<sub>2</sub>. Now solubility (S) of Mg(OH)<sub>2</sub> can be derived by

$$K_{sp} = 4S^3$$

$$\therefore$$
 S =  $\sqrt[3]{K_{sp}} = \sqrt[3]{1.2 \times 10^{-11}} = 1.4 \times 10^{-4} M$ 

$$\therefore$$
 [OH<sup>-</sup>] = 2S = 2.8 × 10<sup>-4</sup> M

Ex. Will a precipitate of Mg(OH)<sub>2</sub> be formed in a 0.002 M solution of Mg(NO<sub>3</sub>)<sub>2</sub>, if the pH of solution is adjusted to 9 ? K<sub>sp</sub> of Mg(OH)<sub>2</sub> =  $8.9 \times 10^{-12}$ .

**Sol.** 
$$pH=9$$

$$\therefore$$
 [H<sup>+</sup>] = 10<sup>-9</sup> M

or  $[OH^{-}] = 10^{-5} M$ 

Now if Mg(NO<sub>3</sub>)<sub>2</sub> 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<sub>sp</sub> of Mg(OH)<sub>2</sub> i.e,  $8.9 \times 10^{-12}$ 

 $\therefore$  Mg(OH)<sub>2</sub> will not precipitate.

### 80 Condition of Precipitation

- ا For precipitation ionic product [IP] should be greater than solubility product k
- Ex. You are given  $10^{-5}$  M NaCl solution and  $10^{-8}$  M AgNO<sub>3</sub> 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<sub>3</sub> 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.

# 8 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<sup>+</sup> ion concentration remains same and hence,

solubility of AgCN in buffer solution can be calculated as  $\frac{K_{sp}}{K_a} = \frac{s^2}{[H^+]_{buffer}}$ .

 $\bigotimes$  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  $H_2S(0.1 \text{ M})$  to precipitate CdS but not ZnS, if  $[Cd^{2+}] = [Zn^{2+}] = 0.1$  initially ?

 $K_{sp} = (ZnS) = 1 \times 10^{-21}$  $K_s = (H_2S) = 1.1 \times 10^{-21}$ 

Sol. In order to prevent precipitation of ZnS

$$\begin{split} & [Zn^{2^+}] \, [S^{2^-}] < K_{sp}(ZnS) = 1 \times 10^{-21} \\ & (\text{ionic product}) \\ & \text{or} \quad (0.1) \, [S^{2^-}] < 1 \times 10^{-21} \\ & \text{or} \quad [S^{2^-}] < 1 \times 10^{-20} \end{split}$$

This is the maximum value of  $[S^{2-}]$  before ZnS will precipitate. Let  $[H^+]$  to maintain this  $[S^{2-}]$  be x. Thus for

$$H_{2}S_{1}^{+} \rightarrow 2H^{+} + S^{2-}$$

$$K_{a} = \frac{[H^{+}]^{2}[S^{2-}]}{[H_{2}S]} = \frac{x^{2}(1 \times 10^{-20})}{0.1}$$
$$= 1.1 \times 10^{-21}$$

or  $x = [H^+] = 0.1 M$ 

 $\therefore$  No ZnS will precipitate at a concentration of H<sup>+</sup> greater than 0.1 M

# 80 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



 $[Cu(NH_3)_4]^{2+}$ 





### Ex.

$$\operatorname{Cu}^{2+}(\operatorname{aq}) + 4\operatorname{NH}_{3}(\operatorname{aq}) \rightleftharpoons [\operatorname{Cu}(\operatorname{NH}_{3})_{4}]^{2+}$$

$$K_{stab} / K_{f} = \frac{[Cu(NH_{3})_{4}^{2^{+}}]}{[Cu^{2^{+}}][NH_{3}]^{4}}$$

Higher is the value of  $K_f/K_{stab}$ , more stable will be the complex and vice-versa.

$$\left[\operatorname{Cu}(\operatorname{NH}_{3})_{4}\right]^{2^{+}} \stackrel{K_{\operatorname{instant}}}{=} \operatorname{Cu}^{2^{+}} + 4\operatorname{NH}_{3}$$

$$\therefore \quad \mathbf{K}_{\text{stab}} \,/\, \mathbf{K}_{\text{f}} = \frac{1}{\mathbf{K}_{\text{instant}}}$$

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  $4 \times 10^{-3} M Ag^+$  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,  $1.8 \times 10^{-10} = [Ag^+][Cl^-]$ 

$$[\mathrm{Ag}^+] = \frac{1.8 \times 10^{-10}}{0.001} = 1.8 \times 10^{-7} \mathrm{M},$$

This quantity is so small that almost all the  $Ag^+$  ion will be consumed.

$$Ag^{+} + 2NH_{3} \ddagger \uparrow \uparrow \uparrow [Ag(NH_{3})_{2}]^{+} K = \frac{10^{8}}{6}$$
  
 $4 \times 10^{-3}$  b 0

$$1.8 \times 10^{-7} \qquad (b - 8 \times 10^{-3}) \qquad 4 \times 10^{-3} \qquad K = \frac{10^8}{6} = \frac{4 \times 10^{-3}}{1.8 \times 10^{-7} \times (b - 8 \times 10^{-3})^2} \implies b = 0.0445$$

**Ex.** The solubility of  $Mg(OH)_2$  is increased by addition of  $NH_4^+$  ion. Find

(i)  $K_c$  for the reaction

For the reaction

$$Mg(OH)_{2} + 2NH_{4}^{+} \stackrel{2}{\uparrow} \stackrel{2}{\uparrow} \stackrel{2}{\to} 2NH_{3} + 2H_{2}O + Mg^{2+}$$

(ii) Calculate solubility of Mg(OH), 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)

$$Mg(OH)_{2} + 2NH_{4}^{+} \stackrel{2}{T} \stackrel{2}{} \stackrel{2}{T} \frac{2}{T} + 2H_{2}O + Mg^{2+}$$

Also for the reaction



$$NH_3 + H_2O$$
  $\ddagger \uparrow \uparrow NH_4^+ + OH^-$ 

[As water is in large excess in both the cases]

Now, 
$$K_{c} \times K_{b}^{2} = \frac{[NH_{3}]^{2}[Mg^{2+}]}{[NH_{4}^{+}]^{2}} \times \frac{[NH_{4}^{+}]^{2}[OH^{-}]^{2}}{[NH_{3}]^{2}}$$
  
=  $[Mg^{+2}] [OH^{-}]^{2} = K_{sp[Mg(OH)]b}$ 

$$\therefore \qquad K_{c} = \frac{K_{sp}}{K_{b}^{2}} = \frac{10^{-11}}{(1.8 \times 10^{-5})^{2}} = 3.08 \times 10^{-2}$$

(ii) Now, let us, assume that 'a' moles of Mg(OH), be dissolved in presence of 
$$0.5 \text{ M NH}_4\text{Cl}$$
.

$$\therefore \qquad K_{c} = \frac{a \times (2a)^{2}}{(0.5 - 2a)^{2}} \approx \frac{4a^{3}}{0.25} = 3.08 \times 10^{-2}$$
  
or a = 0.124 M

Ex. 0.10 mol sample of AgNO<sub>3</sub> is dissolved in one litre of 2.00 M NH<sub>3</sub>. 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. 
$$Ag^+ + 2NH_3 \stackrel{*}{\downarrow} \stackrel{*}{\to} \stackrel{*}{\neq} [Ag(NH_3)_2^+]$$
  
 $0.10 M 2.00 0$   
 $0.10-0.10 (2-0.20 M) 0.10 M$   
 $= 0 = 1.80 M$ 

It is assumed that all Ag<sup>+</sup> ions have been complexed and only x amount is left

$$K_{f} = \frac{[Ag(NH_{3})_{2}^{+}]}{[Ag^{+}][NH_{3}]^{2}} \Longrightarrow 1.6 \times 10^{7} = \frac{0.10}{x(1.80)^{2}}$$

 $x = 1.93 \times 10^{-9} M = [Ag^+]$  undisolved

$$[C1^{-}] = 1.0 \times 10^{-2} M$$

$$[Ag^+] [CI^-] = 1.93 \times 10^{-9} \times 1.0 \times 10^{-2} = 1.93 \times 10^{-11} < 1.8 \times 10^{-10} [K_{sp(AgCI)}]$$
  
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  $(K_{sp} = 6.25 \times 10^{-10} \text{ and its molecular mass is } 128)$ :

(A) 0.0064 g (B) 0.0128 g (C) 0.0032 g (D) 0.0640 gSol. (C)  $[Ca^{2+}][C_2O_4^{-2-}] = 6.25 \times 10^{-10} \text{ so solubility} = 2.5 \times 10^{-5} \text{ mol/L} = 2.5 \times 128 \times 10^{-5} = 3.2 \times 10^{-3} \text{ g/L}$ 

# **CHEMISTRY FOR JEE MAIN & ADVANCED**

Ex	Select the sulphides which has maximum solubility in water?						
	(A) CdS (K <sub>sn</sub>	$=36 \times 10^{-30}$ )		<b>(B)</b> FeS $(K_{sn} = 11)$	× 10 <sup>-20</sup> )		
	(C) HgS (K <sub>sp</sub>	$=32 \times 10^{-54}$ )		( <b>D</b> ) ZnS ( $K_{sp} = 11$	× 10 <sup>-22</sup> )		
Sol.	(B)			sh			
	All salt are A	B type so solul	bility will be $\sqrt{\mathrm{K}_{\mathrm{sp}}}$ . Hig	ther the value of $K_{sp}^{}$ , the	e maximum will be solubility.		
Ex.	If equal volu	mes of the foll	owing solutions are add	ed, precipitation of Ag	CI		
	$(K_{sp} = 1.8 \times 1)$	$0^{-10}$ ) will occur	only with.				
	(A) $10^{-4}$ M (A)	$({ m Ag}^{+})$ and $10^{-4}$ M	ſ (Cl⁻)	<b>(B)</b> $10^{-5}$ M (Ag <sup>+</sup> ) a	and $10^{-5} \mathrm{M}(\mathrm{Cl}^{-})$		
	<b>(C)</b> 10 <sup>-6</sup> M (A	$({ m Ag}^{+})$ and $10^{-6}$ M	ſ (Cl <sup>−</sup> )	<b>(D)</b> $10^{-10}$ M (Ag <sup>+</sup> )	and $10^{-10} \mathrm{M}(\mathrm{Cl}^{-})$		
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, afte	r the dissolution of a sp	paringly soluble salt, then -		
	(A) solubility	y of salt decrea	ises.	(B) solubility of s	(B) solubility of salt increases		
	(C) there wil	l be no effect o	on solubility	(D) question is at	osurd		
Sol.	<b>(B)</b>						
	Dissolution e	equilibria shift	towards right side due	to hydrolysis of cation	or anion.		
Ex.	What is the c that is 0.01 N	oncentration of AgNO <sub>3</sub> , 0.01	$fAg^+$ ions in 0.01 M AgN M NaCl and 1 M NH <sub>3</sub> ?	$\mathrm{NO}_3$ that is also 1.0 M N	H <sub>3</sub> ? Will AgCl precipitate from a solution		
	$K_{d}(Ag[NH_{3}]_{2}^{+}) = 5.88 \times 10^{-8};$						
	$K_{sp}(AgCl) = 1$	$1.8 \times 10^{-10}$ .					
Sol.	Let us first as dissociation.	ssume that 0.0	1 M AgNO <sub>3</sub> shall combi	ine with 0.02 $NH_3$ to for	rm 0.01 M Ag(NH <sub>3</sub> ) $_{2}^{+}$ and the consider its		
	AgNO <sub>3</sub>	+	$2NH_3 \longrightarrow$	$Ag(NH_3)_2^+$	Initial conc.		
	0.01 M		1 M	0			
	0		(1-0.02)=0.98M	0.01 M	at eq. conc.		
	Ag(NH <sub>2</sub> ), <sup>+</sup>	î ^ ∕ <b>*</b>	$Ag^+$ + 2NH.		-		
	(0.01 - x)	+	x = (0.98 + 2x)	c)			
	= 0.01  M		≈ 0.98 M	•) ·			
	0.01		Fauib	conc			
	Since x <<<	1	Lquio.	conc.			
	$K_{d} = \frac{[Ag^{+}][1]}{[Ag(N)]}$	$\frac{\mathrm{NH}_{3}]^{2}}{\mathrm{H}_{3})^{+}_{2}} = 5.88 \times$	10 <sup>-8</sup>				
	$\therefore [Ag^+] = \frac{5}{2}$	$\therefore [Ag^+] = \frac{5.88 \times 10^{-8} \times 0.01}{(0.98)^2} = 6.12 \times 10^{-10} \mathrm{M}$					
	Further, ionic product of AgCl = $[Ag^+][Cl^-] = (6.12 \times 10^{-10})(0.01) = 6.12 \times 10^{-12}$						
	Because the	ionic product i	s smaller than $K_{-} = 1.8$	$\times 10^{-10}$ , no precipitate s	hould form.		
		•	sp	· <b>. 1</b>			
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### **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<sup>+</sup> ions and pink coloured anions.

HPh  $\longrightarrow$  H<sup>+</sup> + Ph<sup>-</sup> Colourless Pink

- 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<sup>+</sup> and the solution remains colourless.

 $HPh \Longrightarrow H^+ + Ph^-$ 

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

 In alkaline medium, the OH<sup>-</sup> ions combine with H<sup>+</sup> ions of the indicator to form water. HPh === H<sup>+</sup> + Ph<sup>-</sup>

 $NaOH \longrightarrow Na^{+} + OH^{-}$ 

Thus Ph<sup>-</sup> ions gives pink colour in alkaline medium.

### (ii) Methyl Orange (MeOH) :- It is a weak base and dissociates as :-

 $MeOH \Longrightarrow Me^+ + OH^-$ 

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<sup>-</sup> and the solution remains yellow.

```
MeOH \Longrightarrow 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.

 $MeOH \Longrightarrow Me^+ + OH^-$ 

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

# **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)

(b) For Phenolphthalein





Colourless benzenoid form (in Acid)

Red quinonoid form (in Alkali)

Red quinonoid form (in acids)

# **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<sup>3</sup> of 0.1 M HCl with 0.1 M NaOH.

 $NaOH(aq) + HCl(aq) \longrightarrow NaCl(aq) + H_2O(\bullet)$ 

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  $49.8 \text{ cm}^3$  of 0.1 M NaOH solution have been added. The pH suddenly changes to 10 after addition of  $50.1 \text{ cm}^3$  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.





# TITRATION OF STRONG ACID AGAINST WEAK ALKALI

The graph (B) shows how pH changes during titration of 50 cm<sup>3</sup> of 0.1 M HCl with 0.1 M NH<sub>3</sub>.

 $HCl(aq) + NH_4OH(aq) \longrightarrow NH_4Cl(aq) + H_2O(\bullet)$ 

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<sup>3</sup> of 0.1 M CH<sub>3</sub>COOH with 0.1 M NaOH.

 $CH_3COOH(aq) + NaOH(aq) \longrightarrow CH_3COONa(aq) + H_2O(\bullet)$ 

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<sup>3</sup> of 0.1 M CH<sub>3</sub>COOH with 0.1 M NH<sub>3</sub>.

 $CH_{3}COOH(aq) + NH_{4}OH(aq) \longrightarrow CH_{3}COONH_{4}(aq) + H_{2}O(\bullet)$ 

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.



# **CHEMISTRY FOR JEE MAIN & ADVANCED**

Indicator	pH range	Colour change	pK <sub>a</sub> Neutral colour pH
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  $\hat{\ddagger} \hat{\uparrow} \hat{\uparrow} H^+ + BPh^-$ 
  - $K_a = \frac{[H^+][BPh^-]}{[HBPh]}$ , when  $BPh^- = HBPh$ , indicator will work. Thus
  - $[H^+] = 6.84 \times 10^{-6}$
  - $\therefore pH = 5.165$
  - Also if pH = 5.84
  - or  $[H^+] = 1.44 \times 10^{-6}$ , then

 $K_{a} = \frac{[H^{+}][BPh^{-}]}{[HBPh]} \text{ or } 6.84 \times 10^{-6} = \frac{1.44 \times 10^{-6}.C\alpha}{C(1-\alpha)} \text{ or } \alpha = 0.83 \text{ or } 83 \%$ 



- 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<sub>2</sub>SO<sub>4</sub>, NaCl, KNO<sub>3</sub> 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<sub>4</sub>OH, CH<sub>3</sub>COOH etc.
- 3. Degree of dissociation :- The fraction of the total amount of an electrolyte which dissociates into ions is called the degree of dissociation ( $\alpha$ ),

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<sup>+</sup> ions in the aqueous solution whereas a base is a substance which gives OH<sup>-</sup> 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 :  $NH_3$ , ROH,  $H_2O$  : etc. (ii) All

negative ions like F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, l<sup>-</sup>, OH<sup>-</sup> etc.

### **Types of Lewis Acids**

- (i) Molecules having central atom with incomplete octet e.g. BF<sub>3</sub>, AlCl<sub>3</sub> 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  $\alpha$  as the degree of dissociation,

$$K_a = \frac{C\alpha^2}{1-\alpha} \approx C\alpha^2$$
 or  $\alpha = \sqrt{K_a / C} = \sqrt{K_a V}$ 

- 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  $25^{\circ}C = 10^{-14}$
- **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, 
$$K_{sn} = [Ag^+] [Cl^-]$$
, for  $Ca_3(PO_4)_2$ ,  $K_{sn} = [Ca^{2+}]^3 [PO_4^{3-}]^2$  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<sup>-</sup> 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

$$pOH = pK_b + log \frac{[Salt]}{[Base]}$$
 and then  $pH = 14 - pOH$ 

- 17. Buffer capacity =  $\frac{\text{No. of moles of the acid or base added to l litre of buffer}}{\text{Change in pH}} = \frac{n}{\Delta pH}$
- **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  $H_2CO_3 + NaHCO_3$ .









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# IONIC EQUILIBRIUM