Ionic Equilibrium-I

Introduction :

Here we deal with the equilibria of species wich are ionic in nature. Generally the concentration of H^+ and OH^- ions is of importance. Also the concentration of ions forming precipitates is focused upon. As like dissolves like, the solvent for production of these ions should be polar. It is generally water.

Table-1









D2: Arrhenius Base : Substance which gives OH- ion from its own molecule on dissolving in an ionising solvent.

Eg : NaOH, Ba(OH)₂, NH₄OH etc.

Table-3



O OH⁻ ion also exists in hydrated form of H₃O₂⁻, H₂O₄⁻, H₅O₃⁻.

- O First group elements of modern periodic table (except Li) form strong bases.
- O Insoluble hydroxides like Fe(OH)₃, Mg(OH)₂, Cr(OH)₃.

Bronsted-Lowry concept (Conjugate acid-base concept / Protonic concept)

D3: Bronsted Lowry Acid : Species which donate H⁺ are Bronsted Lowry acids (H⁺ donor).

D4: Bronsted Lowry Base : Species which accept H⁺ are Bronsted Lowry bases (H⁺ acceptor).



Conjugated acid-base pairs : In a typical acid-base reaction,

Forward reaction : Here HX, being a proton donor is an acid. Here HB, being a proton acceptor is a base

Backward reaction : Here HB⁺, being a proton donor is an acid. Here X⁻, being a proton acceptor is a base.

Acid	Base	Conjugate acidConjugate base			
HCI +	H ₂ O	\rightarrow	H₃O+	+	CI⁻
HSO₄⁻ +	NH₃	\rightarrow	NH_{4}^{+}	+	SO4 ²⁻
[Fe(H ₂ O) ₆] ³⁺ +	H ₂ O	\rightarrow	H₃O+	+	[Fe(H ₂ O) ₅ (OH)] ²⁺

O Conjugate acid-base pair differ by only one proton (H⁺).

O Strong acid will have weak conjugate base. This can be explained as the strong electrolyte will move the equilibrium where it is in dissociated form.

O Weak acid/base will also have weak conjugate base/acid, because weak electrolyte has tendency to be in undissociated form.

O Reaction will always proceed in a direction from stronger acid to weaker acid or from stronger base to weak base.

	Table-4	Some Acid-Base Conjugate Pairs				
	Acid	Conjugate base = A	Acid – H⁺	Base	Conjugate acid = Base + H [⁺]	
Increasing Acidic Strength	Table-4 Acid HClO ₄ HI HBr H ₂ SO ₄ HCl HNO ₃ H ₃ O ⁺ HSO ₄ ⁻ HNO ₂ H ₃ PO ₄ CH ₃ COOH H ₂ CO ₃ H ₂ S NH ₄ ⁺ HCN C ₉ H ₅ OH H ₂ O	Some Acid-Base Conjugate base = A CIO ₄ ⁻ I ⁻ Br ⁻ HSO ₄ ⁻ CI ⁻ NO ₃ ⁻ H ₂ O SO ₄ ²⁻ NO ₂ ⁻ H ₂ PO ₄ ⁻ CH ₃ COO ⁻ HCO ₃ ⁻ HS ⁻ NH ₃ CN C ₈ H ₅ O ⁻ OH	Conjugat Acid – H ⁺	The Pairs Base H_2O C_2H_6OH $NH_3 \text{ or } NH_3.H_2$ $R-NH_2$ CN^- $C_6H_5O^-$ NH_2^- CH_3^-	Conjugate acid = Base + H [*] H_3O^{+} $C_2H_6OH_2$ O NH4 ⁺ R-NH3 ⁺ HCN C_6H_5OH NH3 CH4	
	C_2H_5OH NH $_3$ CH $_4$	C₂H₅O [−] NH₂ CH₃ [−]	Ļ			

Note : In polyprotic acids, the tendency of release of subsequent H⁺ decreases. Eg : Order of acidic strength: $H_3PO_4 > H_2PO_4^- > HPO_4^{2-}$.

D5 : Amphiprotic/Amphoteric Species : Species which can act as an acid as well as a base. Eg : H_2O , NH_3 .

HCl + H₂O \implies H₃O⁺ + Cl⁻ (H₂O acting as base)

 $\begin{array}{ll} NH_3 + H_2O & \longrightarrow \\ NH_4^+ + OH^- & (H_2O \mbox{ acting as acid}; \mbox{ NH}_3 \mbox{ acting as base}) \\ NH_3 + CH_{3^-} & \longrightarrow \\ NH_2^- + CH_4 & (NH_3 \mbox{ acting as acid}) \end{array}$

Lewis Concept (Electronic Concept)

D6: Lewis Acid : An Lewis acid is a species which can accept an electron pair with the formation of coordinate bond.

Acid \leftarrow Electron pair donor \Rightarrow **Acid** : Electron pair acceptor. eg : Electron deficient molecules : BF₃, AlCl₃, H₃BO₃, BeCl₂

Cations : H⁺, Fe³⁺, Na⁺

Molecules with vacant orbitals : SiCl₄, SO₂.

D7 : Lewis Base : A Lewis base is a species wich has a lone pair of electrons available for donation. Base \rightarrow Electron pair acceptor \Rightarrow Base : Electron pair donor

eg : Molecules with donatable lone pairs : NH_3 , $H_2 \ddot{O}$, $CH_3 \ddot{O}H$

lons : X⁻, CN⁻, OH⁻.

Note : (OH)₃B +

 \longrightarrow B(OH)^{Θ}₄ + H^{\oplus}

Here, Boric acid [i.e. B(OH)₃] accepts a lone pair. So, it is a lewis acid.

-Solved Examples -

Ex-1. In which direction will the following equilibria I and II proceed ?

 $I : H_2SO_4 (aq) + NH_3 (aq) \longrightarrow NH_4^+ (aq) + HSO_4^- (aq)$

II : $HCO_{3^{-}}(aq) + SO_{4^{2-}}(aq) \longrightarrow HSO_{4^{-}}(aq) + CO_{3^{2-}}(aq)$

- (A) I forward & II backward
- (C) Both forward

- (B) I backward & II forward
- (D) Both backward

Sol.	Equilibrium proceeds in the direction from strong (Acid/Base) to weak (Acid/Base).					
	Here, acidic strength is compared among the 2 acids in the reaction & basic strength is compared					
	among 2 bases in that reaction only. $WA + WB \longrightarrow SA + SB$					
• •						
Ans. (A	A)					
Ex-2.	For the given reaction, identify the true (T) & false (F) statements. $C_2H_5 \text{ NH}_2 + \text{HI} \implies (C_2H_5 \text{NH}_3)^+ \text{ I}^-$					
	S1: HI is bronsted base.					
	S ₂ : HI is bronsted acid. S ₃ : HI is arrhenius acid.					
	S ₄ : HI is lewis acid.					
	S ₅ : HI is arrhenius base. S ₆ : HI is lewis base.					
	(A) TFFFTT (B) FTTTFF (C) FTTFFF (D) TFFFTF					
Sol.	HI has donated H ⁺ in the above reaction. So it acts as an Arrhenius acid as well as a Bronsted acid.					
Ev_2	In the above question, identify the true (T) & false (E) statements if H is replaced with CaH-NHa in each					
LA-J.	statement.					
Sol	(A) TFFFTT (B) TFFFFT (C) FFTTFF (D) FTTTFF					
501.	Bronsted base accepts H ⁺ from a species. Annual as a species of the species of					
Ex-4.	Ammonium ion is :					
0.1	(A) Lewis acid (B) Lewis base (C) Bronsted acid (D) Bronsted base					
501.	$N \Pi 4' \longrightarrow N \Pi 3 + \Pi' \Rightarrow$ Bronsted Acid Ans. (C)					
Ex-5.	In which of the following reactions, does NH_3 act as an acid?					
	(C) NH ₃ + HCl \longrightarrow NH ₄ Cl (D) None, as NH ₃ is a base					
Sol.	In the reaction, NH_3 changes to NH_2^- . So, NH_3 has donated a proton (H ⁺) and hence acts as an acid.					
	Ans. (B)					
Ex-6.	Sulphanilic acid is a/an : (A) Arrhenius acid (B) Lewis base (C) Neither (A) or (B) (D) Both (A) & (B)					
	S_{PO_3H}					
Sol.	Sulphanilic acid is \bigcirc . Its –SO ₃ H group is capable of donating H ⁺ , and hence it acts as arrhenius					
	\uparrow					
	NH ₂ acid, while –NH2 group's pitrogen has lone pair of electron which can be donated as :					
	acid, write $-iNH_2$ group s nitrogen has ione pair of electron which can be donated as : SO ₃ H SO ₃ ⁻					
	$[0] \rightleftharpoons [0]$					
	Υ					
	NH_2 $\dot{N}H_3^+$					
	Ans. (D)					



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

So, pK_a of $H_2O = pK_b$ of $H_2O = -\log(1.8 \times 10^{-16}) = 15.74$ (at 25°C)

pH Scale :

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• Acidic strength means the tendency of an acid to give H_3O^+ or H^+ ions in water. So greater the tendency to give H^+ , more will be the acidic strength of the substance.

- O Basic strength means the tendency of a base to give OH⁻ ions in water.
 So greater the tendency to give OH⁻ ions, more will be basic strength of the substance.
- **D8**: The concentration of H⁺ ions is written in a simplified form introduced by Sorenson known as pH scale. pH is

defined as negative logarithm of activity of H⁺ ions.

- pH = $-\log a_{H^+}$ (where a_{H^+} is the activity of H⁺ ions)
- O Activity of H⁺ ions is the concentration of free H⁺ ions or H_3O^+ ions in a dilute solution.
- O The pH scale was marked from 0 to 14 with central point at 7 at 25°C taking water as solvent.

F2:
$$pH = -\log [H^+]$$
 or $pH = \log \frac{1}{[H^+]}$ or $pH = -\log [H_3O^+]$

F3:
$$pOH = -\log [OH^{-}]$$
 or $pOH = \log \frac{1}{[OH^{-}]}$

Der3: From, $K_w = [H^+] [OH^-] = 10^{-14}$ (at 25°C) Taking negative log both sides, $-\log [H^+] - \log [OH^-] = -\log (10^{-14}) = -\log k_w = 14$ $pH + pOH = pK_w = 14$ (for an aqueous solution at 25°C) \Rightarrow 0 If the temperature and the solvent are changed, the pH range of the scale will also change. For example : 0 – 14 at 25°C Neutral point pH = 70 – 13 at 80°C ($K_w = 10^{-13}$) Neutral point pH = 6.5Ο pH can also be negative or greater than 14. Ο $pH = -\log [H^+] = 7$ and $pOH = -\log [OH^-] = 7$, for water at 25°C (experimental) Now. pH = 7 = pOH \Rightarrow neutral at 25° C only pH < 7 or pOH > 7acidic \Rightarrow pH > 7 or pOH < 7 \Rightarrow basic

Autoprotolysis :

Some substances like HCOOH, NH₃ etc are observed to be self ionised in pure liquid state as follows : D9: $2HCOOH (\Box) \Longrightarrow HCOO^{-} + HCOOH_{2^{+}}$

This phenomena is called Self-Ionisation or Autoprotolysis and equilibrium constant corresponding to above is called Autoprotolysis constant defined as follows : $K_{eq} = [HCOO^{-}] [HCOOH_2^{+}]$

Relation between K_a and k_b for conjugate acid-base pair (C)

Der4: For any conjugate acid-base pair (HA & A⁻) in aqueous solution :

$$HA + H_2O \Longrightarrow A^- + H_3O^- \qquad : \qquad K_a = \frac{[H_3O^+][A^-]}{[HA]}$$
$$A^- + H_2O \Longrightarrow HA + OH^- \qquad : \qquad K_b = \frac{[HA][OH^-]}{[A^-]}$$

 $K_a \times K_b = K_w \implies pK_a + pK_b = pK_w = 14$ (at 25°C) Now

Eq. pK_a (CH₃COOH) + pK_b (CH₃COO⁻) = pK_w = 14 ; pK_a (NH₄⁺) + pK_b (NH₃) = pK_w = 14.

Degree of dissociation (α)

When an electrolyte is dissolved in a solvent (H₂O), it spontaneously dissociates into ions. Ο 0

It may dissociate partially ($\alpha < 1$) or sometimes completely ($\alpha \approx 1$)

Eq. NaCl + aq \implies Na⁺ (aq) + Cl⁻ (aq) $(\alpha \approx 1)$ $CH_3COOH + aq \implies CH_3COO^-(aq) + H^+(aq)$ $(\alpha < 1)$

D10: The degree of dissociation of an electrolyte (α) is the fraction of one mole of the electrolyte that has dissociated under the given conditions.

α = No. of moles taken initially

The value of $\boldsymbol{\alpha}$ depends on :

- **Nature of electrolyte:** Strong electrolytes dissociate completely ($\alpha = 1$) whereas weak (a) electrolytes dissociate partially. ($\alpha < 1$)
- Nature of solvent: A solvent having high value of dielectric constant will favour dissociation. (b) (Generally polar solvents)
- Dilution: For weak electrolytes, degree of dissociation will increase with dilution (Ostwald's (c) dilution law)
- (d) Temperature: On increasing temperature, generally degree of dissociation increases. (For endothermic dissociations)
- (e) Presence of other solute: When a substance is present in a solution, it may effect the dissociation of another substance. Generally, presence of common ion supresses degree of dissociation of weak electrolyte. (Common ion effect)

(D)	pH Calculation : Strong acid SolutioNs, strong base solutions, solutions containing mixture of two or more strong acids, solutions containing mixture of two or more strong bases, solutions containing mixture of strong acid and strong base				
		If [H+] from strong poid is greater than 10 ⁻⁶ M			
	(1)	In this case, H ⁺ ions coming from water can be neglected.			
F5 :		So, $[H^+]$ = Molarity of strong acid solution × number of H ⁺ ions per acid molecule.			
	(ii)	If [H ⁺]from strong acid is less than 10 ⁻⁶ M			
E6 ·		In this case, H^+ ions coming from water cannot be neglected. So $[H^+] = [H^+]$ from strong acid $\pm [H^+]$ coming from water in presence of this strong acid			
10.		So, $[11] = [11]$ from strong acid $+ [11]$ coming from water in presence of this strong acid.			
		olved Examples			
Ex-7.	Find the	e pH of :			
	(a) 10 ⁻³	M HNO ₃ solution			
	(b) 10 ⁻⁴	4 M H ₂ SO ₄ solution (Take log 2 = 0.3)			
Sol.	(a) pH :	$= -\log[H^+]_{HNO_3} = -\log(10^{-3}) = 3$			
	(b) pH =	$= -\log[H^+]_{H_2SO_4} = -\log(2 \times 10^{-4}) = 4 - \log 2 = 3.7$			
		In both solutions, $[H^+]_{\text{from strong acid}} > 10^{-6}$ M. So H ⁺ from water has not been considered.			
Ex-8.	Calcula	te pH of 10^{-8} M HCl solution at 25°C. (Take log 1.05 = 0.02)			
Sol.	Here, [l	$H^{+}_{ HC } = 10^{-8}$ M (< 10 ⁻⁶ M). So [H ⁺] from water has to be considered. But,			
	[H ⁺] _{from}	$H_{20} \neq 10^{-7}$ M because of common ion effect exerted on it by H ⁺ ions of HCI. So, considering			
	dissocia	ation of H ₂ O :			
		$H_2O \iff H^+ + OH^-$			
		$10^{-0} + XX$ K _w = [H+] [OH ⁻]			
		$10^{-14} = x(x + 10^{-8})$			
		$\Rightarrow x^2 + x \times 10^{-8} - 10^{-14} = 0$			
		$x = \frac{-10^{-8} \pm \sqrt{10^{-16} + 4x10^{-14}}}{100} = \frac{-10^{-8} + 10^{-7}\sqrt{4 + \frac{1}{100}}}{100} = \frac{(\sqrt{401} - 1)10^{-8}}{0.95 \times 10^{-7}}$			
		2 2 2 Itel 405 × 40 ⁻² 40 ⁻⁷ M			
		$[H^{+}] = 10.5 \times 10^{-6} = 1.05 \times 10^{-7} M$ $pH = 7 - \log 1.05 \sim 6.98$			
	Note :	For 10^{-9} M HCl pH ≈ 7 . For 10^{-12} M HCl pH ≈ 7			
	(1) 0/				
	(b) Stro	Dng base solution :			
	(1)	In this case. OH- ions coming from water can be neglected.			
F7 :		So, $[OH^-] = Molarity of strong base solution × number of OH- ions per base molecule.$			
	(ii)	If [OH ⁻]from strong base is less than 10 ⁻⁶ M			
-		In this case OH ⁻ ions coming from water cannot be neglected.			
F8:		So, $[OH^-] = [OH^-]$ from strong base + $[OH^-]$ coming from water in presence of this strong base.			
	S	olved Examples			
Examp	le-9.	What will be the pH of 5 × 10 ⁻⁶ M Ba(OH) ₂ solution at 25 ^o C ?			
Solutio	on.	$[OH^{-}]_{\text{from strong base}} = 2(5 \times 10^{-6}) = 10^{-5} \text{ M}$			
		∴ $pH = 14 - p(OH) = 14 - (-log [OH^-]) = 14 - (-log 10^{-5}) = 14 - 5 = 9$			
Examn	le-10.	Calculate pH of 10^{-7} M of NaOH solution at 25°C. (Take log 0.618= 0.21)			
Solutio	on.	$[OH^-]$ from NaOH = 10^{-7} M (< 10^{-6} M)			
		$[OH^{-}]$ from water = x (< 10 ⁻⁷ M ; due to common ion effect)			
		$H_2O \implies OH^- + H^+$			
		$- (x + 10^{-7}) x$			
		$N_{W} = [\Pi^{+}] [U\Pi^{-}] = 10^{-14} = X (X + 10^{-7})$			

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

⇒ $x = \frac{\sqrt{5} - 1}{2} \times 10^{-7} = 0.618 \times 10^{-7} \text{ M} = [\text{H}^{+}]$ ($\sqrt{5} = 2.236$)
∴ pH = 7.21

pH OF ACIDS/BASES MIXTURES :

Mixture of two strong acids : (A) If V₁ volume of a strong acid solution with H⁺ concentration $[H^+]_1$ is mixed with V₂ volume of another strong acid solution with H⁺ concentration [H⁺]₂, then moles of H⁺ ions from I-solution = M_1V_1 moles of H⁺ ions from II-solution = $M_2 V_2$ If final H⁺ ion concentration is $[H^+]_f$ and final volume is $V_f (= V_1 + V_2)$, then : $[H^+]_f V_f = [H^+]_1 V_1 + [H^+]_2 V_2$ [Dissociation equilibrium of none of these acids will be disturbed as both are strong acids] $[H^+]_f = \frac{[H^+]_1 V_1 + [H^+]_2 V_2}{V_1 + V_2}$ F9: ÷. Mixture of two strong bases : **(B)**

Similar to above calculation,

$$[OH^{-}]_{f} = \frac{[OH^{-}]_{1}V_{1} + [OH^{-}]_{2}V_{2}}{V_{1} + V_{2}} \qquad \& \qquad [H^{+}]_{f} = \frac{10^{-14}}{[OH^{-}]_{f}}$$

Ex-11. Calculate pH of mixture of (400 mL, $\frac{1}{200}$ M H₂SO₄) + (400 mL, $\frac{1}{100}$ M HCl) + (200 mL of water).

Take $\log 2 = 0.3$

Sol.

 \Rightarrow

F10:

$$[H^{+}]_{1}V_{1} = \frac{1}{100} \times \frac{400}{1000} = \frac{4}{1000}, \quad [H^{+}]_{2}V_{2} = \frac{4}{1000}, \quad H^{+} \text{ ions from water can be neglected}$$
$$[H^{+}]_{1}V_{1} + [H^{+}]_{2}V_{2} = 8 \times 10^{-3} \text{ and } V_{f} = 0.4 + 0.4 + 0.2 = 1 \text{ L}$$
$$[H^{+}]_{f} = \frac{8 \times 10^{-3}}{1} = 8 \times 10^{-3} \text{ M} \qquad \therefore \qquad \text{pH} = 3 - \log 8 = 2.1.$$

Ex-12. 500 mL of 10⁻⁵ M NaOH is mixed with 500 mL of 2.5 x 10⁻⁵ M of Ba(OH)₂. To the resulting solution, 99 L water is added. Calculate pH of final solution. Take log 0.303 = -0.52.

Sol.
$$[OH^{-}]_{f} = \frac{(500 \times 10^{-5}) + (500 \times 2 \times 2.5 \times 10^{-5})}{1000} = 3 \times 10^{-5} \text{ M}$$

 $V_f = 100 L$ $V_i = 1 L \&$

no. of moles of [OH-] in resulting solution = no. of moles of [OH-] in final

 $3 \times 10^{-5} = [OH^{-}]_{f} \times 100$ •:•

 $[OH^{-}]_{f} = 3 \times 10^{-7} \text{ M} (< 10^{-6} \text{ M})$

So, OH^{-} ions coming from H_2O should also be considered.

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

x (x + 3 × 10⁻⁷)
K_w = x (x + 3 × 10⁻⁷) = 10⁻¹⁴
∴ x = $\left(\frac{\sqrt{13} - 3}{2}\right) \times 10^{-7} \text{ M} = [\text{H}^+]$

 $pH = 7 - \log 0.303 = 7.52.$ So,

(C) Mixture of a strong acid and a strong base :

0 Acid Base neutralisation reaction will take place.

The solution will be acidic or basic, depending on which component has been taken in excess. \mathbf{O}

If V₁ volume of a strong acid solution with H⁺ concentration [H⁺] is mixed with V₂ volume of a strong Der5: base solution with OH⁻ concentration [OH⁻], then

Number of moles H⁺ ions from I-solution = $[H^+]_1V_1$ Number of moles OH^{-1} ions from II-solution = $[OH^{-1}_{2}V_{2}]$





Ionic	c Equilibrium (Elementary)
Der7 :	We have to use Ostwald's Dilution law (as we have been derived earlier)
	$HA \iff H^+ + OH^-$
	t = t _{eq} $C(1-\alpha)$ $C\alpha$ $C\alpha$ $K_a = \frac{[H^+]}{[HA]} = \frac{C \alpha^2}{1-\alpha}$ (1)
	Assume $\alpha \ll 1 \Rightarrow (1 - \alpha) \approx 1 \Rightarrow K_a \approx C\alpha^2 \Rightarrow \alpha = \sqrt{\frac{K_a}{C}}$ (valid if $\alpha < 0.1$ or 10%)
F15 :	$[H^+] = C\alpha = C\sqrt{\frac{K_a}{C}} = \sqrt{K_a \times C} \implies \text{So, } \mathbf{pH} = \frac{1}{2}(\mathbf{pK}_a - \log C) \qquad \text{(valid if } \alpha < 0.1 \text{ or } 10\%)$
	on dilution \Rightarrow $C \downarrow \Rightarrow \alpha \uparrow$ and $[H^+] \downarrow \Rightarrow pH \uparrow$
Note :	If α obtained from $\sqrt{\frac{K_a}{C}}$ is greater than 0.1, solve quadratic equation (1) and get accurate α .
	Then, $[H^+] = C \alpha$ & now pH calculation can be done.
	— Solved Examples —
Ex-14.	Calculate pH of (a) 10^{-1} M CH ₃ COOH (b) 10^{-3} M CH ₃ COOH (c) 10^{-6} M CH ₃ COOH Take K _a = 2 ×10 ⁻⁵ , at 25°C.
Sol.	(a) $\alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{2 \times 10^{-5}}{10^{-1}}} = \sqrt{2 \times 10^{-4}} (\alpha << 0.1)$
	So, $[H^+] = 10^{-1} \times \sqrt{2} \times 10^{-2} \Rightarrow pH = 3 - \frac{1}{2} \log 2 = 2.85$ Ans.
	(b) $\alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{2 \times 10^{-5}}{10^{-3}}} = \sqrt{2 \times 10^{-2}} (\alpha > 0.1)$
	So, we have to do the exact calculations
	$K_{a} = \frac{C\alpha^{2}}{1-\alpha} \implies 2 \times 10^{-5} = \frac{10^{-3} \times \alpha^{2}}{1-\alpha} \implies \alpha = 13.14\%$
	$[H^+] = 10^{-3} \times 0.1314 = 1.314 \times 10^{-4} \implies pH = 4 - \log(1.314) 3.8$ Ans.
	(c) If approximation is used, then $\alpha = \sqrt{\frac{2 \times 10^{-5}}{10^{-6}}} = \sqrt{20}$ (> 1; not possible)
	So, we have to do the exact calculations, $2 \times 10^{-5} = 10^{-6} \frac{\alpha^2}{1-\alpha} \implies \alpha \ 0.95 \text{ or } 95\%$
о	$[H^+] = 0.95 \times 10^{-6} = 9.5 \times 10^{-7} \implies pH = 7 - \log (9.5) = 6.022$ Ans. At very low concentration (at infinite dilution), weak electrolyte will be almost 100% dissociated, so it will behave as strong electrolyte pH of 10^{-6} M HCl $\approx pH$ of 10^{-6} M CH ₃ COOH ≈ 6)

Weak base (monoacidic) solution :

Proceed similarly as done for weak monoprotic acid.

F16 : ∴ pOH = $\frac{1}{2}$ (pK_b – log C) (if α < 0.1 or 10%)

& then pH = 14 - pOH.

Isohydric solutions:

D11: If the concentration of the common ions in the solution of two electrolytes, for example H⁺ ion concentration in two acid solutions HA₁ and HA₂ or OH⁻ ion concentration in two base solutions B₁OH and B₂OH is same, then on mixing them, there is no change in the degree of dissociation of either of the electrolytes (common ion effect is not exerted by one on other). Such solutions are called isohydric solutions.

Consider two isohydric solutions of weak acids HA₁ and HA₂. Let C₁ and C₂ be their concentration and α_1 and α_2 be their degree of dissociation. Then,

F17: $C_1\alpha_1 = C_2\alpha_2$ (on equating the H⁺ concentrations from both acids).

Relative strength of acids and bases :

In practice, K_a is used to define the strength only of those acids that are weaker than H_3O^+ and K_b is used to define the strength of only those bases that are weaker than OH^- . For two weak acids HA_1 and HA_2 of ionisation constant K_{a1} and K_{a2} respectively at the same concentration C, we have :

F18 :
$$\frac{\text{Acid strength of HA}_1}{\text{Acid strength of HA}_2} = \frac{\alpha_1}{\alpha_2} = \sqrt{\frac{\text{K}_{a_1}}{\text{K}_{a_2}}}$$

Similarly, relative strengths of any two weak bases at the same concentration are given by the ratio of the square-roots of their dissociation constants i.e.,

F19 :
$$\frac{\text{Basic strength of BOH}_1}{\text{Basic strength of BOH}_2} = \frac{\alpha_1}{\alpha_2} = \sqrt{\frac{K_{b_1}}{K_{b_2}}}$$

(F) Salt Hydrolysis, pH calculation : solutions of salt of monoprotic acid and monoacidic base Salt Hydrolysis

D12 : Hydrolysis : The reaction of an ion with water in which either H₃O⁺ or OH⁻ is produced, by dissociation of water molecule.

Salt + Water 💳 acid +base

When acids and bases are mixed so that none of the two is left, then we will have salt solution in water and we have to calculate pH of salt solution.

When a salt is added to water, the solid salt first dissolves and breaks into ions completely (unless otherwise specified). The ions of the salt may or may not react with water. The cations on reaction with water will produce H_3O^+ ions and the anions on reaction with water will produce OH^- ions. Depending on the extent of hydrolysis and on the amounts of H_3O^+ and OH^- ions, the solution can be acidic, basic or neutral. If salt is BA, then :

 $\begin{array}{ll} \mathsf{BA}(s) & \longrightarrow & \mathsf{BA}(aq) & \longrightarrow & \mathsf{B}^+(aq) + \mathsf{A}^-(aq) \\ \mathsf{A}^-(aq) + \mathsf{H}_2\mathsf{O}(l) & \mathchoice{\longleftrightarrow}{\leftarrow}{\leftarrow}{\leftarrow} & \mathsf{HA}(aq) + \mathsf{OH}^-(aq) \\ \mathsf{B}^+(aq) + 2\mathsf{H}_2\mathsf{O}(l) & \mathchoice{\longleftrightarrow}{\leftarrow}{\leftarrow}{\leftarrow} & \mathsf{BOH}(aq) + \mathsf{H}_3\mathsf{O}^+(aq) \end{array} \qquad (anionic hydrolysis) \\ (cationic hydrolysis) \end{array}$

ANIONIC HYDROLYSIS

Anions can function as a base on reaction with water and hydrolyse as follows :

 $A^{-}(aq) + H_2O(I) \iff HA(aq) + OH^{-}(aq)$

The extent of hydrolysis of a given anion depends on its basic strength.

(a) Complete hydrolysis

The anions, which are stronger base than OH⁻ and have conjugate acids weaker than H₂O, will show complete hydrolysis in aqueous medium.

For example : $H^- + H_2O \longrightarrow H_2 + OH^-$; $NH_2^- + H_2O \longrightarrow NH_3 + OH^-$

(b) Hydrolysis to a limited extent

The anions, which are weaker base than OH^- and have conjugate acids stronger than H_2O but weaker acid than H_3O^+ , will hydrolyse to a limited extent in aqueous medium.

For example : $CN^- + H_2O \iff HCN + OH^-$

Other examples are CH₃COO⁻, NO_2^- , S^{2-} etc.

(c) No hydrolysis

The anions, which are weaker base than OH^- and have conjugate acids stronger than both H_2O and H_3O^+ , do not hydrolyse at all.

For example : $CI^- + H_2O \longrightarrow HCI + OH^-$

Other examples include HSO₄⁻, NO₃⁻, ClO₄⁻ etc.

CATIONIC HYDROLYSIS

Cations can function as acid on reaction with water and hydrolyse as follows :

 $B^+(aq) + 2H_2O(I) \iff BOH(aq) + H_3O^+(aq)$

The extent of hydrolysis of a given cation depends on its acidic strength.

(a) Complete hydrolysis

The cations, which are stronger acids than H_3O^+ and their conjugate bases are very much weaker than H_2O will show complete hydrolysis.

For example : $PH_4^+ + H_2O \longrightarrow H_3O^+ + PH_3$

(b) Hydrolysis to a limited extent

The cations, which weaker acid than H_3O^+ ion and their conjugate bases are stonger than H_2O but weaker than OH^- , show hydrolysis to a limited extent.

For example : $NH_4^+ + 2H_2O \implies NH_4OH + H_3O^+$ Other examples are $C_6H_5NH_3^+$, $CH_3NH_3^+$ etc.

(c) No hydrolysis

The cations, which are weaker acid than H_3O^+ and their conjugate bases are stronger than both H_2O and

OH⁻, do not hydrolyze at all. Examples are alkali and alkaline earth metal ions. For example : Na⁺ + 2H₂O \longrightarrow NaOH + H₃O⁺

pH calculation : Solutions of salt of monoprotic acid and monoacidic base. There are four types of salts :

(A) Salt of strong acid and strong base

- Salt of strong acid and weak base
- (C) Salt of weak acid and strong base
- Salt of weak acid and weak base

Salts of first type does not undergo hydrolysis and rest three types undergo hydrolysis. Currently considering only monoprotic acids & monoacidic bases,

(A) Salt of strong acid and strong base

Neither of the ions will undergo hydrolysis, so the solution involves only the equilibrium of ionization of water.

(B)

(D)

 $2H_2O(I) \Longrightarrow H_3O^+ + OH^-$

Thus, the pH of solution will be 7 (neutral solution at 25°C).

(B) Salt of strong acid and weak base

Examples can be NH₄Cl, (NH₄)₂SO₄, C₆H₅NH₃⁺Cl⁻

Only the cation will undergo hydrolysis and the solution will be acidic in nature. Cation is considered responsible for the acidic nature of solution.

 $\mbox{Der8}$: For example, in the solution of $\mbox{NH}_4\mbox{Cl}$ of concentration c, we will have :

$$\begin{array}{c} NH_4^+ + H_2O \Longrightarrow NH_4OH + H^+ \\ t = 0 & c & - & 0 & 0 \\ at eq. & c(1-h) & ch & ch & (h - degree of hydrolysis) \end{array}$$

 $K_{h}=\frac{[NH_{4}OH][H^{+}]}{[NH_{4}^{+}]} = hydrolysis \text{ constant of the salt}$

$$NH_4OH \Longrightarrow NH_4^+ + OH^-, \qquad K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]}$$
$$H_2O \Longrightarrow H^+ + OH^-, \qquad K_w = [H^+] [OH^-]$$

From above equations, we can get :

$$K_h \times K_b = K_w$$

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

F20 : Generally, $h \ll 1 \therefore 1 - h = \sqrt{\frac{K_h}{c}}$

$$\Rightarrow \qquad [H^+] = ch = \sqrt{K_h \times c} = \sqrt{\frac{K_w}{K_b} \times c}$$
$$\Rightarrow \qquad pH = -\log [H^+] = -\frac{1}{2} [\log K_w - \log K_b + \log c]$$

F21: \Rightarrow **pH** = $\frac{1}{2}$ [**pK**_w - **pK**_b - log c] (valid if h < 0.1 or 10%)

Note: (1) c is the concentration of ion undergoing hydrolysis, not the concentration of salt.

(2) If h obtained from $\sqrt{\frac{K_h}{c}}$ is greater than 0.1, solve quadratic equation (2) and get accurate h. Then, $[H^+] = ch \& now pH$ calculation can be done.

Solved Examples

- Ex-15. Calculate degree of hydrolysis, K_h and pH of 1 M urea hydrochloride solution in water, K_b (Urea) = 1.5×10^{-14} at 25°C. Consider urea as a monoacidic base. Take log 0.55 = -0.26.
- Sol. NH₂CONH₃Cl is a salt of SA + WB

 $K_{h} = \frac{K_{w}}{K_{h}} = \frac{10^{-14}}{1.5 \text{ x} 10^{-14}} = 6.667 \text{ x} 10^{-1}$ h = $\sqrt{\frac{K_h}{C}} = \sqrt{\frac{10^{-14}}{1.5 \times 10^{-14} \times 1}}$ Now h = 0.816 (> 0.1)or So we use actual relation $K_{h} = \frac{Ch^{2}}{1-h} = \frac{1}{1.5}$ $1.5 h^2 + h - 1 = 0$ h = 0.55 \Rightarrow $[H^+] = ch = 0.55 M$ pH = 0.26.:.

- **Ex-16.** Equal volume of 0.2 M NH₄OH (or ammonia) and 0.1 M H₂SO₄ are mixed. Calculate pH of final solution. Given : K_b of NH₃ = 1.8 × 10⁻⁵ at 25°C.
- Sol. $C = [NH_4^+] = 0.1 M (\Box$ volume got doubled, so concentration must have been halved)

h =
$$\sqrt{\frac{K_h}{C}} = \sqrt{\frac{10^{-14}}{1.8 \times 10^{-5} \times 0.1}}$$
 (< 0.1)
∴ pH = 1/2 {14 - 4.74 + 1} = $\frac{10.26}{2}$ = 5.13

(C) Salt of weak acid and strong base

 $K_h x$

Der9:

The examples can be CH₃COONa, KCN etc. Proceeding similar to above analysis of salt of weak base & strong acid, we will get :

$$K_h \times K_a = K_w \qquad \& \qquad K_h = \frac{ch \cdot ch}{c(1-h)} = \frac{ch^2}{(1-h)}$$

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

F22:

$$[OH^{-}] = ch = \sqrt{K_{h} \times c} = \sqrt{\frac{K_{w}}{K_{a}} \times c}$$

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

$$pH = -\log [H^{+}] = -\frac{1}{2}[\log K_{w} + \log K_{a} - \log c]$$

$$pH = \frac{1}{2}[pK_{w} + pK_{a} + \log c] \qquad (valid if h < 0.1 or 10\%)$$

F23:

Ο

...

= t a

Solution will be basic in nature due to hydrolysis of anion.

Ex-17. If the equilibrium constant for reaction of HCN with NaOH is 10¹⁰, then calculate pH of 10⁻³ M NaCN solution at 25°C.

Sol.

$$\begin{array}{rcl} & HCN + NaOH \iff H_2O + NaCN & K = 10^{10} \\ & CN^- + H_2O \iff HCN + OH^- & K_h = 10^{-10} \\ & = 0 & 10^{-3}M & 0 & 0 \\ t \ eq. & 10^{-3}(1-h) & 10^{-3}h & 10^{-3}h \\ & K_h = 10^{-10} = \frac{10^{-3}h \times 10^{-3}h}{10^{-3}(1-h)} \implies & h = \sqrt{\frac{K_h}{c}} = \sqrt{10^{-7}} \ (< 0.1) \end{array}$$

$$\Rightarrow \qquad \mathsf{pH} = \mathsf{7} - \frac{1}{2}\log 10^{-10} + \frac{1}{2}\log 10^{-3} = \mathsf{7} + 5 - \frac{3}{2} = 10.5.$$

Ex-18. Calculate degree of hydrolysis(h) and pH of solution obtanied by dissolving 0.1 mole of CH₃ COONa in water to get 100 L of solution. Take K_a of acetic acid = 2 ×10⁻⁵ at 25°C.

Sol.
$$c = \frac{0.1}{100} = 1 \times 10^{-3} \text{ M}$$

 $K_h = \frac{K_w}{K_a} = \frac{10^{-14}}{2 \times 10^{-5}} = 5 \times 10^{-10} \implies h = \sqrt{\frac{K_h}{c}} = \sqrt{\frac{5 \times 10^{-10}}{2 \times 10^{-5}}} = 5 \times 10^{-3} = 0.5\%$
 $\therefore pH = \frac{1}{2} [pK_w + pK_a + \log c] = \frac{1}{2} [14 + 5 - \log 2 + \log 10^{-3}] = \frac{1}{2} [15.7] = 7.85.$

Examples can be CH₃COONH₄, NH₄CN etc.
Der10: CH₃COO⁻ + NH₄⁺ + H₂O
$$\rightleftharpoons$$
 CH₃COOH + NH₄OH
t = 0 c c 0 0 0
at eq. c - ch c - ch ch ch ch
 $K_h = \frac{[CH_3COOH] [NH_4OH]}{[CH_3COO^-] [NH_4^+]}$ (i)
CH₃COOH \rightleftharpoons CH₃COO⁻ + H⁺, $K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$ (ii)
[NH₄⁺]IOH⁻]

$$NH_4OH \implies NH_4^+ + OH^-, \qquad K_b = \frac{[H_4 H_4][OH^+]}{[NH_4OH]} \qquad \dots (iii)$$
$$H_2O \implies H^+ + OH^-, \qquad K_w = [H^+][OH^-] \qquad \dots (iv)$$

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

$$\Rightarrow \qquad K_{h} = \frac{ch \cdot ch}{c(1-h) \cdot c(1-h)} = \left(\frac{h}{1-h}\right)^{2}$$

$$\Rightarrow \qquad \left(\frac{h}{1-h}\right) = \sqrt{K_{h}}$$

$$\rightarrow \qquad \mathsf{Nh} = \mathsf{F24} : \Rightarrow \left(-\frac{\mathsf{h}}{\mathsf{h}} \right)$$

From (ii) equation,

$$[H^+] = K_a \frac{[CH_3COOH]}{[CH_3COO^-]} = K_a \frac{ch}{c(1-h)} = K_a \times \frac{h}{1-h} = K_a \times \sqrt{K_h} = K_a \times \sqrt{\frac{K_w}{K_a} \times K_b} = \sqrt{\frac{K_w \times K_a}{K_b}}$$

F25 :
$$pH = -\log [H^+] = \frac{1}{2} [pK_w + pK_a - pK_b]$$

- 0 This formula is always valid for any Ka and Kb at any temperature, for any h.
- 0 pH is independent of concentration of salt solution.
- Even if K_a of weak acid $\neq K_b$ of week base, degree of hydrolysis of cations & anions are very close to 0 each other when they are getting hydrolysed in presence of each other. So, for numerical analysis, they are taken same.

Solved Examples

- **Ex-19.** Calcluate pH and degree of hydrolysis of 10⁻² M NH₄CN solution.
 - Given that K_a of HCN = 5 x 10⁻¹⁰ and K_b of (aq.NH₃) = 2 x 10⁻⁵ at 25°C.

Sol.
$$pH = \frac{1}{2} [14 + pK_a - pK_b] = \frac{1}{2} [14 + 10 - \log 5 - 5 + \log 2] = \frac{1}{2} [18.6] = 9.3$$

$$\frac{h}{1 - h} = \sqrt{K_h} = \sqrt{\frac{K_w}{K_a \times K_b}} = \sqrt{\frac{10^{-14}}{5 \times 10^{-10} \times 2 \times 10^{-5}}} = 1$$
$$\Rightarrow \qquad 2h = 1$$

$$\Rightarrow$$
 h = $\frac{1}{2}$ = 0.5

Table-5

Types of salt	Expression for K _h	Expression for h	Expression for pH
(i) Salt of weak acid and strong base	$K_{h} = \frac{K_{w}}{K_{a}}$	$h = \sqrt{\left(\frac{K_{h}}{C}\right)}$ (h < 0.1)	$pH = \frac{1}{2} [pK_w + pK_a + \log C]$
(ii) Salt of strong acid and weak base	$K_{h} = \frac{K_{w}}{K_{b}}$	$h = \sqrt{\left(\frac{K_{h}}{C}\right)}$ (h < 0.1)	$pH = \frac{1}{2} \left[pK_w - pK_b - \log C \right]$
(iii) Salt of weak acid and weak base	$K_{h} = \frac{K_{w}}{K_{a}K_{b}}$	$\frac{h}{1-h} = \sqrt{(K_h)}$	$pH = \frac{1}{2} \left[pK_w + pK_a - pK_b \right]$

Ionic Equilibrium-II

(A) Buffer Solution: Definition and identification

D13 : Buffer solutions are those solutions which resist a change in pH upon addition of small amount of small amount of acid or base.

This does not mean that the pH will not change, all it means is that the pH change would be less than the change that would have occurred had it not been a buffer.

There are various types of buffers :

(i)

- Buffer of a weak acid and its salt with a strong base : Can be prepared by
 - (a) Mixing weak acid solution and solution of its salt with a strong base.

(b) Mixing weak acid solution and lesser amount of strong base solution than that required for neutralization.

(c) Mixing salt solution of a weak acid and strong base with lesser amount of strong acid solution than that required for complete reaction.

Eg. A solution containing CH₃COOH & CH₃COONa.

(ii) Buffer of a weak base and its salt with a strong acid : Can be prepared by

(a) Mixing weak base solution and solution of its salt with a strong acid.

(b) Mixing weak base solution and lesser amount of strong acid solution than that required for neutralization

(c) Mixing salt solution of a weak base and strong acid with lesser amount of strong base solution than that required for complete reaction.

- Eg. A solution containing NH4OH & NH4CI.
- (iii) **Solution of salt of a weak acid and a weak base :** Eg. A solution of CH₃COONH₄.

(B) pH calculation: Buffer solutions generated from monobasic acid / monoacidic base

Der11: To calculate the pH of a buffer solution consisting of a weak acid (CH₃COOH; C₁ concentration) and its salt with a strong base (CH₃COONa; C₂ concentration of anion), we have :

$$\begin{array}{c} CH_{3}COOH & \stackrel{\longrightarrow}{\longleftarrow} CH_{3}COO^{-} + H^{+} \\ t = 0 & C_{1} & C_{2} & 0 \\ t = eq & C_{1}(1-\alpha) & C_{2} + C_{1}\alpha & C_{1}\alpha \\ K_{a} = \frac{[CH_{3}COO^{-}] & [H^{+}]}{[CH_{3}CO_{2}H]} = \frac{(C_{2} + C_{1}\alpha) & C_{1}\alpha}{C_{1}(1-\alpha)} & \dots(1) \end{array}$$

Expecting $\alpha \ll 1$ (due to common ion effect exerted by CH₃COO⁻ on dissociation of CH₃COOH),

$$\alpha = \frac{\mathsf{K}_{\mathsf{a}}}{\mathsf{C}_{\mathsf{2}}}$$

$$\therefore \qquad [\mathsf{H}^+] = \mathsf{C}_1 \alpha = \mathsf{K}_a \times \frac{\mathsf{C}_1}{\mathsf{C}_2}$$

Taking log of both sides,

 $\log [H^+] = \log K_a + \log \frac{[Acid]}{[Anion of Salt]}$

...(2)

F26: ÷. $pH = pK_a +$

This is known as the Henderson's equation of a buffer.

NOTE : If α from (2) comes greater than 0.1, calculate exact α by solving quadratic (1) & then [H⁺] = $C_{1\alpha}$

For a buffer made up of weak base and its salt with a strong acid, the Henderson's equation looks like this:

 $pOH = pK_{I}$ F27:

$$L_b + \log \frac{[Cattorior Sat}{[Base]}$$

Base] - Solved Examples –

- Ex-20. Calculate the amount of (NH₄)₂SO₄ in grams which must be added to 500 ml of 0.2 M NH₃ to give a solution of pH = 9.3. Given pK_b for NH₃ = 4.7
- Sol. This is a buffer solution made up of weak base and its salt with a strong acid. On checking α (refer derivation), it comes less than 0.1 (can be considered negligible).

 $pOH = pK_b + log \frac{[Conjugate acid]}{[Base]}$ (Cation of salt here is same as conjugate acid) ÷.

4.7 = 4.7 + log $\frac{x}{0.2}$ \Rightarrow x = [NH₄⁺] = 0.2, so concentration of (NH₄)₂SO₄ required = 0.1 M moles of $(NH_4)_2SO_4$ needed = 0.1 x 0.5 = 0.05

- *.*.. weight of $(NH_4)_2SO_4$ needed = $132 \times 0.05 = 6.6$ g *.*..
- Ex-21. Calculate [H⁺] in a 0.20 M solution of dichloroacetic acid (K_a= 5 × 10⁻²) that also contains 0.1 M sodium dichloroacetate. Neglect hydrolysis of sodium salt.

Sol. CHCl₂COOH ← CHCl₂COO-H+ Before dissociation 0.2 After dissociation (0.2 - x)х х $CHCl_2COONa \longrightarrow CHCl_2COO^-$ Na⁺ 0.1 01

For the dissociation of acid

 $K_a = 5 \times 10^{-2} = \frac{[CHCl_2COO^-][H^+]}{[CHCH_2COOH]}$ or

$$0.05 = \frac{[0.1 + x] [x]}{[0.2 - x]}$$

x = 0.05 or $[H^+] = 0.05$ M.

Ionic Equilibrium-III

(A) Solubility, Solubility Product and simple solubility calculations

Solubility product (K_{sp}) is a type of equilibrium constant, so will be dependent only on temperature for a particular salt.

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

Simple solubility

Let salt $A_x B_y$ be dissolved in water. Let its solubility in $H_2 O = s' M$. Then :

 $A_x B_y \implies xA^{y+} + yB^{-x}$

F28:
$$\therefore$$
 $K_{sp} = (xs)^{x} (ys)^{y} = x^{x} . y^{y} . (s)^{x+y}$

_Solved Examples -

Ex-22. Calculate K_{sp} of Fe₄[Fe(CN)₆]₃ at a particular temperature, where solubility in water = s mol/L

Sol. $K_{sp} = 4^4 \cdot 3^3 \cdot (s)^{3+4} = 6912 \ s^7$

(B) Condition of precipitation, common ion effect on solubility Condition of precipitation

- O Consider ionic product (K_{IP}) similar to reaction quotient Q in chemical equilibrium.
- For precipitation, ionic product (K_{IP}) should be greater than solubility product K_{sp} . This will make the equilibrium of undissolved salt and dissolved salt shift in backward direction leading to precipitation.
- After precipitation, solution will become saturated and $K_{IP} = K_{sp}$.
- Remember to modify the concentration of the precipitating ions because of volume change occouring upon mixing both solutions.

- **Ex-23.** You are given 10⁻⁵ M NaCl solution and 10⁻⁸ M AgNO₃ solution. They are mixed in 1:1 volume ratio. Predict whether AgCl will be precipitated or not, if solubility product (Ksp) of AgCl = 10⁻¹⁰.
- **Sol.** Upon mixing equal volumes, volume of solution will get doubled. So concentration of each ion will get halved from original value.

Ionic product K_{IP} = ([Ag⁺] [CI⁻])_{upon mixing} = $\frac{10^{-5}}{2} \times \frac{10^{-8}}{2} = 25 \times 10^{-15} (< K_{sp})$

Hence, no precipitation will take place.

Common Ion effect on solubility

- Because of the presence of common ion in solution, the solubility of the sparingly soluble salt generally decreases.
- Neglect the concentration of common ion coming from sparingly soluble salt with respect to that coming from completely soluble salt.

-Solved Examples –

- **Ex-24.** Calculate solubility of silver oxalate in 10^{-2} M potassium oxalate solution. Given that K_{sp} of silver oxalate = 10^{-10} .
- Sol. Let the solubility be x mol/L $Ag_2C_2O_4 \implies 2Ag^+ + C_2O_4^{2-}$

$$K_{sp} = 10^{-10} = 10^{-2} \times (2x)^2 \qquad \qquad 2x \qquad x + 10^{-2} (\approx 10^{-2}) \\ K_{sp} = 10^{-10} = 10^{-2} \times (2x)^2 \qquad \qquad \Rightarrow \qquad \frac{10^{-8}}{2 \times 2} = x^2 \qquad \Rightarrow \qquad x = 5 \times 10^{-5} \text{ M}$$



	Check List					
D1 D2 D3 D4 D5 D6 D7 D8 D9 D10 D11 D12 D13	Definitions (D) Arrhenius Acid Arrhenius Base Brönsted–Lowry Acid Brönsted–Lowry Base Amphiprotic species Lewis Acid Lewis Base pH & pH scale Autoprotolysis Degree of dissociation (α) Isohydric Solutions Hydrolysis Buffer solution	F14 F15 F16 F17 F18 F19 F20 F21 F22 F23 F24 F25 F26 F26 F26 F27	Concentrations of ions produced by weak electrolyte (with $\alpha < 0.1$) [H ⁺] & pH of a weak monoprotic acid solution pOH of a weak monoacidic base solution Condition for two solution to be isohydric Relative strength of two weak acids Relative strength of two weak bases Degree of hydrolysis (h) of a salt of WB & SA (< 0.1) pH of a solution of a salt of WB & SA (< 0.1) Degree of hydrolysis (h) of a salt of WA & SB (< 0.1) pH of a solution of a salt of WA & SB (< 0.1) Degree of hydrolysis (h) of a salt of WA & WB pH of a solution of a salt of WA & WB pH of a solution of a salt of WA & WB pH of a buffer solution of WA & its conjugate base			
=1 =2 =3 =4 =5	Formulae (F) Ionic Product of Water (K_w) pH pOH α [H ⁺] in strong acid solution (H ⁺ from H ₂ O negligible) [H ⁺] in strong acid solution (H ⁺ from H ₂ O negligible)	F28 Der1 Der2 Der3	Relation between solubility(s) & solubility product (K _{sp}) for sparingly soluble salts Derivation (Der) Absolute dissociation constant of water (K _a or K _b) Relation between pH & pOH for an aqueous solution			
-0 -7 -8 -9 -10 -11 -12	[H ⁺] in strong base solution (H ⁺ norm H ₂ O significant) [OH ⁻] in strong base solution (OH ⁻ from H ₂ O significant) [H ⁺] in a solution containing mixture of two strong acids [OH ⁻] in a solution containing mixture of two strong bases [H ⁺][OH ⁻] in a solution containing mixture of a strong acid & a strong base K_{eq} for a weak electrolyte (in terms of C & α)	Der4 Der5 Der6 Der7 Der8 Der9 Der10 Der11	Relation between $pK_a \& pK_b$ for a conjugate acid base pair $[H^+]/[OH^-]$ in a solution containing mixture of SA & SB Ostwald's Dilution Law Equilibrium of a weak monoprotic acid Hydrolysis of cation in a salt solution of WB & SA Hydrolysis of cation in a salt solution of WA & SB Hydrolysis of cation & anion in a salt solution of WA & WB pH calculation of a buffer solution consisting of a weak acid & its salt with SB			

MISCELLANEOUS SOLVED PROBLEMS (MSPs)

1.	Which of the following is the strongest base?						
A mo	(A) $C_2 H_5^-$	(B) $C_2H_5COO^-$	(C) C ₂ H₅O ⁻	(D) OH⁻			
Ans.	(A)						
501.	Weakest acid wil	$_{2}\Pi_{6} < C_{2}\Pi_{5}O\Pi < \Pi_{2}O < C_{2}I$ I have strongest conjugate	base.				
2.	A solution of HCI	has a $pH = 5$. If one mL of	it is diluted to 1 litre, w	hat will be pH of result	ing solution.		
Sol.]	HCI] _i = 10 ⁻⁵ M	since pH = 5	-	-		
	Since volume of original solution has been made 1000 times, so concentration of solution will decrease by 1000 times.						

- $[HCl]_{f} = 10^{-8}$ M. So H⁺ from water should also be considered (as done in solved example-8) *.*.. Then, pH of resulting solution = **6.96**
- 3. Calculate the pH of 0.001 M HOCI having 25% dissociation. Also calculate dissociation constant of the acid. Take log 2 = 0.3

Sol.

HOCI
$$\longrightarrow$$
 H⁺ + OCI⁻
t=0 a 0 0
t=eq a - aa aa aa
So, [H⁺] = aa = 10⁻³ × $\frac{25}{100}$ = 2.5 × 10⁻⁴
So, pH = **3.6**

Now,
$$K_a = \frac{(a\alpha)}{a} \frac{(a\alpha)}{(1-\alpha)} = \frac{a\alpha^2}{1-\alpha} = \frac{1}{12} \times 10^{-3}$$

4. The solubility product of SrF₂ in water is 8×10⁻¹⁰. Calculate its solubility in 0.1 M NaF aqueous solution. Sol.
$$\begin{split} &K_{sp} = [Sr^{2+}] \, [F^{-}]^2 \\ &8 \times 10^{-10} = s[2s+0.1]^2 = s[0.1]^2 \ (\text{neglecting the } F^- \text{coming from sparingly soluble salt } SrF_2) \end{split}$$

10 - 10

:.
$$s = \frac{8 \times 10^{-10}}{(0.1)^2} = 8 \times 10^{-8} M$$