IONIC EQUILIBRIUM

4.0 **INTRODUCTION**

Formulae :

In $x = \log_e x = 2.303 \log_{10} x = 2.303 \log x$ (i) (ii) $\log(x \times y) = \log x + \log y$ (iii) log $= \log x - \log y$ $\log x^{y} = y \log x$ (iv) Ex. $\log 6 = \log (2 \times 3)$ (i) $= \log 2 + \log 3$ = 0.3010 + 0.47711 = 0.7781 $\log 30 = \log (3 \times 10)$ (ii) $= \log 3 + \log 10$ $= \log 0.4771 + 1 = 1.4771$ $\log 1000 = \log 10^3$ (iii) $= 3\log 10 = 3 \times 1 = 3$ A. Some values of log : $\log 1 = 0$

log2 = 0.3010log3 = 0.4771log4 = 0.6020 $\log 5 = 0.699$ log6 = 0.7781log7 = 0.8451log8 = 0.9030log9 = 0.9542log10 = 1log11 = 1.04log100 = 2log1000 = 3

Some terms which are used in ionic equilibrium : Antilog : Antilog $(x) = 10^{x}$

Antilog (2) = $10^2 = 100$ Ex. Antilog $(0.3010) = 10^{.3010} 2$ Antilog $\left[\log(2)\right]$ = Antilog (0.3010) = 2

pH - Scale : Given by - Sorenson

pH Scale is called Sorenson scale.

pH scale is a measuring scale used to measure strength of acid and base and its value is equal to $-\log[H^+]$

3

i.e.
$$pH = -\log[H^+] = \log \frac{1}{[H^+]}$$

Ex. $[H^+] = 10^{-3}$
 $pH = -\log 10^{-3} = +3 \log 10 =$

Conclusion :

If
$$pH = x$$

then $[H^+] = 10^{-x}$ or Vice versa

i.e. If $[H^+] = 10^{-x}$ then pH = x **pOH** \rightarrow It is equal to $-\log [OH^-]$ i.e. pOH = $-\log [OH^-] = \log \frac{1}{[OH^-]}$

Ex. If
$$X = \frac{a}{b} \times 10^{-c}$$
, then find pX?
Sol. $pX = -\log X = -\log \left(\frac{a}{b} \times 10^{-c}\right)$
 $pX = -\left[\log \frac{a}{b} + \log 10^{-c}\right] = -[\log a - \log b - c]$
 $pX = c + \log b - \log a$

pH scale at 25°C

Figure

According to conductivity substances are of two types :

(1) Non-Conductor – Those substance which do not show the flow of current or electricity.

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

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

- (2) **Conductors** Those substance which show conductivity or flow of current are called conductors and these are of two types :
 - (a) Metallic conductor –Those conductor which show conductivity due to motion of free electrons.
 - (b) Ionic conductors 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 ion Movement of ions through the solution of electrolyte (AgNO₃) towards oppositely charged electrodes.

Figure

According to strength, ionic conductors are of two types-

Ex.

(1) **Strong electrolytes** – Those ionic conductors which are completely ionized in aqueous solution are called as strong electrolytes.

For strong electrolyte the value of degree of ionization is 100% i.e. $\alpha = 1$

- (a) Strong acid \rightarrow H₂SO₄, HCl, HNO₃, HClO₄, HBr, HI
 - (b) Strong base \rightarrow KOH, NaOH, Ba(OH)₂, CsOH, RbOH
- (c) All salts \rightarrow NaCl, KCl, CuSO₄.....
- (2) Weak electrolytes Those electrolytes which are partially ionized in aqueous solution are called as weak electrolytes. For weak electrolytes the value of α is less that one.

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↓ H₃BO₃

(Boric acid)

(b) Weak base
$$\rightarrow$$
 NH₄OH, Cu(OH)₂, Zn(OH)₂, Fe(OH)₃, Al(OH)₃ etc.

4.1 ARRHENIUS CONCEPT :

- (a) According to Arrhenius when an electrolyte dissolves in water it splits up into two oppositely charge particles i.e. cation and anion.
- (b) In an electrolytic solution (Aqueous solution of electrolyte), total +ve charges is equal to total -ve charge i.e. solution is electrically neutral.
- \Rightarrow In an electrolytic solution number of +ve ions may or may not be equal to the number of negative ions.
- (c) Properties of an electrolytic solution are defined by its ions. **Ex.** Blue colour of $CuSO_4$ aqueous solution is due to Cu^{+2} ion (dark blue colour)
- (d) When electric current is pass in aqueous solution of electrolyte then cation shows migration towards cathode where as anion shows migration towards anode.
- (e) When a weak electrolyte is dissolved in water an equilibrium is set up between unionized moles and ionized moles.

This condition of the reversible ionic reaction is known as ionic equilibrium.

AB(Aq.) $\frac{1}{2}$ $\hat{T} A^+ + B^-(Aq.)$

According to L.M.A.

Ionisation constant $K = \frac{[A^+][B^-]}{[A B]}$

Illustrations

Illustration 1. If $[H^+] = \frac{5}{3} \times 10^{-4}$ then find pH?

p

Solution

$$H = -\log[H^{+}] = -\log\left(\frac{5}{3} \times 10^{-4}\right)$$
$$= -\left[\log\frac{5}{3} + \log 10^{-4}\right] = -[\log 5 - \log 3 - 4]$$
$$= [0.699 - 0.4771 - 4] = -[-3.778] = 3.778$$

Illustration 2. Assertion : H₂SO₄ is a strong acid.

Reason : H_2SO_4 undergoes almost completely ionized in aqueous solution. (1) A (2) B (3) C (4) D

Solution Ar

Ans. (1)

4.2 OSTWALD'S DILUTION LAW

 \Rightarrow Ostwald dilution law is applicable only for weak electrolytes.

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Statement : According to Ostwald when solution of weak electrolyte is diluted then degree of ionization of solution is increased, is called dilution law.

AB(Aq.) $\frac{1}{2}$ $\hat{}$ $\hat{}$ $A^+(Aq.) + B^-(Aq.)$ Let 0 Initial concentration С 0 $(C - C\alpha)$ Degree of ionization (α) $(C\alpha)$ $(C\alpha)$ According to L.M.A $\mathbf{K} = \frac{[\mathbf{A}^+][\mathbf{B}^-]}{[\mathbf{A}\mathbf{B}]}; \mathbf{K} = \frac{\mathbf{C}\alpha \times \mathbf{C}\alpha}{\mathbf{C}(1-\alpha)} = \frac{\mathbf{C}\alpha^2}{(1-\alpha)}$ **Ionisation constant** If $\alpha < < < < 1$ then $1-\alpha \propto 1$ $K = C\alpha^2$ or $\alpha = \sqrt{\frac{K}{C}}$ (K = constant, At constant temperature) $\alpha \propto \frac{1}{\sqrt{C}}$ (C $\propto \frac{1}{V}$) $\alpha \propto \sqrt{V}$ Volume = dilution $\alpha \propto \sqrt{\text{dilution}}$ by dilution law dilution $\uparrow \alpha \uparrow$ At infinite dilution, $\alpha = 100\%$ Thus for weak electrolytes the degree of ionization is directly proportional to square root of dilution or inversely proportional to square root of concentration. This law is known as Ostwald Dilution Law.

GOLDEN KEY POINTS

- At infinite dilution the value of a becomes equal to one.
- The value of concentration should be in terms of normality for calculation of pH.

Application of Ostwald's Dilution Law : $K = C\alpha^2$

- (a) For mono basic weak acid (HA)
- (i) Ionisation constant (K_a)

HA
$$\frac{2}{3}$$
 \hat{T} H⁺ + A⁻

Initial concentrationC00At equilibrium $C - C\alpha$ $C\alpha$ $C\alpha$

If degree of ionization is α

$$\begin{split} \mathbf{K}_{a} &= \frac{[\mathbf{H}^{+}][\mathbf{A}^{-}]}{[\mathbf{H}\mathbf{A}]} = \frac{\mathbf{C}\alpha \times \mathbf{C}\alpha}{\mathbf{C} - \mathbf{C}\alpha} \\ \mathbf{K}_{a} &= \frac{\mathbf{C}^{2}\alpha^{2}}{\mathbf{1}(1 - \alpha)} = \frac{\mathbf{C}\alpha^{2}}{(1 - \alpha)} \\ \boldsymbol{\Theta} & \alpha < < < 1 \quad \therefore \quad (1 - \alpha) \approx 1 \\ \therefore \quad \mathbf{K}_{a} &= \mathbf{C}\alpha^{2} \end{split}$$

Where K_a → Ionisation constant of weak acid
 K_b → Ionisation constant of weak base
 Both K_a and K_b depends only on temperature
 (ii) [H⁺] (Concentration of H⁺)

$$[H^{+}] = C\alpha \qquad \dots \dots (1)$$

$$K_{a} = C\alpha^{2} \qquad \text{or} \qquad a = \sqrt{\frac{K_{a}}{C}} \qquad \dots \dots (2)$$
From Eq. (1) and (2) $[H^{+}] = C \times \frac{\sqrt{K_{a}}}{\sqrt{C}}$

$$[H^{+}] = \sqrt{K_{a} \times C}$$
(iii) $pH = -log[H^{+}]$
Put the value of $[H^{+}]$
Put the value of $[H^{+}]$
 $pH = -log(\sqrt{K_{a} \times C}) = -log(K_{a} \times C)^{1/2}$
 $pH = -\frac{1}{2}[log K_{a} + log C]$
 $pH = -\frac{1}{2}log K_{a} - \frac{1}{2}log C$
 $pH = \frac{1}{2}pK_{a} - \frac{1}{2}log C$

- (b) For mono acidic weak base (BOH)
- (i) Ionisation constant (K_b)

	BOH 🔒 ^	$\mathbf{\dot{T}} \mathbf{B}^+ + \mathbf{OH}^-$
Initial concentration	С	0 0
At equilibrium	$C - C\alpha$	C α C α
If degree of ionization is a		
$K_{b} = \frac{[B^{+}][OH^{-}]}{[BOH]} = \frac{C\alpha \times C}{C - C}$	$\frac{\alpha}{\alpha}$	
$K_{b} = \frac{C^{2}\alpha^{2}}{C(1-\alpha)} = \frac{C\alpha^{2}}{(1-\alpha)}$		

$$\Theta \qquad \alpha < < < 1 \qquad \therefore \qquad (1 - \alpha) \approx 1$$

$$\therefore \qquad K_b = C\alpha^2$$

Where $K_a \rightarrow$ Ionisation constant of weak acid $K_b \rightarrow$ Ionisation constant of weak base Both K_a and K_b depends only on temperature (ii) $[OH^-]$ (Concentration of OH^-) $[OH^-] = C\alpha$ (1) $K_b = C\alpha^2$ or $\alpha = \sqrt{\frac{K_b}{C}}$ (2)

From Eq. (1) and (2) [OH⁻] = C×
$$\frac{\sqrt{K_b}}{\sqrt{C}}$$

$$[OH^{-}] = \sqrt{K_{b} \times C}$$

pOH = -log[OH^{-}]
put the value of [OH^{-}]

$$pOH = -\log\left(\sqrt{K_b \times C}\right) = -\log(K_b \times C)^{1/2}$$
$$pOH = -\frac{1}{2} \left[\log K_b + \log C\right]$$
$$pOH = -\frac{1}{2} \log K_b - \frac{1}{2} \log C$$
$$pOH = \frac{1}{2} pK_b - \frac{1}{2} \log C$$

In summary :

1.
$$K_a = C\alpha^2$$

2. $[H^+] = C\alpha = \sqrt{K_a \times C}$
3. $pH = -log[H^+]$
or $pH = \frac{1}{2}pK_a - \frac{1}{2}logC$

1. $K_b = C\alpha^2$ 2. $[OH^-] = C\alpha = \sqrt{K_b \times C}$ 3. $pOH = -log[OH^-]$ or $pOH = \frac{1}{2}pK_b - \frac{1}{2}logC$

Limitation of Ostwald Dilution Law :

It is not applicable for strong electrolytes.

Factors affecting the Value of Degree of ionization :

- (1) Temperature \rightarrow On increasing temperature, ionization increases so a increases because dissociation is endothermic process.
- (2) Dilution $\rightarrow \alpha \propto \sqrt{V}$ so on dilution, α increases.
- (3) Nature of electrolytes
 - (i) Strong electrolytes $\alpha = 100\%$
 - (ii) Weak electrolytes $\alpha < 100\%$
- (4) Nature of solvent

If dielectric constant m of solvent increases then the value of α increases.

$$H_2O \rightarrow \mu = 81$$

$$D_2O \rightarrow \mu = 79$$

$$H_6O_6 \rightarrow \mu = 2.5$$

$$CCl_4 \rightarrow \mu = 0$$

Mixing of ions :-

(a) Common ion effect	(b) Odd ion effect
When a strong electrolyte having a common	When a strong electrolyte having a odd ion, is
ion, is mixed with weak electrolyte then the	mixed with weak electrolyte then the degree
degree ionization (∞) of weak electrolyte is	ionization (∞) of weak electrolyte is
decreased. This effect is called common ion	increased. This effect is called odd ion effect.
effect.	

Common ion : On mixing CH₃COONa with CH₃COOH solution

Initially CH_3COOH $\ddagger \uparrow \uparrow CH_3COO^- + H^+$

(On mixing) $CH_3COONa \longrightarrow CH_3COO^- + Na^+$; $[CH_3COO^-]$ increases so $[H^+]$ decreases respectively.

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Odd ion : On mixing, NaOH with CH₃COOH solution Initially $CH_3COOH \stackrel{?}{\ddagger} \stackrel{\land}{\uparrow} CH_3COO^- + H^+$ (On mixing) NaOH \longrightarrow Na⁺ + OH⁻ \longrightarrow Water Due to odd ion effect H⁺ + OH⁻ \rightarrow Water

Illustrations	
Illustration 3 For which dilution law is applicable :	
(1) NaCl (SASB salt) (2) HCl (SA)	
(3) CH ₃ COONa (WASB salt) (4) None of these	
Solution Ans. (4)	
Illustration 4. Find out the value of α of 10^{-2} M HCN solution if $[H^+] = 10^{-3}$.	
Solution $[H^+] = C\alpha$	
$10^{-3} - 10^{-2}$ or $\alpha = \frac{10^{-3}}{10^{-3}} = 10^{-1}$ or $\alpha = 0.1$	
$10^{-10} - 10^{-10} - 10^{-2} - 10^{-10} - 10^{-10} - 0.1$	
$\alpha = 10\%$	
Illustration 5. For 10 M CH ₃ COOH solution if $K_a = 10^{-5}$ then find out :	
(i) α (ii) [H ⁺] (iii) pH	
Solution (i) α	
(Degree of ion ionization) : $K_a = C\alpha^2$	
$10^{-5} = 10\alpha^2$ or $\alpha^2 = \frac{10^{-5}}{10^{-5}} = 10^{-6}$ or $\alpha = 10^{-3}$	
(ii) $[H^+] = C\alpha = 10 \times 10^{-3} = 10^{-2}$	
(iii) $pH = -log[H^+] = -log10^{-2} = 2$	
Illustration 6. For 10 ° M H ₂ CO ₃ if $\alpha = 10\%$ then find out the value of pH?	
Solution Normality = $M \times V.F. = 10^{-3} \times 2 = 2 \times 10^{-4}$	
$[H^{+}] = C\alpha = 2 \times 10^{-5} \times 0.1 = 2 \times 10^{-7}$	
$pH = -log[H] = -log(2 \times 10^{-}) = -log2 - log10^{-} = 0.3010 + 4 = 3.7$	
Illustration 7 Assertion :- NaCl + HCl does not experience common ion effect	
Reason :- Both NaCl and HCl are strong electrolytes	
(1) A (2) B (3) C (4) D	
Solution Ans. (1) $(1)^{2}$	
4.3 EXPLANATION OF WATER	
a. Nature of water is neutral. $[H^+] = [OH^-] = [=10^{-7}M \text{ (at } 25^{\circ}C)]$	
i.e. at 25° C pH = 7 and pOH = 7	
\therefore pH = pOH	
b Number of H ₂ O moles in 1 litre water $=\frac{1000}{1000}=55.5$ moles	
$\frac{18}{18}$	
c. Molar concentration of $H_2O = 55.5 \text{ mol } L^{-1}$	
d. Number of H_2O molecules in 1 litre water = 55.5 N _A (N _A = AVOGADO'S NUME	ER)
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e. Concentration of H² and OH ions in 1 litre water

$$[H^{-}] = 10^{-7} \text{ mol } L^{-1} \text{ and } [OH^{-}] = 10^{-7} \text{ mol } L^{-1}$$
f. Number of H¹ and OH² ions in 1 litre water
Number of H¹ and OH² ions in 1 litre water
Number of H² ions = 10⁻⁷ N_A and Number of OH² ions = 10⁻⁷ N_A
g. In water (Number of H₂O molecules : Number of H² ions
= 55.5 × 10⁷ : 1
i.e. one H² ion is obtained from 55.5 × 10⁷ H₂O molecules
h. **Degree of ionization of water (a)**:
H₂O $\frac{1}{2}$ ⁵ [†] H⁺ + OH⁻
According to Ostwald's dilution law
[H²] = C α
 $\alpha = \frac{10^{-7}}{55.5} = 1.8 \times 10^{9}$
 $[\alpha = 1.8 \times 10^{-7} \%]$
Hence, water is a very weak electrolyte.
i. **K** (Ionisation constant of water):
H₂O $\frac{1}{4}$ ⁵ [†] H⁺ + OH⁻
 $K = \frac{[H^{+1}](OH^{-1}]}{[H_2O]}$
 $K = \frac{10^{-7} \times 10^{-7}}{55.5}$ or $K = 1.8 \times 10^{-78}$
j. Ionic product of water K_w:
H₂O $\frac{1}{4}$ ⁵ [†] H⁺ + OH⁻
 $K = \frac{[H^{+1}](OH^{-1}]}{[H_2O]}$
 $K_{+}[H_{+}O] = [H^{+1}](OH^{-1}]$
Since, dissociation takes place to a very small extent, [H₂O] may be regarded as constant.
Thus, the product K.[H₂O] gives another constant which designated as K_w. So,
 $K_w = [H^{-1}](OH^{-1}]$
 $At 25^{\circ}C - K_w = 10^{-7} \times 10^{-7} = 10^{-14}$
 $K[H_2O] = K_w \Rightarrow K_w > K (always)$
Various forms of K_w
(a) $K_w = [H^{-1}](OH^{-1}]$
(b) $K_w = [H^{-1}](OH^{-1}]$
(c) $K_w = [OH^{-1}]^{-1}$
(d) $K_w = [H_3O^{-1}](H_1O^{-1}] = [H^{-1}]^{-1}$
(e) $K_w = [H_3O^{-1}](H_1^{-1}] = [OH^{-1}]^{-1}$
(f) $K_w = [H_3O^{-1}](H_1^{-1}] = [OH^{-1}]^{-1}$
(g) $K_w = [H_3O^{-1}](DH^{-1}]$
(h) $K_w = [H_3O^{-1}](DH^{-1}]$
(h) $K_w = [H_3O^{-1}](DH^{-1}]$
(c) $K_w = [H_3O^{-1}](DH^{-1}]^{-1}$
(f) $K_w = [H_3O^{-1}](DH^{-1}]^{-1}$
(g) $K_w = [H_3O^{-1}](DH^{-1}]^{-1}$
(h) $K_w = [H_3O^{-1}](DH^{-1}]^{-1}$
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(h) $K_w = [H_3O^{-1}](DH^{-1}]^{-1}$
(c) $K_w = [H_3O^{-1}](DH^{-1}]^{-1}$
(d) $K_w = [H_3O^{-1}](DH^{-1}]^{-1}$
(e) $K_w = [H_3O^{-1}](DH$

• Nature of water is neutral so, [pH = pOH] $pK_{W} = pH + pH$ $2pH = pK_{W}$ $pH = \frac{pK_{W}}{2}$ $pH = pOH = \frac{pK_{W}}{2}$ $pH = pOH = \frac{pK_{W}}{2}$ $At 25^{\circ}C, K_{W} = 10^{-14} \text{ or } pK_{W} = 14$ $\therefore pH + pOH = 14 \text{ or } pH = pOH = 7$ k. Effect of temperature :-

 $H_2O_{\frac{1}{2}}^{\uparrow\uparrow}H^+ + OH^-$

Ionization of water is endothermic process so, on increasing temperature a increases or $[H^+]$ and $[OH^-]$ increases or $[H^+][OH^-]$ increases i.e. K_w increases means pH decreases or pOH decreases.

 $T \uparrow = \alpha \uparrow = [H^+][OH^-]\uparrow = K_W \uparrow \Rightarrow pK_W \downarrow$ At 25°C, $K_W = 10^{-14}$ At 90°C, $K_W = 10^{-12}$

Parameters	At 25°C	At 90°C	
K _W	10^{-14}	10^{-12}	
pK _W	14	12	
$pH = \frac{pK_w}{2} = pOH$	7	6	
$[\mathrm{H}^+] = [\mathrm{OH}^-] = \sqrt{\mathrm{K}_\mathrm{w}}$	10^{-7}	10 ⁻⁶	
$pH + pOH = pK_W$	14	12	

GOLDEN KEY POINTS

• On increasing temperature, both [H⁺] and [OH⁻] increases equally so water remains neutral but neutral pH changes from 7 to 6 at 90°C.

Illustrations

Illustration 8. Dissociation constant of water at 25°C is

(1) $10^{-14} \times (55.5)^{-1}$ (3) $10^{-14} \times (18)^{-1}$

 $\begin{array}{c} (2) \ 10^{-7} \times (18)^{-1} \\ (4) \ 10^{-7} \times (55.4)^{-1} \end{array}$

Solution Ans. (1)

Illustration 9. What should be the number of H^+ ions in 1 mL of distilled water, if the number of H^+ ions in 1 L is 6.023×10^{16} ?

Solution Number of H⁺ ions in 1 mL distilled water = $\frac{6.023 \times 10^{16}}{1000} = 6.023 \times 10^{13}$

BEGINNER'S BOX-1

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1.	The pH of a 0.005 M (1) 3.3	H ₂ SO ₄ solution is - (2) 5.0	(3) 2.0	(4) 4.0
2.	If pure water has pK _w (1) 6.68	f = 13.36 at 50°C, the p (2) 7.0	pH of pure water will b (3) 7.13	e- (4) 6.0
3.	How many H^+ ions at (1) 10^{-16}	re present in 1 mol of a (2) 6.022×10^{13}	a solution whose pH is (3) 6.22×10^7	13? (4) 6.22×10^{23}
4.	The pH of solutions solution is -	A, B, C and D are 9	9.5, 2.5, 3.5 and 5.5 r	respectively. The most acidic
	(1) D	(2) C	(3) A	(4) B
5.	Calculate the concersolution at equilibrium	ntration of the formation $(K_a = 1.7 \times 10^{-4})$	t ion present in 0.10	0 M formic acid (HCOOH)
	(1) 4.1×10^{-3} M	(2) 3.1×10^{-3} M	(3) 2.1×10^{-3} M	(4) 5.1×10^{-3} M
6.	Which of the followin (1) Phenol ($K_a = 1.3 \times$ (3) Acetic acid ($K_a =$	ng is the weakest acid? (10^{-10}) 1.8×10^{-5})	(2) Hydrocyanic acid (4) Benzoic acid (K _a	$(K_a = 4.9 \times 10^{-10})$ = 6.5×10 ⁻⁵)
7.	The pH of 0.1 M more $(1) \ 1.0 \times 10^{-7}$	nobasic acid is 4.50. Th (2) 1.0×10 ⁻⁵	the acidity constant (K_a) (3) 1.0×10^{-4}) of the monobasic acid is - (4) 1.0×10^{-8}
8.	Which of the followin (1) $C_6H_5NH_2$ (pK _b = (3) $C_6H_5N(CH_3)_2$ (pK	ng is the strongest base 9.42) $X_b = 8.94$)	$(2) C_6H_5$ NHCH ₃ (pK (4) C ₆ H ₅ NHC ₂ H ₅ (pk	$b_b = 9.15)$ $C_b = 8.89)$
9.	Value of dissociation acid is 10^{-5} . Which of (1) 10	f constant of acetic ac f the following will be (2) +1	id is 10^{-6} , where as di the value of pKa (acet (3) 10^{-1}	ssociation constant of formic ic acid) – pKa (formic (acid) (4) –1
10.	A solution has pOH e (1) highly acidic (3) moderately basic	equal to 13 at 298 K. T	he solution will be (2) highly basic (4) unpredictable	
11.	What would be $[H^+] = (1) 0.6 \times 10^{-4}$	of 0.006 M benzoic act (2) 6×10 ⁻⁴	id (K = 6×10^{-5}) (3) 0.6×10^{-3}	(4) 3.6×10 ⁻⁴
4.4	SALTS, TYPES OF (A) SALT : Salts	SALT AND CONJU are regarded as comp comes from a base	GATE THEORY pounds made up of po	sitive and negative ions. The

positive part comes from a base while negative part from an acid. Salts are ionic compounds.

i.e. A Compound formed by the combination of acid and base is known as salt.

Acid + Base \rightarrow Salt + water; $\Delta H = -ve$

 $HCl + NaOH \rightarrow NaCl (Salt + H_2O)$

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(B) TYPES OF SALT

(a) Normal / general salts :- The salts formed by the loss of all possible protons. (Replaceable hydrogen ions as H⁺) are called normal salts. Such a salt doesnot contain either a replaceable hydrogen ion or a hydrgoxyl (OH⁻) group.

Ex. : NaCl, NaNO₃, K_2SO_4 , Ca₃(PO₄)₂, Na₂HPO₃, NaH₂PO₂ etc.

- (b) Acid salts :- Salts formed by incomplete neutralisation of poly basic acids are called acid salts. Such salts still contain one or more replaceable hydrogen ions (H⁺).
 Ex. NaHCO₃, NaHSO₄, NaH₂PO₄, Na₂HPO₄ etc.
- (c) Basic salts :- Salts are formed by incomplete neutalisation of poly acidic base are called basic salts. Such salts still contain one or more hydroxyl ion group.
 Ex. Zn(OH)Cl, Mg(OH)Cl, Fe(OH)₂Cl, Bi(OH)₂Cl etc.
- (d) **Double salts :-** The addition compounds formed by the combination of two simple salts are termed double salts. Such salts are stable in solid state only i.e. when dissolved in water they break into simple ions.

Ex. : $FeSO_4.(NH_4)_2SO_4.6H_2O$,

 $K_2SO_4.Al_2(SO_4)_3.24H_2O$ etc. (Potast alum)

(e) **Complex salts :-** These salts when dissolved in water give complex ions. Complex ions stable in solid state as well as in solutions.

Ex.: $K_4[Fe(CN)_6]$, $[Co(NH_3)_6]SO_4$, $[Ag(NH_3)_2Cl$ etc

(Ferrous ammonium sulphate)

(f) Mixed salts :- The salts which furnishes more than one type of cations or more than one type of anions when are called mixed salts.

These are formed by the neutralization of more than one acids and bases.

Ex. (i)
$$H_{2}SO_{4} + NaOH \longrightarrow NaHSO_{4} + H_{2}O$$

 $acidic salt$
 $NaHSO_{4} + KOH \longrightarrow NaKSO_{4} \longrightarrow Na^{+}K^{+}SO_{4}^{-2}$
 $acidic salt$
(ii) $Ca \swarrow OCl$
(iii) $Na \swarrow S$
(iv) $NH_{4} \longrightarrow PO_{4}$
(a) Types of general salts :
(i) SASB
(ii) SAWB
(iii) WASB
(iv) WAWB

(C) Conjugate acid-base pair :

(i) Conjugate acid-base pairs means difference between two species of only one H^+ or OH^- ion.

(ii) When an acid loses a proton, the residual part of its has a tendency toregain a proton. Therefore it behaves as a base.

î^† CH₃COOH H^+ CH_3COO^- + Weak acid Conjugate strong base $(K_a = 1.85 \times 10^{-5})$ or acceptor ion <u>}</u>^† NH₄OH NH_4^+ OH^{-} +Weak base Conjugate strong acid $(K_b = 1.85 \times 10^{-5})$ or acceptor ion HCl H^+ Cl^{-} +

 Strong acid
 Conjugate weak base (spectator ion)
Accepting tendency of $H^+ \propto 0$

 NaOH
 \longrightarrow Na⁺
 + OH^-

 Strong base
 Conjugate weak acid
(spectator ion)
 (spectator ion)

Note : Strong acids have weak conjugate base while weak acids have strong conjugate bases. Similarly, strong bases have weak conjugate acids while weak bases have strong conjugate acids.

(D) Relation between conjugate acid-base pair :-Example -CH₃COOH <u>}</u>^† CH₃COO⁻ H^+ Acid Conjugate base NH₄OH $\hat{f} \wedge \hat{f} NH_4^+ +$ OH^{-} Base Conjugate acid CH₃COOH CH₃COO⁻ Acid conjugate base $CH_3COOH + H_2O f CH_3COO^- + H_3O^+$ $CH_3COO^- + H_2O f CH_3COOH + OH^ \mathbf{K}_{\mathbf{a}} = \frac{[\mathbf{CH}_{3}\mathbf{COO}^{-}][\mathbf{H}_{3}\mathbf{O}^{+}]}{\mathbf{H}_{3}\mathbf{O}^{+}}$ $\mathbf{K}_{\mathrm{b}} = \frac{[\mathrm{CH}_{3}\mathrm{COO}^{-}][\mathrm{OH}^{-}]}{[\mathrm{CH}_{3}\mathrm{COO}^{-}]}$(i) ...(ii) [CH₃COOH] In both the reactions H_2O in excess quantity so active mass of H_2O is one Now multiply the equation (i) and (ii) $\mathbf{K}_{a} \times \mathbf{K}_{b} = [\mathbf{H}^{+}][\mathbf{OH}^{-}]$ $\overline{\mathbf{K}_{a}\times\mathbf{K}_{b}}=\mathbf{K}_{w}$ We know $[H^+] \times [OH^-] = K_W$ (Ionic product of water) $pK_a + PK_b = pK_w$ Taking -log on both sides $K_W = 10^{-14} \text{ or } pK_W = 14$ We know that for water at 25°C, $K_{a} \times K_{b} = 10^{-14}$ $pK_{a} + pK_{b} = 14$ So or Above relation is applicable only for conjugate acid-base pairs.

Illustrations

Illustratio	on 10 Which	salt is not an example o	f acidic salt :-	
(1)) HCOONa	(2) NaH_2PO_2	(3) NaHS	(4) (1) and (2) both
Solution	Ans. (4)			

Illustration 11 Calculate the number of ions in Bohr's salt [FeSO₄.(NH₄)₂SO₄.6H₂O] or Ferrous Ammonium Sulphate

Solution FeSO₄.(NH₄)₂SO₄.6H₂O \longrightarrow Fe⁺² + SO₄⁻² + 2 NH₄⁺ + SO₄⁻² + 6H₂O

Total number of ions = 5

4.5 HYDROLYSIS OF SALTS

Salt hydrolysis is defined as the process in which water reacts with cation or anion or both or a salt to change the concentration of H^+ and OH^- ions of water.

Salt hydrolysis is reverse process of neutralization.

Water + Salt $\frac{1}{2}$ \hat{T} Acid + Base ; $\Delta H = +ve$

(A) Hydrolysis of strong acid and strong base [SA – SB] types of salt –
 Ex. NaCl, BaCl₂, Na₂SO₄, KClO₄, BaSO₄, NaNO₃, KBr, KCl etc.

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 $NaCl + H_2O \longrightarrow NaOH + HCl$ $Na^+ + Cl^- + H_2O \longrightarrow Na^+ + OH^- + H^+ + Cl^ H_2O \stackrel{\circ}{\pm} \stackrel{\wedge}{\uparrow} H^+ + OH^- (It is not salt hydrolysis)$

- (i) Hydrolysis of salt of [SA SB] is not possible as both cation and anion are not reactive.
- (ii) Aqueous solution of these type of salt is neutral in nature. (pH = pOH = 7)
- (iii) pH of the solution is 7.
- (iv) No effect on litmus paper.

(B) Hydrolysis of strong acid and weak base [SA –WB] Types of salt

Ex. CaSO₄, NH₄Cl, (NH₄)₂SO₄, Ca(NO₃)₂, ZnCl₂, CuCl₂, CaCl₂, AgCl, AgI, AgNO₃ etc.

 $NH_4Cl + H_2O$ \div \uparrow $NH_4OH + HCl$

 $NH_4^+ + Cl^- + H_2O_{1}^{+} \uparrow NH_4OH + H^+ + Cl^-$

$$NH_4^+ + H_2O_{\frac{1}{2}}^{\uparrow\uparrow} NH_4OH + H^-$$

(i) In this type of salt hydrolysis, cation reacts with H_2O therefore called as cationic hydrolysis. The cation of the salt which has come from weak base is reactive.

(ii) Solution is acidic in nature as [H⁺] is increased.

(iii) pH of the solution is less than 7.

(iv) Solution turns blue litmus paper red.

 $K_h = Hydrolysis constant$

 K_W = Ionic product of water

K_a = Ionisation constant of acid

 $K_b =$ Ionisation constant of base

h = Degree of hydrolysis

- C = Concentration of salt (Concentration of ions)
- (a) Relation between K_h, K_W and K_b

 $B^+ + H_2O_{\frac{1}{2}}^{\uparrow} T BOH + H^+$

$$NH_4^+ + H_2O$$
 \hat{f}^* $NH_4OH + H^+$

Hydrolysis constant [K_h]

$$K_{h} = \frac{[NH_{4}OH][H^{+}]}{[NH_{4}^{+}]} \qquad \dots \dots (1)$$

For weak Base NH₄OH $\frac{2}{2}$ $^{+}$ NH₄⁺ + OH⁻

$$K_{b} = \frac{NH_{4}^{+}[OH^{-}]}{[NH_{4}OH]} \qquad \dots \dots \dots (2)$$

For water $H_2O_{\ddagger}^{\uparrow\uparrow}H^+ + OH^-$

$$K_{W} = [H^{+}][OH^{-}]$$
(3)

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

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

i.e.
$$K_h \times K_b = K_W$$

 $K_h = \frac{K_W}{K_b}$ (4)
(b) Degree of hydrolysis – Represented by h
 $NH_4^r + H_2O \frac{2}{7}^{\uparrow \uparrow} NH_4OH + H^+$
Initial concentration of salt C 0 0 0
 $K_h = \frac{[NH_4OH][H^+]}{[NH_4^r]} = \frac{Ch \times Ch}{C - Ch} = \frac{C^2h^2}{C(1 - h)} = \frac{Ch^2}{(1 - h)}$
Since $h < < <1$ then $(1 - h) \approx 1$
 \therefore $K_h = Ch^2$ (5)
 $h^2 = \frac{K_h}{C} \Rightarrow h = \sqrt{\frac{K_h}{C}}$ (6)
 \therefore $K_h = \frac{K_W}{K_b} \Rightarrow h = \sqrt{\frac{K_W}{C}}$ (7)
(c) pH of the solution : pH = -log[H^+]
 $[H^+] = Ch = C\sqrt{\frac{K_W}{K_b \times C}} \Rightarrow [H^+] = \sqrt{\frac{K_W \times C}{K_b}}$ (8)
Taking -log on the both sides
 $-log[H^+] = -log\sqrt{\frac{K_W \times C}{K_b}} \Rightarrow pH = -log(\frac{K_W \times C}{K_b})^{1/2}$
 $pH = -\frac{1}{2} [log K_W + logC - log K_b]$
 $pH = -\frac{1}{2} log K_W - \frac{1}{2} log C - \frac{1}{2} pK_b$
 $pH = 7 - \frac{1}{2} pK_b - \frac{1}{2} log C$ (9)
Hydrolysis of weak acid and strong base [WA - SB] types of salt –

(C) Hydrolysis of weak acid and strong base [WA - SB] types of salt – Ex. CH₃COONa, HCOONa, KCN, NaCN, K₂CO₃, BaCO₃, K₃PO₄ etc. CH₃COONa + H₂O $\ddagger \uparrow \uparrow$ CH₃COOH + NaOH CH₃COO⁻ + Na⁺ + H₂O $\ddagger \uparrow \uparrow$ CH₃COOH + Na⁺ + OH⁻ CH₃COO⁻ + H₂O $\ddagger \uparrow \uparrow$ CH₃COOH + Na⁺ + OH⁻ CH₃COO⁻ + H₂O $\ddagger \uparrow \uparrow$ CH₃COOH + OH⁻

(i) In this type of salt hydrolysis, anion reacts with water therefore called as anionic hydrolysis. The anion of the salt which has come from weak acid is reactive.

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(ii) Solution is basic in nature as [OH⁻] increases. (iii) pH of the solution is greater than 7. (iv) Solution turns red litmus paper blue. Relation between K_h, K_W, and K_a **(a)** $CH_{3}COO^{-} + H_{2}O \text{ f} \text{ f} CH_{3}COOH + OH^{-}$ $K_{h} = \frac{[CH_{3}COOH][OH^{-}]}{[CH_{3}COO^{-}]}$(1) For weak acid CH₃COOH $\frac{1}{2}$ \uparrow CH₃COO⁻ + H⁺ $K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$(2) For water $H_2O_{\frac{1}{2}}^{\uparrow} \uparrow H^+ + OH^-$(3) $K_{W} = [H^{+}][OH^{-}]$ Now multiply eq. (1) \times eq. (2) = eq. (3) $\frac{[CH_{3}COOH][OH^{-}]}{[CH_{3}COO^{-}]} \times \frac{[CH_{3}COO^{-}][H^{+}]}{[CH_{3}COOH]} = [H^{+}][OH^{-}]$ $\underline{\mathbf{K}_{\mathrm{h}} \times \mathbf{K}_{\mathrm{a}}} = \mathbf{K}_{\mathrm{W}}$ $K_{h} = \frac{K_{W}}{K_{a}}$(4) Degree of hydrolysis (h) : **(b)** $CH_3COO^- + H_2O_{\frac{1}{2}}^{+} \uparrow^{+} CH_3COOH + OH^-$ 0 Initial concentration of salt 0 С Ch Ch $K_{h} = \frac{[CH_{3}COOH][OH^{-}]}{[CH_{3}COO^{-}]} = \frac{Ch \times Ch}{C - Ch} = \frac{C^{2}h^{2}}{C(1-h)}$ $K_{h} = \frac{Ch^{2}}{(1-h)}$ Since h < < < 1 then $(1 - h) \approx 1$ $K_{h} = Ch^{2} \qquad \dots \dots (5)$ $h^{2} = \frac{K_{h}}{C} \qquad \text{or } h = \sqrt{\frac{K_{h}}{C}} \qquad \dots \dots (6)$ · . pH of the solution (c) $[OH^-] = Ch$ $[OH^{-}] = C \times \sqrt{\frac{K_{w}}{K_{a} \times C}} \text{ or } [OH^{-}] = \sqrt{\frac{K_{w} \times C}{K_{a}}} \dots (8)$ taking -log on both sides

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$$-\log[OH^{-}] = -\log\left(\frac{K_{W}.C}{K_{a}}\right)^{1/2}$$

$$pOH = \frac{1}{2} [\log K_{W} + \log C - \log K_{a}]$$

$$pOH = \frac{1}{2} pK_{W} - \frac{1}{2} pK_{a} - \frac{1}{2} \log C \quad \text{or } pOH = 7 - \frac{1}{2} pK_{a} - \frac{1}{2} \log C$$

$$\Theta \quad pH + pOH = 14$$

$$pH = 14 - pOH$$

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

(D) Hydrolysis of weak acid and weak base (WA - WB) type of salt :

Ex. CH₃COONH₄, AgCN, NH₄CN, CaCO₃, [NH₄]₂CO₃, ZnHPO₃ etc CH₃COONH₄ + H₂O $\stackrel{2}{+}$ $\stackrel{\wedge}{\uparrow}$ CH₃COOH + NH₄OH WB

 $CH_3COO^- + NH_4^+ + H_2O_{1}^{\uparrow} CH_3COOH + NH_4OH$

(i) Maximum hydrolysis occurs of the salt of (WA – WB) as both the cation and anion are reactive.

(ii) Solution is almost neutral but it may be acidic or basic depending upon the nature of acid base

(iii) pH of the solution is near to 7.

For WA – WB types of salt :

Terms	$K_a > K_b$	$K_b > K_a$	$\mathbf{K}_{\mathbf{a}} = \mathbf{K}_{\mathbf{b}}$
1. Hydrolysis	Cation anionic	Anionic-cationic	Neutral hydrolysis
2. Nature	Acidic	Basic	Neutral
3. pH	pH < 7	pH > 7	pH = 7

```
(a) Relation between K_h, K_W, K_a and K_b

CH_3COO^- + NH_4^+ + H_2O \stackrel{+}{2} \stackrel{\wedge}{\uparrow} CH_3COOH + NH_4OH

K_h = \frac{[CH_3COOH][NH_4OH]}{[CH_3COO^-][NH_4^+]} .....(1)

For weak base

NH_4OH \stackrel{+}{2} \stackrel{\wedge}{\uparrow} NH_4^+ + OH^-

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

For weak acid

CH_3COOH \stackrel{+}{2} \stackrel{\wedge}{\uparrow} CH_3COO^- + H^+

K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} .....(3)
```

For water

OII

 $H_2O_{\uparrow}^{\uparrow} H^+ + OH^ K_W = [H^+][OH^-]$(4) Multiply Eq. (1)×Eq. (2)×Eq.(3) = Eq.(4)

NTT T+

тт

(b) Degree of hydrolysis (h) -

$$pH = -\frac{1}{2} [logK_w] - \frac{1}{2} [logK_a] - \frac{1}{2} [-logK_b]$$

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

$$pH = 7 + \frac{1}{2}pK_{a} - \frac{1}{2}pK_{b}$$
.....(9)

• Degree of hydrolysis, pH of weak acid and weak base [WA – WB] type salts do not depend on the concentration of salt.

•	1)	

	SA SB salts	SA WB salts	WA WB salts	WA WB salts
1.	Neutral	Acidic solution	Basic solution	Almost neutral
	solution			solution
2.	No	Cationic hydrolysis	Anionic hydrolysis	Hydrolysis by both
	Hydrolysis			cation and anion
3.	-	$K_{h} = \frac{K_{W}}{K_{b}}$	$K_{h} = \frac{K_{W}}{K_{a}}$	$K_{h} = \frac{K_{W}}{K_{a} \times K_{b}}$
4.	-	$h = \sqrt{\frac{K_{w}}{K_{b}.C}}$	$h = \sqrt{\frac{K_{w}}{K_{a}.C}}$	$\mathbf{h} = \sqrt{\frac{\mathbf{K}_{\mathrm{W}}}{\mathbf{K}_{\mathrm{a}}.\mathbf{K}_{\mathrm{b}}}}$
5.	-	$[H^+] = Ch = \frac{K_w.C}{K_b}$	$[OH^{-}] = C.h = \sqrt{\frac{K_{w}.C}{K_{a}}}$	$[H^{+}] = K_{a}.h = $ $\sqrt{\frac{K_{w}.K_{a}}{K_{b}}}$
6.	-	$pH = 7 - \frac{1}{2}pK_b - \frac{1}{2}\log C$	$pH = 7 + \frac{1}{2}pK_a + \frac{1}{2}\log C$	$pH = 7 + \frac{1}{2} pK_a -$
				$\frac{1}{2} \mathbf{p} \mathbf{K}_{\mathbf{b}}$

Illustrations

 Illustration 12. What is the pH of 1 M CH₃COONa solution? Ka of acetic acid = 1.8×10^{-5} , K_w = 10^{-14} mol² L⁻²

 (1) 2.4
 (2) 3.6
 (3) 4.8
 (4) 9.4

 Solution Ans. (4)

Illustration 13. Calculate the degree of hydrolysis of a mixture containing 0.1N NH₄OH and 0.1N HCN. If $K_a = 10^{-5}$ and $K_b = 10^{-5}$

Solution Salt is [WA – WB]

$$h = \sqrt{\frac{K_{w}}{K_{a} \times K_{b}}} = \sqrt{\frac{10^{-14}}{10^{-5} \times 10^{-5}}} = \sqrt{10^{-14} \times 10^{+10}} = \sqrt{10^{-4}} = 10^{-2}$$

Illustration 12. Assertion : An aqueous solution of NH_4NO_3 is acidic in characters.Reason : NH_4NO_3 in an aqueous solution undergoes anionic hydrolysis.(1) A(2) B(3) C(4) D

Solution Ans. (3)

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1. When sodium acetate (CH ₃ COONa) is added to aqueous solution of acetic acid (CH ₃ COOI the- (1) the pH value becomes zero (2) pH value remains unchanged (3) pH value decreases (4) pH value increases 2. Which of the following cations is not hydrolyzed in aqueous solution? (i) Mg ²⁺ (ii) Ca ²⁺ (iii) Na ⁺ (iv) K ⁺ (1) (i), (ii) (2) (iii), (iv) (3) (i), (iii), (iv) (4) (i), (iii), (iii) 3. Which of the anions is not hydrolyzed in aqueous solution? (i) Cl ⁻ (ii) NO ₃ (iii) Br ⁻ (iv) ClO ₄ (1) (i), (ii), (iii), (iv) (2) (ii), (iv) (3) (i), (ii), (iv) (2) KCl (3) NH ₄ NO ₃ (4) FeCl ₃ .6H ₂ O 5. Which of the following salts does not undergo hydrolysis? (1) KCN (2) KCl (3) NH ₄ NO ₃ (4) FeCl ₃ .6H ₂ O 5. Which of the following salts undergoes anionic hydrolysis? (1) AlCl ₃ (2) CuSO ₄ (3) Na ₂ CO ₃ (4) NH ₄ Cl 6. For cationic hydrolysis, pH is given by - (1) pH = $\frac{1}{2}$ pK _w + $\frac{1}{2}$ pK _a + $\frac{1}{2}$ logC (2) pH = $\frac{1}{2}$ pK _w + $\frac{1}{2}$ pK _b - $\frac{1}{2}$ logC (3) pH = $\frac{1}{2}$ pK _w + $\frac{1}{2}$ pK _a + $\frac{1}{2}$ pK _b (4) pH = $\frac{1}{2}$ pK _w + $\frac{1}{2}$ pK _b + $\frac{1}{2}$ logC 7. Which of the following salts is neutral in water? (1) KCl (2) NH ₄ SO ₃ (3) NH ₄ CN (4) NH ₄ OH 4.6 SOLUBILITY AND SOLUBILITY PRODUCT (K _{SP}) (a) Definition At constant temperature the maximum number of moles of solute which c			BEGINNE	CR'S BOX-2		
the- (1) the pH value becomes zero (2) pH value remains unchanged (3) pH value decreases (4) pH value increases 2. Which of the following cations is not hydrolyzed in aqueous solution? (i) Mg ²⁺ (ii) Ca ²⁺ (iii) Na ⁺ (iv) K ⁺ (1) (i), (ii) (iii), (iv) (2) (iii), (iv) (3) (i), (iii), (iv) (4) (i), (ii), (iii) 3. Which of the anions is not hydrolyzed in aqueous solution? (i) Cl ⁻ (ii) NO ₃ (iii) Br ⁻ (iv) ClO ₄ (1) (i), (iii), (iv) (2) (ii), (ivi) (3) (i), (iii), (ivi) (2) (ii), (ivi) (3) (i), (iii), (ivi) (4) (ii), (iv) (3) (i), (iii), (ivi) (4) (ii), (iv) (3) (i), (iii), (ivi) (2) KCl (3) NH ₄ NO ₃ (4) FeCl ₃ .6H ₂ O 5. Which of the following salts undergoes anionic hydrolysis? (1) KCN (2) KCl (3) NH ₄ NO ₃ (4) FeCl ₃ .6H ₂ O 5. Which of the following salts undergoes anionic hydrolysis? (1) AlCl ₃ (2) CuSO ₄ (3) Na ₂ CO ₃ (4) NH ₄ Cl 6. For cationic hydrolysis, pH is given by- (1) pH = $\frac{1}{2}$ pKw + $\frac{1}{2}$ pKa + $\frac{1}{2}$ logC (2) pH = $\frac{1}{2}$ pKw + $\frac{1}{2}$ pKb - $\frac{1}{2}$ logC (3) pH = $\frac{1}{2}$ pKw + $\frac{1}{2}$ pKa + $\frac{1}{2}$ pKb (4) pH = $\frac{1}{2}$ pKw + $\frac{1}{2}$ pKb + $\frac{1}{2}$ logC 7. Which of the following salts is neutral in water? (1) KCl (2) NH ₄ SO ₃ (3) NH ₄ CN (4) NH ₄ OH 4.6 SOLUBILITY AND SOLUBILITY PRODUCT (K _{SP}) (A) Definition At constant temperature the maximum number of moles of solute which c	1.	When sodium acetat	e (CH ₃ COONa) is add	led to aqueous solution	n of acetic acid (CH ₃ COOH),	
(1) the pH value becomes zero (2) pH value remains unchanged (3) pH value decreases (4) pH value increases 2. Which of the following cations is not hydrolyzed in aqueous solution? (i) Mg ²⁺ (ii) Ca ²⁺ (iii) Na ⁺ (iv) K ⁺ (1) (i), (ii) (ii), (iii) (iv) (2) (iii), (iv) (3) (i), (iii), (iv) (4) (i), (ii) Br ⁻ (iv) ClO ₄ ⁻ (1) (i), (iii), (iv) (2) (ii), (iii), (iv) (3) (i), (ii), (iv) (2) (ii), (iii), (iv) (3) (i), (iii), (iv) (2) (ii), (iv) (3) (i), (iii), (iv) (2) KCl (3) NH ₄ NO ₃ (4) FeCl _{3.6} H ₂ O 5. Which of the following salts undergoes anionic hydrolysis? (1) ACl ₃ (2) CuSO ₄ (3) Na ₂ CO ₃ (4) NH ₄ Cl 6. For cationic hydrolysis, pH is given by - (1) pH = $\frac{1}{2}$ pK _w + $\frac{1}{2}$ pK _a + $\frac{1}{2}$ logC (2) pH = $\frac{1}{2}$ pK _w + $\frac{1}{2}$ pK _b - $\frac{1}{2}$ logC (3) pH = $\frac{1}{2}$ pK _w + $\frac{1}{2}$ pK _a + $\frac{1}{2}$ pK _b (4) pH = $\frac{1}{2}$ pK _w + $\frac{1}{2}$ logC 7. Which of the following salts is neutral in water? (1) KCl (2) NH ₄ SO ₃ (3) NH ₄ CN (4) NH ₄ OH 4.6 SOLUBILITY AND SOLUBILITY PRODUCT (K _{SP}) (a) Definition At constant temperature the maximum number of moles of solute which c		the-				
(3) pH value decreases (4) pH value increases (4) pH value increases (i) Mg ²⁺ (ii) Ca ²⁺ (iii) Na ⁺ (iv) K ⁺ (1) (i), (ii), (iii), (iv) (2) (iii), (iv) (3) (i), (ii), (iv) (2) (ii), (iii), (iv) (3) (i), (ii), (iii) (iv) (2) (ii), (iii), (iv) (3) (i), (ii), (iii) (4) (ii), (iv) (4) (ii), (iv) (5) (H) cf the following salts does not undergo hydrolysis? (1) KCN (2) KCl (3) NH ₄ NO ₃ (4) FeCl _{3.6} H ₂ O (1) AlCl ₃ (2) CuSO ₄ (3) Na ₂ CO ₃ (4) NH ₄ Cl (4) For cationic hydrolysis, pH is given by - (1) pH = $\frac{1}{2}$ pK _w + $\frac{1}{2}$ pK _a + $\frac{1}{2}$ logC (2) pH = $\frac{1}{2}$ pK _w + $\frac{1}{2}$ pK _b - $\frac{1}{2}$ logC (3) pH = $\frac{1}{2}$ pK _w + $\frac{1}{2}$ pK _a + $\frac{1}{2}$ pK _b (4) pH = $\frac{1}{2}$ pK _w + $\frac{1}{2}$ pK _b + $\frac{1}{2}$ logC (3) pH = $\frac{1}{2}$ pK _w + $\frac{1}{2}$ pK _a + $\frac{1}{2}$ pK _b (4) pH = $\frac{1}{2}$ pK _w + $\frac{1}{2}$ pK _b + $\frac{1}{2}$ logC (3) pH = $\frac{1}{2}$ pK _w + $\frac{1}{2}$ pK _a + $\frac{1}{2}$ pK _b (4) pH = $\frac{1}{2}$ pK _w + $\frac{1}{2}$ pK _b + $\frac{1}{2}$ logC (3) pH = $\frac{1}{2}$ pK _w + $\frac{1}{2}$ pK _a + $\frac{1}{2}$ pK _b (4) pH = $\frac{1}{2}$ pK _w + $\frac{1}{2}$ pK _b + $\frac{1}{2}$ logC (4) NH ₄ OH (5) SOLUBILITY AND SOLUBILITY PRODUCT (K _{SP}) (6) Definition At constant temperature the maximum number of moles of solute which c		(1) the pH value beco	omes zero	(2) pH value remains	unchanged	
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3. Which of the anions is not hydrolyzed in aqueous solution? (i) CT (ii) NO ₃ (iii) Br ⁻ (iv) ClO ₄ (1) (i), (iii), (iv) (2) (ii), (iii), (iv) (3) (i), (iii) (iii) (4) (ii), (iv) 4. Which of the following salts does not undergo hydrolysis? (1) KCN (2) KCl (3) NH ₄ NO ₃ (4) FeCl ₃ .6H ₂ O 5. Which of the following salts undergoes anionic hydrolysis? (1) AlCl ₃ (2) CuSO ₄ (3) Na ₂ CO ₃ (4) NH ₄ Cl 6. For cationic hydrolysis, pH is given by - (1) pH = $\frac{1}{2}$ pK _w + $\frac{1}{2}$ pK _a + $\frac{1}{2}$ logC (2) pH = $\frac{1}{2}$ pK _w + $\frac{1}{2}$ pK _b - $\frac{1}{2}$ logC (3) pH = $\frac{1}{2}$ pK _w + $\frac{1}{2}$ pK _a + $\frac{1}{2}$ pK _b (4) pH = $\frac{1}{2}$ pK _w + $\frac{1}{2}$ pK _b + $\frac{1}{2}$ logC 7. Which of the following salts is neutral in water? (1) KCl (2) NH ₄ SO ₃ (3) NH ₄ CN (4) NH ₄ OH 4.6 SOLUBILITY AND SOLUBILITY PRODUCT (K _{SP}) (a) Definition At constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which cons		(3) (i), (ii), (iii), (iv)		(4) (i), (ii), (iii)		
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(1) AlCl ₃ (2) CuSO ₄ (3) Na ₂ CO ₃ (4) NH ₄ Cl 6. For cationic hydrolysis, pH is given by - (1) pH = $\frac{1}{2}$ pK _w + $\frac{1}{2}$ pK _a + $\frac{1}{2}$ logC (2) pH = $\frac{1}{2}$ pK _w + $\frac{1}{2}$ pK _b - $\frac{1}{2}$ logC (3) pH = $\frac{1}{2}$ pK _w + $\frac{1}{2}$ pK _a + $\frac{1}{2}$ pK _b (4) pH = $\frac{1}{2}$ pK _w + $\frac{1}{2}$ pK _b + $\frac{1}{2}$ logC 7. Which of the following salts is neutral in water? (1) KCl (2) NH ₄ SO ₃ (3) NH ₄ CN (4) NH ₄ OH 4.6 SOLUBILITY AND SOLUBILITY PRODUCT (K _{SP}) (A) SOLUBILITY (a) Definition At constant temperature the maximum number of moles of solute which c	5.	Which of the followi	ng salts undergoes anic	onic hydrolysis?		
 6. For cationic hydrolysis, pH is given by - (1) pH = ¹/₂ pK_w + ¹/₂ pK_a + ¹/₂ logC (2) pH = ¹/₂ pK_w + ¹/₂ pK_b - ¹/₂ logC (3) pH = ¹/₂ pK_w + ¹/₂ pK_a + ¹/₂ pK_b (4) pH = ¹/₂ pK_w + ¹/₂ pK_b + ¹/₂ logC 7. Which of the following salts is neutral in water? (1) KCl (2) NH₄SO₃ (3) NH₄CN (4) NH₄OH 4.6 SOLUBILITY AND SOLUBILITY PRODUCT (K_{SP}) (A) Definition At constant temperature the maximum number of moles of solute which characterized is product to obtain 1 litra of a details (in product of poly) is called a solution (in poly). 		(1) AlCl ₃	(2) $CuSO_4$	$(3) \operatorname{Na_2CO_3}$	(4) NH ₄ Cl	
(1) $pH = \frac{1}{2}pK_W + \frac{1}{2}pK_a + \frac{1}{2}logC$ (2) $pH = \frac{1}{2}pK_W + \frac{1}{2}pK_b - \frac{1}{2}logC$ (3) $pH = \frac{1}{2}pK_W + \frac{1}{2}pK_a + \frac{1}{2}pK_b$ (4) $pH = \frac{1}{2}pK_W + \frac{1}{2}pK_b + \frac{1}{2}logC$ 7. Which of the following salts is neutral in water? (1) KCl (2) NH ₄ SO ₃ (3) NH ₄ CN (4) NH ₄ OH 4.6 SOLUBILITY AND SOLUBILITY PRODUCT (K _{SP}) (A) SOLUBILITY (a) Definition At constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature tempera	6.	For cationic hydrolys	sis, pH is given by -			
(c) $PP = \frac{1}{2} PP = \frac{1}{2}$		(1) $pH = \frac{1}{p}K_w + \frac{1}{p}$	$pK_{a} + \frac{1}{-}\log C$	(2) $pH = \frac{1}{pK_w} + \frac{1}{2}$	$pK_{\rm b} - \frac{1}{2}\log C$	
(3) $pH = \frac{1}{2}pK_w + \frac{1}{2}pK_a + \frac{1}{2}pK_b$ (4) $pH = \frac{1}{2}pK_w + \frac{1}{2}pK_b + \frac{1}{2}\log C$ 7. Which of the following salts is neutral in water? (1) KCl (2) NH ₄ SO ₃ (3) NH ₄ CN (4) NH ₄ OH 4.6 SOLUBILITY AND SOLUBILITY PRODUCT (K _{SP}) (A) SOLUBILITY (a) Definition At constant temperature the maximum number of moles of solute which c			2			
 2¹ 2¹ 2¹ 2¹ 2¹ 2¹ 2¹ 2¹		(3) $pH = \frac{1}{2}pK_W + \frac{1}{2}$	$pK_a + \frac{1}{2}pK_b$	(4) $pH = \frac{1}{2}pK_W + \frac{1}{2}$	$pK_b + \frac{1}{2}\log C$	
 7. Which of the following salts is neutral in water? (1) KCl (2) NH₄SO₃ (3) NH₄CN (4) NH₄OH 4.6 SOLUBILITY AND SOLUBILITY PRODUCT (K_{SP}) (A) SOLUBILITY (a) Definition At constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature temperature temperature for a solution (i.e., and the solution) is constant temperature temp		2 2 2	2	2 2 2	2	
 (1) KCl (2) NH₄SO₃ (3) NH₄CN (4) NH₄OH 4.6 SOLUBILITY AND SOLUBILITY PRODUCT (K_{SP}) (A) SOLUBILITY (a) Definition At constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature tempera	7.	Which of the followi	ng salts is neutral in w	ater?		
 4.6 SOLUBILITY AND SOLUBILITY PRODUCT (K_{SP}) (A) SOLUBILITY (a) Definition At constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature tempe		(1) KCl	(2) NH_4SO_3	$(3) \text{ NH}_4\text{CN}$	(4) NH ₄ OH	
 4.6 SOLUBILITY AND SOLUBILITY PRODUCT (K_{SP}) (A) SOLUBILITY (a) Definition At constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature the maximum number of moles of solute which constant temperature t						
(a) Definition At constant temperature the maximum number of moles of solute which c	4.6	SOLUBILITY AND) SOLUBILITY PRO	DUCT (K _{SP})		
the disc best to be the share in the maximum of a share of a share of the share of	(A)	SULUBILITY (a) Definition At constant temperature the maximum number of moles of solute which can				
be dissolved in a solvent to obtain 1 litre of solution (i.e. saturated solution) is call						
solubility.						
$S(M) = \frac{\text{Number of moles of solute}}{\text{Number of moles of solute}}$ $S = \frac{x}{100000000000000000000000000000000000$		Number of moles of solute $x = 1 L^{-1}$				
Volume of solution (L) $M_{W} \times V_{L}$ Hor L		5(11)	Volume of solution	$n(L) = M_W \times V_L$		
$\mathbf{S}_{g/\lambda} = \mathbf{S}_{\mathbf{M}} \times \text{molar mass}$		$S_{g/\lambda} =$	$S_M \times molar \; mass$			
COLDEN KEV POINTS			COLDENK	TV POINTS		

- Solubility does not depend on amount of substances and volume of solution where as depends on the following
 - (i) Temperature
 - (ii) Presence of common ion
 - (iii) Nature of solvent (Molecular wt. of AgCl = 143.5)

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(Molecular wt. of $BaSO_4 = 233$)

• Solubility can be expressed in terms of molarity.

(B) SOLUBILITY PRODUCT (K_{sp}) :

When a sparingly soluble salt such as AgCl is put into water, a very small amount of AgCl dissolves in water and most of the salt remains undissolved in its saturated solution.

• The salt AgCl is an electrolyte, its dissociation occurs in solution. Hence, the quantity of AgCl that dissolves in water dissociates into Ag^+ and Cl^- ions. Thus, in the saturated solution of AgCl an equilibrium exists between undissolved solid AgCl and its ions, Ag^+ and Cl^- ions.

$$\operatorname{AgCl}_{(s)}$$
 \ddagger $\operatorname{AgCl}_{\operatorname{Precipitation}}$ $\operatorname{Ag}_{(aq)}^{+} + \operatorname{Cl}_{(aq)}^{-}$

According to law of mass action $K = \frac{[Ag^+].[Cl^-]}{[AgCl]}$

Since, the concentration of undissolved solid AgCl is constant. Thus, the product K.[AgCl] gives another constant which is designated as Ksp.

So,
$$K.[AgCl] = [Ag^+].[Cl^-]$$
 \therefore $K_{sp} = [Ag^+].[Cl^-]$

At constant temperature product of concentrations of ions in a saturated solution of substance is called solubility product of that substance. (Saturated solution is that solution in which solid solute and the ions in solution remain in equilibrium with each other.

• \mathbf{K}_{sp} for CaCl₂ CaCl₂(s) $\frac{2}{3}$ \hat{T} Ca⁺²(aq) + 2Cl⁻(aq)

Solubility product in terms of concentration of ions $K_{sp} = [Ca^{+2}][Cl^{-}]^2$

• $\mathbf{K_{sp}}$ for AlCl₃ AlCl₃(s) $\frac{2}{3}$ $\frac{1}{7}$ $\frac{1}{7}$ Al⁺³(aq) + 3Cl⁻(aq)

Solubility product in terms of concentration of ions $K_{sp} = [AI^{+3}][CI^{-3}]^3$

• General form $AxBy \stackrel{2}{\ddagger} \stackrel{2}{\uparrow} XA^{+y}(aq) + yB^{-x}(aq)$ $K_{sp} = [A^{+y}]^{x}[B^{-x}]^{y}$

4.7 APPLICATION OF SOLUBILITY PRODUCT (K_{sp})

(A) To find out the solubility (S) :

- (i) K_{sp} of AB (Mono-mono, di-di, tri-tri, valency) type salt-
 - **Ex.** NaCl, BaSO₄, CH₃COONa, CaCO₃, NaCN, KCN, NH₄CN, NH₄Cl etc.

$$AB(s) \stackrel{2}{\pm} \stackrel{2}{\uparrow} \stackrel{*}{\dagger} A^+(aq) + B^-(aq)$$

a 0 0
(a-s) s s
$$K_{sp} = [A^+][B^-]$$

 $K_{sp} = s^2$ or $s = \sqrt{K_{sp}}$

Ex. CaCl₂, CaBr₂, K₂S, $(NH_4)_2SO_4$, K₂SO₄, K₂CO₃ etc

 $AB_2(s)$ $\ddagger \uparrow \uparrow A^{+2}(aq) + 2B^{-}(aq)$

a 0 0 (a-s) s 2s $K_{sp} = [A^{+2}][B^{-}]^2$ $K_{sp} = s \times (2s)^2 = s \times 4s^2 = 4s^3$

$$s = \left(\frac{K_{sp}}{4}\right)^{1/2}$$

K_{sp} of AB₃ or A₃B (Mono-tri or tri-mono valency) type salt-(iii) FeCl₂, AlCl₃, K₃PO₄ etc Ex. $AB_3(s) \stackrel{2}{\pm} \stackrel{2}{\uparrow} \stackrel{1}{\mp} A^{+3}(aq) + 3B^{-}(aq)$ a 0 0 (a–s) 3s $K_{sp} = [A^{+3}][B^{-}]^{3}$ $K_{sp} = s \times (3s)^{3} = 27s^{4}$ $s = \left(\frac{K_{sp}}{27}\right)^{1/4}$ (iv) K_{sp} of A₂B₃ or A₃B₂ (Di-tri or tri-di valency) type salt- $Al_2(SO_4)_3$, $Ba_3(PO_4)$ etc Ex. $A_2B_3(s)$ $\frac{1}{2}$ $\frac{1}{7}$ $\frac{1}{7}$ $2A^{+3}(aq) + 3B^{-2}(aq)$ a 0 0 $(a-s) = [A^{+3}]^2 [B^{-2}]^3$ 3s $K_{sp} = 2s \times 2s \times 3s \times 3s \times 3s = 108s^5$ $s = \left(\frac{K_{sp}}{108}\right)^{1/5}$ **(v) General form :** $A_x B_y(aq) \stackrel{2}{\ddagger} \stackrel{2}{\uparrow} \overset{1}{\uparrow} x A^{+y}(aq) + y B^{-x}(aq)$ 0 0 $a-s \\ K_{sp} = [A^{+y}]^{x} . [B^{-x}]^{y} \\ K_{sp} = (xs)^{x} . (ys)^{y} \\ K_{sp} = x^{x} . y^{y} . s^{(x+y)}$ XS ys

Illustrations

Illustration. 15 What will be the solubility product of following in terms of solubility (mol L^{-1}) (i) Al₂(SO₄)₃(s) (ii) Na₂KPO₄(s) (iii) NaKrbPO₄(s)

Solution

(i)

Al₂(SO₄)₃(s) $\ddagger \uparrow \uparrow 2Al^{+3} (aq) + 3SO_4^{-2} (aq)$ Ksp = $2^2 \times 3^2 \times (S)^{2+3} = 4 \times 27 \times S^5 = 108 S^5$

(ii) $Na_2KPO_4(s) \ddagger \uparrow \dagger 2Na^+(aq) + K^+(aq) + PO_4^{-3}(aq)$ $Ksp = 2^2 \times 1^1 \times 1^1(S)^{2+1+1} = 4s^4$

(iii) NaKRbPO₄(s)
$$\frac{2}{3}$$
 $\stackrel{\wedge}{}$ Na⁺(aq) + K⁺(aq) + Rb⁺(aq) + PO₄⁻³ (aq)
Ksp = 1¹ × 1¹ × 1¹ × 1¹ × (S)¹⁺¹⁺¹⁺¹ = S⁴

Illustration. 16 If solubility product of the base $M(OH)_3$ is 2.7×10^{-11} , the concentration of OH^{-1} will be

(1) 3×10^{-3}	(2) 3×10 ⁻⁴	(3) 10^{-3}	(4) 10^{-11}
------------------------	------------------------	---------------	----------------



|--|

Illustration. 17 Assertion : For a sparingly soluble salt, K_{sp} is the maximum dissolved value of solute in a solution. **Reason :** K_{sp} corresponds to the ionic product of the salt in a saturated solution. (1) A (2) B(3) C(4) D Solution Ans. (1) **Illustration. 18** The solubility of BaSO₄ in water is 1.07×10^{-5} mol dm⁻³. Estimate its solubility product. Solubility equilibrium for BaSO₄ is BaSO₄(s) $\frac{1}{2}$ $\frac{1}{7}$ Ba²⁺(aq) + SO²⁻(aq) Solution $K_{sp} = [Ba^{2+}][SO_4^{2-}]$ The solubility product is, If S is the molar solubility of BaSO₄ then $K_{sp} = S^2$ because x = 1 = y. Now, $S = 1.07 \times 10^{-5} M$ Hence, $K_{sp} = (1.07 \times 10^{-5})^2 = 1.145 \times 10^{-10}$ **Illustration. 19** The solubility product of AgBr is 5.2×10^{-13} . Calculate is solubility in mol dm⁻³ and g dm^{-3} . (Molar mass of AgBr = 187.8 g mol⁻¹) The solubility equilibrium of AgBr is $AgBr(s) \stackrel{+}{2} \stackrel{\wedge}{T} Ag^+(aq) + Br^-(aq)$ Solution and $K_{sp} = [Ag^+][Br^-] = S^2$ because x = 1 = y. The molar solubility S of AgBr is given by $S = \sqrt{K_{sn}} = \sqrt{5.2 \times 10^{-13}} = 7.2 \times 10^{-7} \text{ mol dm}^{-3}$ The solubility in g dm⁻³ = molar solubility (mol dm⁻³) × molar mass (g mol⁻¹)

Hence, solubility = $7.2 \times 10^{-7} \text{ (mol dm}^{-3}) \times 187.8 = 1.35 \times 10^{-4} \text{ g dm}^{-3}$.

(B) Condition of precipitation / Ionic product (IP or Q_{sp}):

Ionic product (IP) of an electrolyte is defined in the same way as K_{sp} . The only difference is that ionic product expression contains the initial concentration of ions or the concentration at any time where as the expression of K_{sp} contains only equilibrium concentration. Thus, for AgCl.

 $Q_{sp} = IP = [Ag^+], [CI^-]$ and $K_{sp} = [Ag^+]_{eq}[CI^-]_{eq}$

- Ionic product changes with concentration but K_{sp} does not. K_{sp} is applicable for saturated solution of the sparingly soluble electrolyte.
- To decide whether an ionic compound will precipitate, its K_{sp} is compared with the value of ionic product. The following three cases arise :

(i) $Q_{sp} < K_{sp}$: The solution is unsaturated and precipitation will not occur.

(ii) $Q_{sp} = K_{sp}$: The solution is saturated and solubility equilibrium exists.

(iii) $Q_{sp} > K_{sp}$: The solution is supersaturated and hence precipitation of the compound will occur.

Thus, a salt is precipitated when its ionic product exceeds the solubility product of the salt.

(C) Common ion effect on solubility :

Important point :- Solubility of substances always decreases in the presence of common ion. According to Le-Chatelier's principle on increasing common ion concentration equilibrium shifts in backward direction until the equilibrium is re-

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established so, the solubility of substances decreases but K_{sp} remains same because it is an equilibrium constant which depends only on temperature.

Illustrations

Illustration. 20 Find out the solubility of AgCl in the presence of C molar NaCl solution?

AgCl \hat{f} \hat{f} Ag⁺ Solution + Cl^{-} S S S (Let solubility of AgCl is S mol L^{-1}) $Ksp = [Ag^+][Cl^-]$ $Ksp = S^2$ In NaCl solution NaCl \longrightarrow Na⁺ Cl^{-} +С С С Let solubility of AgCl in the presence of NaCl solution is S' mol L^{-1} . $AgCl \hat{\ddagger} \hat{\uparrow} Ag^+ +$ Cl^{-} S' S' S' + CAccording to L.M.A. $Ksp = [Ag^{+}]' [Cl^{-}]'$ $Ksp = S'(S' + C) = S'^2 + S'C$ (Neglecting the higher power terms of S') $S' = \frac{Ksp}{C}$ Ksp = S'C

Illustration. 21 Find out the solubility of $CaCl_2$ solution in the presence of C NaCl solution? **Solution** $CaCl_2$ $\frac{2}{7}$ $^{+}$ Ca^{+2} + $2Cl^{-}$

S S 2S(Let solubility of $CaCl_2$ is S mol L⁻¹) $Ksp = [Ca^{+2}][Cl^{-}]^2 = 4s^3$ For NaCl solution NaCl \longrightarrow Na⁺ Cl^{-} +С C С Let solubility of $CaCl_2$ in the presence of NaCl solution is S' mol L⁻¹. $CaCl_2$ $\hat{\ddagger}$ $\hat{\uparrow}$ Ca^{+2} + $2Cl^{-}$ S' S' 2S' + CAccording to L.M.A. $Ksp = [Ca^{+2}]' [Cl^{-}]'^{2}$ $Ksp = S'(2S' + C)^2 = S' (4S'^2 + 4S'C + C^2)$ $Ksp = 4S'^3 + 4S'^2C + S'C^2$ (Neglecting the higher power terms of S') Ksp

 $\begin{array}{c} \mbox{Illustration. 22 Find out the solubility of NaCl in the presence of C CaCl_2 solution?} \\ \mbox{Solution} & CaCl_2 \longrightarrow Ca^{+2} + 2Cl^- \\ C & C & 2C \\ \mbox{Let solubility of NaCl in the presence of CaCl_2 solution is S' mol L^{-1}.} \end{array}$

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NaCl $\hat{\ddagger}$ $\hat{\uparrow}$ Na⁺ + Cl⁻ S' S' S' + 2C According to L.M.A. Ksp = [Na⁺]' [Cl⁻]' Ksp = S'(S' + 2C) = S'² + 2S'C S' = $\frac{Ksp}{2C}$

(Neglecting the higher power terms of S')

GOLDEN KEY POINTS

• Group precipitation of Salt

Group	Radicals	Condition for	Forms of precipitation
Group	Kaulcais	nrecipitation	rorms or precipitation
		(Group reagent)	
Zero	$Na^{+}, K^{+}, NH_{4}^{+}$	1-2 drops of	-
	7	CH ₃ COOH	
First	$Pb^{+2}, Hg^{+1}, Hg^{+2}, Ag^{+}$	By mixing of dilute	Chloride
		HCl	
Second II(A)	Pb ⁺² , Cu ⁺² , Hg ⁺² , Cd ⁺² , Bi ⁺³	H ₂ S gas passed in the	Sulphide
Second II(B)	As^{+3} , Sb^{+3} , Sn^{+2} , Sn^{+4}	presence of acidic	PbS, HgS, CuS, CdS, SnS,
		medium	SnS_2 , As_2S_3 , Sb_2S_3 , Bi_2S_3
Third	$Al^{+3}, Cr^{+3}, Fe^{+3}$	NH ₄ OH mixed in the	Hydroxide
		presence of NH ₄ Cl	$Al(OH)_3$, $Fe(OH)_3$, $Cr(OH)_3$
Fourth	Zn^{+2} , Ni ⁺² , Mn ⁺² , Co ⁺²	H_2S gas passed in	Sulphide
		presence of basic	MnS, CoS, NiS, ZnS
		medium	
Fifth	Ba^{+2} , Sr^{+2} , Ca^{+2}	$(NH_4)_2CO_3$ mixed in	Carbonate
		the presence of NH ₄ Cl	BaCO ₃ , SrCO ₃ , CaCO ₃
Sixth	Mg ⁺²	By mixing of Na ₂ HPO ₄	Hydrogen phosphate
			(MgHPO ₄)

• $Hg^{+1}(us) \rightarrow Unstable in aqueous solution$ [Stable in dimer form $(Hg_2^{+2}) \Rightarrow Hg_2Cl_2$]

$$Hg_{2}Cl_{2} \stackrel{2}{\ddagger} \stackrel{\wedge}{\uparrow} Hg_{2}^{+2} + 2Cl^{-}$$

$$S \qquad S \qquad 2S$$

$$K_{sp} = \left[Hg_{2}^{+2}\right]\left[Cl^{-}\right]^{2}$$

$$= (S)(2S)^{2}$$

$$Ksp = 4S^{3}$$

• Hg^{+2} (is) \rightarrow stable in aqueous solution $HgCl_2$ $\frac{2}{5}$ $\overset{\wedge}{\dagger}$ $Hg^{+2} + 2Cl^{-}$ S S 2S

$$Ksp = 4S^3$$

• For precipitation of II group, H_2S gas is passed in acidic medium to decrease S^{-2} concentration by common ion effect. So that ionic product of cations of group II and S^{-2} ions exceed the

solubility product of their corresponding metal sulphides. Therefore only the cations of group II gets precipitated. But the sulphides of the cation of the other groups (III, IV & V) are not precipitated under these conditions because their solubility products are quite high. When H_2S gas is directly passed through solution then IV group is also precipitated with II group.

$$H_2S_{\frac{1}{2}}^{\hat{1}} = 2H^+ + S^{-2}$$

 $Ksp_{II} < Ksp_{IV} < [radicals of II and IV group][S^{-2}]$

When H_2S gas pass in acidic medium [H⁺] then only II group radicals are precipitated.

 $H_2S \ \hat{\ddagger} \ \hat{\uparrow} \ DH^+ + S^{-2}$

 $Ksp_{II} < [radicals of II and IV group] [S^{-2}] < Ksp_{IV}$

- For precipitation of group III, NH₄OH is added in the presence of NH₄Cl to decrease the concentration of OH⁻ by common ion effect so that ionic product of cations of group III and hydroxides ions exceed the solubility product of their corresponding metal hydroxides and only group III cations will precipitated. On the other hand cations of group IV, V, and VI, which require large concentration of OH⁻ due to their high solubility product, will not be precipitated.
- In IV group, H_2S gas is passed in basic medium to increase S^{-2} ion concentration by odd ion effect, so that the ionic product of cations of group IV and S^{-2} ions exceed the solubility product of their corresponding metal sulphide and hence gets precipitated.

$$\begin{array}{cccc} H_2S & \swarrow & 2H^+ + S^{-2} \\ NH_4OH & \swarrow & NH_4^+ + OH^- \end{array} \rightarrow H_2O \end{array} Odd ion effect$$

$$So \quad [SO^{-2}] \uparrow$$

$$Var = (ID a dische of ereme WU [S^{-2}])$$

 $Ksp_{IV} < [Radicals of group IV] [S^{-2}]$

• In V group, order of K_{sp} is $BaCO_3 < SrCO_3 < CaCO_3$ but order of precipitation is $BaCO_3 > CaCO_3$.

(D) Precipitation of soap and salt (NaCl)

(i) **Precipitation of NaCl (common salt) :**

For the precipitation of NaCl, HCl gas passed in saturated solution of NaCl to increase the concentration of Cl^- ion by common ion, so ionic product of concentration of Na⁺ and Cl⁻ ion becomes more than Ksp of NaCl and NaCl easily precipitated.

Saturated solution of NaCl NaCl $\hat{\ddagger} \hat{} \hat{} Na^+ + Cl^-$

$$Ksp = [Na^+] [Cl^+]$$

By passing HCl gas $HCl \longrightarrow H^+ + Cl^-$ Due to common ion $Ksp < [Na^+] [Cl^-]^{\uparrow}$

(ii) **Precipitation of soap :**

Ex.

For precipitation of soap, NaCl mixed in saturated solution of soap to increase the concentration of Na⁺ ion by common ion. So ionic product of concentration of Na⁺ and stearate ions is more than Ksp of soap and soap is easily precipitated. $C_{17}H_{35}COONa$ (Sodium stearate)

Saturated solution of $C_{17}H_{35}COONa \Rightarrow C_{17}H_{35}COONa^+ \frac{1}{2} \stackrel{\wedge}{\uparrow} C_{17}H_{35}COO^- + Na^+$

By mixing NaCl solutionNaClDue to common ion $Ksp < [C_{1'}]$

NaCl \longrightarrow Na⁺ + Cl⁻ Ksp < [C₁₇H₃₅COO⁻] [Na⁺] \uparrow

	Illustrations
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Illustration 23. Solubility products of $M(OH)_3$ and 10^{-23} and 10^{-14} respectively. Which will be precipitated first on adding NH₄OH, If M^{+2} and M^{+3} both the ions are in solution? (1) M^{+2} (3) Both M^{+2} and M^{+3} together (4) Precipitation will not take place.

Solution Ans. (2)

Illustration 24. Solubility of CaCl₂ is 4×10^{-8} , then find out its K_{sp} and its new solubility in the presence of 10^{-2} M Ca(OH)₂.

Solution

 $CaCl_2$ \hat{f}^{\uparrow} Ca^{+2} + $2Cl^{-}$ 1 $\frac{1}{K_{sp}} = 4s^3 = 4(4{\times}10^{-8})^3 = 256{\times}10^{-24}$ (Initial solubility = s)(i) $Ca(OH)_2 \longrightarrow Ca^{+2} + 2OH^{-1}$ 0 C С 0 0 2C $CaCl_2$ $\hat{\ddagger}$ $\hat{\uparrow}$ $Ca^{+2} + 2OH^{-1}$ s'+C 2s' (New solubility = s') 1 $K_{sp} = [Ca^{+2}]' [Cl^{-}]^{2'}$ Ksp = $[s' + C][2s']^2 = 4s'^3 + 4s'^2C$ (s'³ = negligible) $Ksp = 4s'^2C$(ii) From equation (i) and (ii)

$$s'^{2} = \frac{Ksp}{4C} = \frac{256 \times 10^{-24}}{4 \times 10^{-2}} = 64 \times 10^{-22}$$

s' = 8×10¹¹ mol L⁻¹

4.8 FEW IMPORTANT POINTS

Isohydric solution :- If different- different solution has same pH are called isohydric **(A)** solution.

Sp. Point :- Isohydric condition for two given weak acids HA_1 and HA_2 which has concentration C_1 and C_2 and ionization constants are Ka₁ and Ka₂ respectively.

Then
$$[H^+]_1 = \sqrt{Ka_1C_1}$$
 and $[H^+]_2 = \sqrt{Ka_2C_2}$

According to given condition for isohydric solution pH of different solution is same. Hence $[H^+]_1 = [H^+]_2$

$$\sqrt{Ka_1C_1} = \sqrt{Ka_2C_2}$$

$$\underline{Ka_1C_1 = Ka_2C_2} \text{ or } \text{ If } n = 1 \text{ mole then } \boxed{\frac{Ka_1}{V_1} = \frac{Ka_2}{V_2}} \qquad \Theta \boxed{C \propto \frac{1}{V}}$$

Relative strength of Acids :- It indicates that how many times an acid is stronger than

(B)

the other acid

We know Strength of acid \propto [H⁺]

If there are two weak acids HA_1 and HA_2 which has concentration C_1 and C_2 , degree of ionization α_1 and α_2 and ionization constants Ka₁ and Ka₂ respectively then ration of their strength of acids.

 $[H^+] = C\alpha = \sqrt{KaC}$ We know

 a_1C

$$\frac{\text{Strength of weak acid HA}_1}{\text{Strength of weak acid HA}_2} = \frac{[\text{H}^+]_1}{[\text{H}^+]_2} = \frac{\text{C}_1\alpha_1}{\text{C}_2\alpha_2} = \frac{\sqrt{\text{K}}}{\sqrt{\text{K}}}$$

If $C_1 = C_2$

R.S. =
$$\frac{\text{Strength of weak acid HA}_1}{\text{Strength of weak acid HA}_2} = \sqrt{\frac{\text{Ka}_1}{\text{Ka}_2}} = \frac{\alpha_1}{\alpha_2}$$

Thus the relative strength of two acids of equimolar concentration can be compared by taking square root of the ratio of their ionization constants.

Illustrations

Illustration 2	25. Which of	the following solv	vents will undergo self-io	onization ?	
(1) H	$_2O$	(2) NH ₃	(3) HF	(4) All of these	
Solution	Ans. (4)				

Illustration 26. For two acids A and B, $pKa_1 = 1.2$, $pKa_2 = 2.8$ respectively in value, then which is true (1) A & B both are equally acidic (2) A is stronger than B

(3) B is stronger than A

(4) None of these

Solution Ans. (2)

Illustration 27. pH values of two acids A and B 4 and 5. The strengths of these two acids are related as :-

- (1) The strengths of the two acids cannot be compared
- (2) Acid B is 10 times stronger than acid A.
- (3) Strength of acid A : Strength of acid B = 4.5
- (4) Acid A is 10 times stronger than acid B.

Solution Ans. (4)

BEGINNER'S BOX-3

- The units of solubility product of silver chromate (Ag₂CrO₄) will be -1. (1) $mol^2 L^{-2}$ (2) $mol^{3}L^{-3}$ (3) mol L^{-1} (4) $mol^{-1} L$
- At a certain temperature, the solubility of the salt $A_x B_y$ is S moles per liter. The general 2. expression for its solubility product will be-(1)

)
$$K_{sp} = x^y y^x S^{x+y}$$
 (2) $K_{sp} = (xy)^{x+y} S^{x+y}$ (3) $K_{sp} = (x^x y^y) S^{x+y}$ (4) $K_{sp} = x^x y^y S^{x+y}$

The molar solubility of silver sulphate is 1.5×10^{-2} mol L⁻¹. The solubility product of the salt 3. will be -(2) 1.35×10^{-5} (3) 1.7×10^{-6} (4) 3.0×10^{-3} (1) 2.25×10^{-4}

The precipitate of CaF₂ ($K_{sp} = 1.7 \times 10^{-10}$) is obtained when equal volumes of the following are 4. mixed : (1) 10^{-3} M Ca²⁺ + 10^{-5} M F⁻ (2) 10^{-5} M Ca²⁺ + 10^{-3} M F⁻ (3) 10^{-2} M Ca²⁺ + 10^{-4} M F⁻ (4) 10^{-4} M Ca²⁺ + 10^{-4} M F⁻

If S₀, S₁, S₂ and S_a are the solubilities of AgCl in water, 0.01 M CaCl₂, 0.01 M NaCl and 0.5 M 5. AgNO₃ solutions, respectively, then which of the following is true?

(1) $S_0 > S_2 > S_1 > S_a$	(2) $S_0 = S_2 = S_1 > S_a$
(3) $S_a > S_1 > S_2 > S_0$	(4) $S_0 > S_2 > S_a > S_1$

6. Given K_{sp} (AgI) = 8.5×10⁻¹⁷. The solubility of AgI in 0.1 M KI solution is-(1) 0.1 M (2) 8.5×10^{-16} M (3) 8.5×10^{-17} M (4) 8.5×10^{-18} M

4.9 pH

1. INTRODUCTION

pH of some important substance :-

- (i) Blood \longrightarrow 7.4
- (ii) Tear \longrightarrow 7.4
- (iii) Gastric Juice \longrightarrow 1 to 3
- (iv) Soft drink \longrightarrow 2 to 4
- (v) Acidic rain $\longrightarrow 6$
- (vi) Milk \longrightarrow 6.3 to 6.6
- (vii) Water $\longrightarrow 7$

2. TYPES OF pH

- (i) pH of SA and SB. $[H^+] = C, [OH^-] = C$
- (ii) pH of WA and WB. $[H^+] = C\alpha$, $[OH^-] = C\alpha$
- (iii) pH of very dilute solution. (Consider H^+ & OH⁻ of H₂O also)
- (iv) pH of salt solution.

(a)	SA	SB	Type	Salt	(always 7)
(b)	SA	WB	Туре	Salt	(< 7)
(c)	WA	SB	Type	Salt	(>7)
(d)	WA	WB	Type	Salt	(Almost 7)

(3) pH of mixture of acid and base.

- (a) pH of mixture of strong acids :
 - $N_1V_1 + N_2V_2 + N_3V_3 + \dots = NV$
 - $V = Volume of final solution = V_1 + V_2 + V_3 + \dots$
 - N = Normality of final solution = $[H^+]$ in final solution.
- (b) pH of mixture of strong base :

 $N_1V_1 + N_2V_2 + N_3V_3 + \dots = NV$

- $V = Volume of final solution = V_1 + V_2 + V_3 + \dots$
- N = Normality of final solution = [OH⁻] in final solution.
- (c) pH of mixture of strong acids and strong bases : For acid :

$$N_1V_1 + N_2V_2 + N_3V_3 + \dots = (NV)_{Acid}$$

For base :

 $N_1V_1 + N_2V_2 + N_3V_3 + \dots = (NV)_{Base}$

- (i) If $(NV)_{Acid} > (NV)_{Base}$ then solution is acidic. $NV = (NV)_{Acid} - (NV)_{Base}$ and $[H^+] = N$
- (ii) If $(NV)_{Base} > (NV)_{Acid}$ then solution is basic. $NV = (NV)_{Base} - (NV)_{Base}$ and

 $[OH^-] = N$

- (iii) If $(NV)_{Acid} = (NV)_{Base}$ then solution is neutral.
- (d) pH of mixture of (WA + SB); when equivalent of WA > SB] pH of mixture of (SA + WB); when equivalent of WB > SA] $\downarrow\downarrow$

Gives rise to concept of buffer solution.

4.10 **BUFFER SOLUTION**

(A) **Definition :** A solution which resist the change in pH and pH does not change significantly on addition of small amount of strong acid or strong base is called buffer solution.

(B) Properties of buffer solution :

(i) The pH of buffer solution does not change appreciably upon the addition of small amount of either strong acid or strong base.

(ii) The pH of buffer solution does not depend on the volume of solution. Hence, solution can be diluted without change in pH.

(iii) The pH of buffer solution remains constant even if it is kept for a long time.

(C) Buffer solutions are used in

- (a) Qualitative analysis of mixture
- (b) Qualitative analysis of mixture
- (c) Digestion of food
- (d) Preservation of food and fruits.
- (e) Agriculture and diary product preservation.
- (f) Industrial process such as manufacture of paper, dyes inks paints, drugs etc.

TYPES OF BUFFER SOLUTION

- (A) Simple buffer solution
- (B) Mixed buffer solution :-
- (i) Acidic buffer solution (ii) Basic buffer solution
- (A) Simple buffer solution : Aqueous solution of weak acid-weak base (WA WB) types of salt.

Ex. CH₃COONH₄, NH₄CN, AgCN etc.

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

pH does not depend on concentration.

 $CH_3COO^- + NH_4^+ + H_2O_{1}^{+} ^{+} CH_3COOH + NH_4OH$

Buffer Action :

Case 1 When mixing of acid $[H^+]$ CH₃COO⁻ + H⁺ $\ddagger \uparrow \uparrow CH_3COOH$ NH₄OH + H⁺ $\ddagger \uparrow \uparrow NH_4^+ + H_2O$ Case 2 When mixing of base [OH⁻] $NH_4^+ + OH^- \hat{\ddagger} \hat{\uparrow} NH_4OH$ $CH_3COOH + OH^- \hat{\ddagger} \hat{\uparrow} CH_3COO^- H_2O$

(B) Mixed buffer solution :

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(i) Acidic buffer solution :- The solution in which weak acid and its conjugate base are present.

OR

Aqueous solution of mixture of weak acid and salt of same weak acid with any strong base is called acidic buffer solution.

Ex. CH₃COOH + CH₃COONa WA WASB CH₃COOH $\stackrel{?}{\downarrow} \stackrel{\land}{\uparrow} CH_3COO^- + H^+$ CH₃COONa \longrightarrow CH₃COO⁻ + Na⁺ $\left[CH_3COOH + CH_3COO^- \\ _{WA} CBase - \right] + Na^+ (Spectator ion)$

BUFFER ACTION :-

Case 1. If a small amount of acid is added to the buffer solution. The H^+ ions of the acid react with CH_3COO^- ions and produce CH_3COOH and most of the added H^+ ions are consumed so there is no appreciable change in pH.

 $CH_3COO^-_{(aq)} + H^+ \stackrel{2}{t} \stackrel{\wedge}{T} CH_3COOH_{(aq)}$

Case 2. If small amount of base is added to the buffer solution, the OH[−] ions are consumed by CH₃COOH

$$CH_3COOH_{(aq)} + OH_{(aq)} \stackrel{?}{t} \stackrel{\land}{t} CH_3COO_{(aq)} + H_2O_{(\lambda)}$$

So, there is no appreciable change in pH.

(a) pH of acidic buffer solution :

$$CH_{3}COOH + CH_{3}COONa$$

$$Acid + Salt$$

$$CH_{3}COOH \stackrel{2}{+} \stackrel{\wedge}{}^{+} CH_{3}COO^{-} + H^{+}$$

$$CH_{3}COONA \longrightarrow CH_{3}COO^{-} + Na^{+}$$

$$K_{a} = \frac{[CH_{3}COO^{-}][H^{+}]}{[CH_{3}COOH]}$$
or
$$[H^{+}] = \frac{Ka[CH_{3}COOH]}{[CH_{3}COO^{-}]} = \frac{Ka[Acid]}{[Conjugate base]}$$

$$pH = pKa - \log \frac{[Acid]}{[Conjugate base]} \text{ or } pH = pKa + \log \frac{[Conjugate base]}{[Acid]}$$

Henderson's equation :

nH – nKa	+ log [Salt] or	[Conjugate base]
pri – pra	$+\log\frac{1}{[\text{Acid}]}$	[Acid]

- [Conjugate base]_{eq} \propto [Salt] because CH₃COO⁻ mainly comes from salt since dissociation of CH₃COOH in presence of CH₃COONa is appreciably decreased.
- $[Acid]_{aq} \propto initial concentration of acid since it is almost unionized in presence of salt due to common ion effect.$

(b) **pH range of acidic buffer solution :** It depends on pK_a of acid and ratio of salt to acid

concentrations.

 $\begin{array}{lll} [CH_{3}COOH] & : & [CH_{3}COONa] \Rightarrow & pH = pKa + \log \frac{[CH_{3}COONa]}{[CH_{3}COOH]} \\ (i) & If, & 1 & : & 10 \Rightarrow & pH = pKa + \log \frac{10}{1} = pKa + 1 \\ (i) & If, & 10 & : & 1 \Rightarrow & pH = pKa - 1 \\ & & So pH range & & \\ & & pH = pKa \pm 1 \end{array}$

(c) Maximum buffer action condition of acidic buffer solution :

[CH₃COOH] : [CH₃COONa]

 $1 \qquad : \qquad 1 \qquad \Rightarrow pH + pK_a + \log \frac{1}{1}$ pH = pKa

(ii) **Basic buffer solution :**

Definition : The solution in which weak base and its conjugate acid are present . **OR** Aqueous solution of mixture of weak base and salt of same weak base with any strong acid is called basic buffer solution.

 $NH_{4}OH + NH_{4}Cl$ $NH_{4}OH \stackrel{2}{\ddagger} \stackrel{\wedge}{\uparrow} NH_{4}^{+} + OH^{-}$ $NH_{4}OH \stackrel{2}{\ddagger} \stackrel{\wedge}{\uparrow} NH_{4}^{+} + Cl^{-}$ $\left[NH_{4}OH + NH_{4}^{+} _{WB} C.acid \right] + Cl^{-} [Spectator ion]$

BUFFER ACTION :-

Ex.

Case 1. If a small amount of the acid is added to the buffer solution, the H^+ ions are consumed by NH_4OH .

 $NH_4OH(aq) + H^+(aq) \stackrel{2}{\ddagger} \stackrel{2}{\uparrow} MH_4^+(aq) + H_2O(\lambda)$

So there is no appreciable change in pH.

Case 2. If small amount of base is added to the buffer solution, the OH^- ions react with NH_4^+ ions to produce NH_4OH .

 $NH_4^+(aq) + OH^-(aq) \stackrel{\circ}{\ddagger} \stackrel{\wedge}{\uparrow} NH_4OH(aq)$

Hence most of the added OH⁻ ions are consumed. So there is no appreciable change in pH.

(a) **pOH of basic buffer solution :**

$$\frac{\rm NH_4OH + \rm NH_4Cl}{\rm Base}$$

 $NH_4OH \hat{\ddagger} \hat{\uparrow} MH_4^+ + OH^-$

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

$$K_{b} = \frac{[NH_{+}^{1}][OHT]}{[NH_{0}OH]} \text{ or } [OHT] = \frac{K_{b}[NH_{0}OH]}{[NH_{1}^{1}]}$$
Taking -log on both sides $pOH = pK_{b} + \log \frac{[NH_{1}^{1}]}{[NH_{1}OH]}$
Henderson's equation :
 $pOH = pK_{b} + \log \frac{[Salt]}{[Base]} \text{ or } \frac{[Conjugate acid]}{[Base]}$
(b) pOH range of basic buffer solution : It depends on pK_{b} of base and ratio of salt to base concentrations.
 $[NH_{0}OH]$: $[NH_{4}CI] \Rightarrow pOH = pK_{b} + \log \frac{[NH_{1}CI]}{[NH_{4}OH]}$
(i) If, 1 : $10 \Rightarrow pOH = pK_{b} + \log \frac{[NH_{1}CH]}{[NH_{4}OH]}$
(i) If, 1 : $10 \Rightarrow pOH = pK_{b} + 1$
(ii) If, $10 \div 1 \Rightarrow pOH = pK_{b} - 1$
So, pOH range : $\underline{pOH} = \underline{pK_{b} \pm 1}$
(c) Maximum buffer action condition of basic buffer solution :
 $NH_{4}OH$: $NH_{4}CI$
 $\frac{1}{pOH} = \underline{pK_{b}}$
3. BUFFFER CAPACITY
Definition:
(ii) It is defined as the number of moles of strong acid (or strong base) added to one litre of a buffer solution to change its pH by one unit.
(iii) It measures the effectiveness of a buffer.
(iii) Larger the value of buffer capacity more resistant is the solution to pH change.
Buffer capacity = Number of moles of acid or base added per litre
Change in pH of buffer solution
Buffer solution is one which has-
(1) reserved acid (2) reserved base (3) constant pH (4) pH equal to 7
2. Which of the following solutions cannot act as a buffer system?
(1) KH₂PO₄/H₂PO₄ (2) NaCO₄/HCO₄
(3) C₃H₃N/C₃H₃NHHCI (4) Na₂CO₃/NAHCO₃

An acidic buffer solution can be prepared by mixing equimolar amounts of(1) B(OH)₃ and Na₂B₄O₇.10H₂O
(2) NH₃ and NH₄Cl
(3) HCl and NaCl
(4) CH₃COOH and CH₃COONa

Which of the following salt solution will act as a buffer?
(1) CH₃COONH₄ (aq)
(2) NH₄Cl (aq)
(3) CH₃COONa (aq)
(4) NaCl (aq)

5. Which of the following combinations will make a buffer solutions?
(i) CH₃COONa (2mol) + HCl (1mol)
(ii) CH₃COOH (2 mol) + NaOH (1 mol)
(iii) CH₃COOH (1 mol) + CH₃COONa (1 mol)
(1) (iii)
(2) (i), (ii)
(3) (ii), (iii)
(4) (i), (ii), (iii)

6. The pH of blood circulating in a human body is maintained around 7.4 by the action of the buffer system-(1) CH₃COOH / CH₃COONa (2) NH₄Cl / NH₃ (3) H₂PO₄²⁻ (4) H₂CO₃/HCO₃⁻

4.11 INDICATOR

- (A) **Definition :-** An indicator is a substance that undergoes changes in its colour to show end point of an acid-base titration.
- Titration involves neutralization of an acid and base.

(B) Types of indicators :

(a) Acidic indicator (HIn)

Ex. Phenolphthalein (HPh)

HPh $\hat{f}_{\pm} \hat{f} H^+ + Ph^-$

pink

- (b) **Basic indicator (InOH)**
 - **Ex.** Methyl orange (MeOH)

Colourless

 $\begin{array}{cccc} MeOH & & & \uparrow & Me^+ & + & OH^- \\ Yellow & orange red & & \end{array}$

OSTWALD THEORY OF INDICATORS

(i) According to this theory, all th indicators are weak organic acid or base.

(ii) Every indicator has light colour in its unionized form and dark colour in ionized form.

(iii) Every indicator has one colour in acidic medium and an altogether different colour in basic medium due to common ion effect and odd ion effect.

Ex. Acidic indicator [HPh]

Case 1. HPh $\frac{2}{2}$ \hat{T} H⁺ + Ph⁻

In acidic medium $[H^+]$

[HPh] > [Ph⁻] Colourless due to common ion effect

Case 2. HPh $\frac{2}{2}$ $\hat{\uparrow}$ $H^+ + Ph^-$

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	In bas	sic medium [OH ⁻]		$[Ph^{-}] >$	[HPh]		
			Pink co	lour due	to odd ion effect		
(a)	pH of	f acidic indicator –					
	HIn 🗿	$\dot{T} H^+ + In^-$					
	K _a or	$K_{I} = \frac{[H^{+}][In^{-}]}{[HIn]}$					
	[H ⁺] =	$=\frac{K_{I}[HIn]}{[In^{-}]}$					
	Takin pH =	$p_{I} = \log on both sides$ $p_{I} = \log [HIn] + \log[1]$	n_]				
	pH =	$pK_{I} + \log \frac{[In^{-}]}{[HIn]}$]	pH = pk	$K_{I} + \log \frac{[\text{Ionised forr}]}{[\text{Unionised form}]}$	n] rm]	
(b)	рОН	of basic indicator –				-	
(~)	InOH	$1 \div 1 H^+ + OH^-$					
	K _b or	$K_{I} = \frac{[In^{+}][OH^{-}]}{[InOH]}$	pOH =	pK _I + lo	[Ionised form] [Unionised form]		
(c)	pH ra Indica	ange of indicators : ators show colour cha	nge for a	ı certain	pH range not at a	definite	e pH which is
	(i)	nH range of acidic i	ndicator	:			
	(-)	[HIn]	:	[In ⁻]			
		1	:	10			
		10	:	1	$pH = pK_1 \pm 1$		
	(ii)	pOH range of basic	indicato	r:			
		[InOH]	:	$[In^+]$			
		1	:	10			
	/ •••	10	:	1	$pOH = pK_1 \pm$	1	
	(iii)	Neutral condition for	or indicat	tors (No	working condition))	
		For acidic indicator	(T. ⁻ 1		For basic indi	cators	гт., ⁺ 1
			[In] 1		[InOH] 1	:	LIN J 1
		$nH = nK_1$	1		$nOH = nK_1$	•	1
		h h. I			$\mathbf{k} \circ \mathbf{m} = \mathbf{k} \mathbf{m} \mathbf{l}$		
C M	NT	e 1. (0.1	•		***	TT

S	5. No.	Name of indicator	Colour in	Colour in basic	Working pH range
			acidic medium	medium	of indicators
1		Methyl orange (MeOH)	Orange red	Yellow	3.1 to 4.5
2	2.	Methyl red	Red	Yellow	4.2 to 6.2
3	i.	Phenol red	Yellow	Red	6.2 to 8.2
4		Phenolphthalein (HPh)	Colourless	Pink	8.2 to 10.2

3. ACID-BASE TITRATION

	S. No. Type of titration		pH range of titration	Suitable indicators			
	1.	SA/SB	3 – 11	All indicators (MeOH, HPh etc.)			
	2.	SA/WB	3 – 7	Methyl orange (MeOH) and methyl red			
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3.	WA/SB	7 – 11	Phenolphthlein (HPh)
4.	WA/WB	6.5 – 7.5	Phenol red

Important points of titration :

- (i) Titration is always possible in two opposite solution. (i.e. one is acidic and other is basic).
- (ii) For any titration only that indicator is suitable if their working pH range is in pH range of titration.
- (iii) At the end point of titration equivalents of acids and bases are always same.
- (iv) At the equivalence point, nature of solution depends on the type of titration.

SA/SB	-	Neutral $(pH = 7)$
SA/WB	-	Acidic
WA/SB	-	Basic
WA/WB	-	Any one possible

4.12 ACID AND BASE

(1) **INTRODUCTION**

The earliest classification of substances into acids and bases was bases upon the characteristic properties possessed by each one of them. For example.

Acid was defined as a substance whose aqueous solution possesses the following characteristic properties :

- (i) conducts electricity,
- (ii) reacts with active metals like zinc, magnesium etc. to give hydrogen,
- (iii) turns blue litmus red.
- (iv) has a sour taste.
- (v) whose acidic properties disappear on reaction with a base.

Base was defined as a substance whose aqueous solution possessed the following the following characteristic properties :

- (i) conducts electricity,
- (ii) reacts with active metals like zinc, magnesium etc. to give hydrogen,
- (iii) turns red litmus blue,
- (iv) has a bitter taste
- (v) whose basic properties are destroyed on reaction with an acid.

The above definitions of acids and bases are called operational definitions as they are based certain operations (i.e. tests) to be performed on the substances. However, these have been replaced by conceptual definitions (put forward by Arrhenium, Bronsted-Lowry and Lewis) which go into the causes of the observed behavior, based upon structure and composition of the substances.

(2) Arrhenius Concept (1884)

(a) Acid :- According to this concept, those substance which produce free H⁺ ions in aqueous solution are called acid.

Example HCl, HNO₃, H₂SO₄, H₃PO₄, H₂CO₃, H₂S, CH₃COOH etc.

 $HCl + H_2O \longrightarrow H^+(aq) + Cl^-(aq)$

 $H_2SO_4 + H_2O \longrightarrow 2H^+(aq) + SO_4^{-2}(aq)$

 $CH_3COOH + H_2O \iff CH_3COO^-(aq) + H^+(aq)$

(b)	Base :- Those substances which produce free OH ⁻ ions in aqueous solution are
	called base.
	Example NaOH, KOH, Cs(OH), Rb(OH), NH ₄ OH, Ba(OH) ₂ , Ca(OH) ₂ ,
	$Al(OH)_3$ etc.
	$NaOH + H_2O \longrightarrow Na^+ (aq) + OH^-(aq)$
	$Ba(OH)_2 + H_2O \longrightarrow Ba^{+2}(aq) + 2OH^{-}(aq)$
(c)	Nature of water :- According to this concept nature of water is neutral and act
	as a solvent.
(d)	Neutralization Reaction :- Those reactions in which acid and base react
	together to form water molecule are called neutralization reactions.
	i.e. $Na^+ + OH^- + H^+ + Cl^- \longrightarrow NaCl + H_2O$
	$\mathrm{H^{+}} + \mathrm{OH^{-}} \longrightarrow \mathrm{H_{2}O}$
(e)	Strength of acids and bases :- This concept explains the strength of acids and
	bases depending upon the basis of degree of ionization.
	Example For strong electrolytes $\alpha \propto 100 \%$
	For weak electrolytes $\alpha \propto 100 \%$
(f)	Advantage :- This concept explains the acids and bases practically i.e. To find
	out the pH, ionization constant, hydrolysis constants, heat of neutralization etc.
(g)	Disadvantage :-
(8)	(i) It explains the behavior of acids and bases only in aqueous (water)
	solvents.
	(ii) It does not explain the stability of proton (H^+)

- (ii) It does not explain the stability of proton (H^+)
- (iii) It does not explain the conjugate acid-base theory.
- (iv) It does not explain the acidic and basic behavior of aprotic acid and base for example SO₂, CO₂, SiCl₄, AlCl₃ etc.

Illustrations

Illustration 29. Gaseous hydrogen chloride is a very poor conductor of electricity but a solution of hydrogen choride in water is a good conductor. This is due to the fact that :-

- (1) Water is a good conductor of electricity
- (2) Hydrogen chloride ionizes in water
- (3) A gas cannot conduct electricity but a liquid can
- (4) HCl does not obey Ohm's law where as the solution does
- **Solution** (2)

Illustration 30. Which is acid in the following pairs according to Arrhenius concept?

(1) HCl(g) and HCl(aq)

(2) $CH_3COOH(\lambda)$ and $CH_3COOH(aq)$

Solution (1) HCl (aq)

(3) **Bronsted-Lowry Concept (1923)**

It is based upon the exchange of proton.

(a) Acid :- According to this concept those substance which have tendency to donate the proton (H⁺) by any method in any solvent are called acid.

Example (i) neutral molecules – HCl, HNO₃, H_2SO_4 , H_2CO_3 , H_2S , CH₃COOH, H_3PO_3 etc.

(ii) Anions – HS^- , HCO_3^- , HSO_4^- , HPO_4^{-2} , H_2O etc.

- (iii) Cations NH_4^+ , H_3O^- , PH_4^+ , $CH_3COOH_2^+$ etc.
 - $[Al(H_2O)_6]^{+3}$, $[Ag(H_2O)_2]^{+1}$, $[Fe(H_2O)_6]^{+3}$ etc.
- Ex. 1 HCl (Acid) + H₂O (Solvent) \longrightarrow H₃O⁺ + Cl⁻
- \longrightarrow H₃O⁺ + S⁻² Ex. 2 HS^{-} (Acid) + H₂O (Solvent)
- \longrightarrow NH₃ + H₃O⁺ Ex. 3 NH_4^+ (Acid) + H₂O (Solvent)

Ex. 4 $[Al(H_2O)_6]^{+3}$ (Acid) + H₂O (Solvent) $\longrightarrow [Al(H_2O)_5OH]^{+2} + H_3O^{+1}$

- Base :- Those substance which have tendency to accept the proton by any method in **(b)** any solvent are called the bases.
 - (1) HS^- , HCO_3^- , HSO_4^- , $\text{H}_2\text{PO}_4^{-2}$, O^{-2} , SO_4^{-2} , CO_3^{-2} , CI^- , Br^- , Γ , CN^- etc.
 - (2) NH₃, RNH₂, R₂NH, R₃N, C₆H₅NH₂, C₅H₅N, H₂N-NH₂ etc.

Example

- (i) $HS^{-}(Base) + H_2O(Solvent) \longrightarrow H_2S + OH^{-}$
 - (ii) $NH_3(Base) + H_2O (Solvent) \longrightarrow NH_4^+ + OH^-$
 - (iii) NH₃ (Base) + H₂O (Solvent) \longrightarrow NH₄⁺ + OH⁻
 - (iv) CO_3^{-2} (Base) + H₂O (Solvent) \longrightarrow HCO₃ + OH⁻
- Nature of water :- According to this concept nature of water is amphoteric or (c) amphiprotic i.e. water can act as both acid and base.

(i) HCl (Acid) + H₂O (Base)
$$\longrightarrow$$
 Cl⁻ + H₃O⁺

(ii) NH₃ (Base) + H₂O (Acid)
$$\longrightarrow$$
 NH₄⁺ + OH

(d) Neutralization Reaction :- According to this concept those reaction in which acid and base react together and convert into their respective conjugate acid and base are called neutralization reactions.

	\checkmark	\checkmark		
Example	$HCl + NH_3$	\sim C	- +	${ m NH_4}^+$
	अम्ल क्षार	संयर्ग्	ो क्षार र	नंयग्मी आम्ल

Strength of acids and bases :- This concept explain the strength of acid and base **(e)** depending upon the basis of relative tendency to accept or donate the proton.

((i) HCl	O_4	(ix) H ₃	PO ₄		(xvii) l	H–OH		•
	(ii) HI		(x) HF			(xviii) C ₂ H ₅ –OH			
(1	(iii) <mark>HB</mark>	Br	(xi) CH ₃ COOH		H	(xix) C	C ₆ H ₅ NH	2	
((iv) H ₂ S	SO_4	(xii) H ₂ CO ₃		(xx) N	H ₃			
((v) HCl		(xiii) H ₂ S		(xxi) R–NH ₂				
((vi) HN	IO_3	(xiv) NH_4^+		(xxii) (CH_4			
((vii) H ₃	$\rm O^+$	(xv) Ho	CN		(xxiii)	H_2		
((viii) HSO ₄		(xvi) C ₆ H ₅ OH						
I	Example								
((i)	HCl	+	H_2O	<u>}</u> ^†	Cl^{-}	+	$H_{3}O^{+}$	
		Strong acid		Strong	base	Weak	base	Weak a	acid
((ii)	CH ₃ COOH	+	H_2O	<u>}</u> ^†	CH ₃ CO	00^{-1}	+	H_3O^-
		Weak acid		Weak	base	Strong	base		Strong acid
((iii)	NH ₃	+	H_2O	<u>}</u> ^†	NH_4^+	+	OH^-	
		Weak base		Weak	acid	Strong	acid	Strong	base
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									Edubull
	(iv)	HCl	+	CH ₃ CO	JOH	<u>^</u> ^ †	Cl^{-}	$+ CH_3$	3COOH ₂ ⁺
		Weak acid		Weak	base	•	Weal	k base	Weak acid
	(v)	HCl	+	NH ₃	<u></u> 4 ^ ↓	Cl^{-}	+	NH^+	
		Strong agid		Strong	+ '	Wook	haco	Wook	acid
	(11)		I	NLL				vv cak	NILI+
	(VI)		Ŧ	INП ₃	1	СП3С	.00	Ŧ	
		Strong acid		Strong	base	Weak	base		Weak acid
			GOI	DFN K	FV PC	INTS			
Type	es of Sol	vent	001						
(a)	Proto	genic or acidi	c solver	t :- The	y have	a tende	ncy to	generate	or donate the protons.
	Exan	iple CH ₃ C	COOH, I	HCI, HN	O_3, H_2	SO ₄ etc			
(b)	Proto	philic or basic	solven	t :- They	/ have a	a tender	ncy to a	accept th	e protons.
	Exan	uple NH ₃ ,	CH ₃ OH	I, RNH ₂	etc				
(c)	Amp	hiprotic or an	nphoter	ic solver	nts :- 7	They ha	ave the	e tenden	cy to accept or donate
	the pr	otons or they a	re eithe	r protopł	ilic or	protoge	enic.		
	Example H_2O , HS^- , HSO_4^- , HCO_3^- etc								
(d)	Apro	tic solvents :- '	They ne	ither dor	nate nor	r acc <mark>ept</mark>	t the pr	otons.	
	Exan	$\mathbf{ple} \qquad \mathbf{C}_{6}\mathbf{H}_{6}$	$CCl_4, CCl_4, $	CHCl ₃ , B	rF ₃ , N	O_2, CO	Cl ₂ etc		
(e)	Amp	holyte solvents	s- Those	e solvent	s in wl	nich the	e same	molecul	e acts as proton donar
	and p	roton acceptor	·						
	Exan	ple (i) H ₂ N–C	H ₂ –CO	он —	\rightarrow H	2^+N-C	H ₂ –CO	O^{-}	
		(ग्लाइ	सीन)		(Zwitte	r ion)		
		SO₃H (प्रो	टोन दात	TT)					
	(ii)								
		। NH2 (प्रो	टोन ग्राई	cf					
		(सल्फ्रेनिलिक	थम्ल)	,					
(f)	Adva	ntage ·-	01.61)						
(1)	(i) It e	explain the beh	avior of	acids an	d base	s in anv	type o	of solven	t.
	(ii) It	explain the sta	bility of	proton (H ⁺).	, w	JPC 0	1 501 01	
(g)	Disad	lvantage :-	5	1					
	(i) It o	loes not explai	n the ac	id and ba	ise prac	ctically	•		
	(ii) It	does not expl	ain acid	lic behav	vior of	aprotic	acid.	(SO_2, SO_2)	O ₃ , CO ₂ , AlCl ₃ , SiCl ₄ ,
	etc.)								
		F							
				Illustr	ation	IS			

Illustration 31. In the process : $NH_3 + NH_3 \stackrel{2}{\ddagger} \stackrel{2}{\uparrow} MH_2^- + NH_4^+$, The nature of ammonia is :-

(1) Acidic Solution

(2) Basic

(4) None

Ans. (3)

(3) Amphoteric

Illustration 32. Which of the following behave both as Bronsted acid as well as Bronsted bases? H₂O, HCO₃⁻, H₂SO₄, H₃PO₄, HS⁻, NH₃

Solution. H_2O , HCO_3^- , HS^- , NH_3

(4) Lewis Concept (1939)

(a) Lewis Acid :- According to this concept those species which have self tendency to accept the lone pair of electrons are called acids. i.e. Lewis acid is an electron pair acceptor (electrophilic)

$$H^{+} + \bigcup_{gg}^{gg} \underset{x}{gg} H^{-} \longrightarrow H \underset{gg}{gg} \underset{x}{gg} \underset{x}{gg} H$$

Acid Base

Classification of Lewis Acids :-

(i) Compounds whose central atom have an incomplete octet (electron deficient) **Example** BF₃, BBr₃, BCl₃, BI₃, B(CH₃)₃, B(OH)₃, AlCl₃, GeCl₃ etc.



(ii) Compounds whose central atom have vacant d-orbitals and can accept one or more pair of lone electrons.

Example SF₄, SF₆, SnCl₂, SnCl₄, PX₃, PX₅, GeX₄, TeX₄, IF₅, IF₇ etc.



(iii) Molecules with a multiple bond between atoms of different electronegaticities. **Example** CO₂, SO₂, SO₃ etc

$$\overset{-\delta}{O} = \overset{+\delta}{C} = \overset{-\delta}{O} \qquad \overset{-\delta}{O} = \overset{+\delta}{S} = \overset{-\delta}{O} \qquad \overset{-\delta}{O} = \overset{+\delta}{S} = \overset{-\delta}{O} \qquad \overset{-\delta}{O} = \overset{+\delta}{S} = \overset{-\delta}{O} \qquad \overset{-\delta}{U} = \overset{+\delta}{S} = \overset{-\delta}{O} \qquad \overset{-\delta}{U} = \overset{+\delta}{S} = \overset{-\delta}{O} \qquad \overset{-\delta}{U} = \overset{-\delta}{S} = \overset{-\delta}{O} = \overset{-\delta}{O} = \overset{-\delta}{S} = \overset{-\delta}{O} = \overset{-\delta}{O}$$

(iv) Cations :-

Example Ag^+ , Na^+ , Li^+ , Al^{+3} , Be^{+2} , Mg^{+2} , I^+ , Cl^+ , H^+ etc **False cations :- Example** NH_4^+ , H_3O^- , $CH_3COOH_2^+$, PH_4^+ etc

Example $Ag^+ + 3 : NH_3 \stackrel{2}{\ddagger} \stackrel{2}{\uparrow} \stackrel{1}{\intercal} [Ag(:NH_3)_2]^+$

(v) Elements which have six electrons in their outermost shell or valence shell. O-family (O, S, Se, Te) Po-Radioactive element

$$\operatorname{SO}_{3}^{-2} + \operatorname{O}_{4\operatorname{cid}}^{\mathfrak{s}} g \longrightarrow [\operatorname{SO}_{3} \longrightarrow \operatorname{O}]^{-2}$$

(b) Lewis Base :- Those species which have self tendency to donate the lone pair of electrons are called bases. i.e. base is an electron pair (lone pair) donor (nucleophile).

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Classification of Lewis Bases
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(i) Those species whose central atom have lone pair of elect4rons and have self tendency to donate them -

Example $\dot{N}H_3$, $R-\dot{N}H_2$, $R_2-\dot{N}H$, $C_6H_5-\dot{N}H_2$, $C_5H_5-\dot{N}$, $H_2\dot{N}-\dot{N}H_2$, $H-\dot{O}-H$, $R-\dot{O}-H$

,
$$R - O - R$$
, $R - S - R$, $R - S - H$ etc.

Explain :- $\underset{+I}{R \longrightarrow O} \stackrel{-\delta}{\leftarrow} \underset{+I}{R}$ (Electron density on O, increases due to +I effect)

(ii) Anions-

Example O^{-2} , SO_4^{-2} , CO_3^{-2} , CI^- , Br^- , F^- , Γ , N^{-3} , P^{-3} , NO_3^- , S^{-2} , CN^- etc.

- (c) Nature of water :- According to this concept nature of water is basic i.e. water is a base.
- (d) Neutralisation Reaction :- According to this concept those reactions in which acid and base react together to form a co-ordinate bond between them are called neutralization reactions.

Example
$$F_{3}B + \ddot{N}H_{3} \longrightarrow [F_{3}B \leftarrow NH_{3}]$$

 $H^{+} + \ddot{N}H_{3} \longrightarrow [H \rightarrow NH_{3}]^{+} \rightarrow NH_{4}^{+}$
 $H^{+} + H_{2}\dot{O} \longrightarrow \left[H \leftarrow O \swarrow H_{H}\right] \rightarrow H_{3}O^{+}$
 $Ag^{+} + 2\ddot{N}H_{3} \longrightarrow \left[H_{3}\dot{N} \rightarrow Ag \leftarrow 2\ddot{N}H_{3}\right]^{-} \rightarrow [Ag(NH_{3})_{2}]$

(e) Strength of acids and bases :- This concept explain the strength of acids and bases depending upon the basis of self tendency. To accept or donate the lone pair of electrons (e⁻).

Example $SO_2 < SO_3$ (Strong acid)

(f) Advantage :-

(a) This concept explains the acid and base without any solvent.

(b) This concept explains those acids and bases which are not explained by other concepts

(g) Disadvantage :-

(a) This concept fails to explain the acid and base practically.

(b) According to this concept forming of co-ordinate bond in neutralization reaction of acid and base is a slow process, where as neutralization reaction oif acids and bases is actually fast process.

(c) This concept fails to explain the real acids and bases

Example HCl, HNO₃, H₂SO₄, NaOH, KOH etc

• All the Lewis bases are Bronsted bases but all the Lewis acids are not Bronsted acids.

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All Arrhenius acids are Bronsted acids but it is not so for bases. •

POLYACIDIC BASE AND POLYBASIC ACIDS (6) (a) **Polyacidic Base** Al(OH)₃ $\frac{1}{2}$ $\hat{}$ $\hat{}$ $Al^{+3} + 3OH^{-} \longrightarrow K_b$ Al(OH)₃ $\div \uparrow \uparrow$ [Al(OH)₂]⁺¹ + OH⁻ \longrightarrow K_b $\left[\operatorname{Al}(\operatorname{OH})_2\right]^{+1} \stackrel{\circ}{:} \stackrel{\circ}{\to} \stackrel{\circ}{\operatorname{I}} \left[\operatorname{Al}(\operatorname{OH})\right]^{+2} + \operatorname{OH}^- + \longrightarrow K_{h}.$ $[Al(OH)]^{+2}$ $\div \uparrow \uparrow Al^{+3} + OH^{-} \longrightarrow K_{h}$ $\mathbf{K}_{b} = \mathbf{K}_{b_{1}} \times \mathbf{K}_{b_{2}} \times \mathbf{K}_{b_{2}}$ Taking -log on both sides $pK_{b} = pK_{b_{1}} + pK_{b_{2}} + pK_{b_{3}}$ i.e. $\overline{\mathbf{K}_{\mathbf{b}_1} > \mathbf{K}_{\mathbf{b}_2} > \mathbf{K}_{\mathbf{b}_3}} \implies \overline{\mathbf{p}\mathbf{K}_{\mathbf{b}_1} + \mathbf{p}\mathbf{K}_{\mathbf{b}_2} + \mathbf{p}\mathbf{K}_{\mathbf{b}_3}}$ **Polybasic Acid (b)** $H_3PO_4 \stackrel{\circ}{\ddagger} \stackrel{\sim}{\uparrow} \stackrel{\bullet}{} 3H^+ + PO_4^{-3} \longrightarrow K_a$ $H_3PO_4 \stackrel{\circ}{\pm} \stackrel{\wedge}{\uparrow} H_2PO_4^{-1} + H^+ \longrightarrow K_a$ $H_2PO_4^{-1} \stackrel{\circ}{\ddagger} \stackrel{\wedge}{\uparrow} HPO_4^{-2} + H^+ \longrightarrow K_{a_2}$ $\mathbf{K}_{a} = \mathbf{K}_{a_{1}} \times \mathbf{K}_{a_{2}} \times \mathbf{K}_{a_{2}}$ Taking -log on both sides $\mathbf{pK}_{\mathbf{b}} = \mathbf{pK}_{\mathbf{b}_{1}} + \mathbf{pK}_{\mathbf{b}_{2}} + \mathbf{pK}_{\mathbf{b}_{2}}$ $K_{a_1} > K_{a_2} > K_{a_3} \implies pK_{b_1} < pK_{b_2} < pK_{b_3}$

Illustrations

Illustration 33. In the dissoc	iation, $H_2A \stackrel{\circ}{\ddagger} \stackrel{\sim}{}^{K} \stackrel{\circ}{\uparrow} \stackrel{\bullet}{\uparrow}$	$H^+ + HA^-; HA^- \hat{\ddagger}^{K_2}$	$H^+ + A^{-2}$
(1) K_1 is equal to K_2		(2) K_1 is smaller than	1 K ₂

- (1) K_1 is equal to K_2
- (3) K_1 is greater than K_2
- Solution Ans. (3)

Illustration 34. Calculate the pH of 2.0×10^{-4} M H₃X solution assuming first dissociation to be 100%, second to be 50% and third to be negligible :

(4) K_1 is negligible

First dissociation : $H_3X \stackrel{\circ}{\ddagger} \stackrel{\sim}{\uparrow} H_2X^- + H^+$ Solution

- H^+ ion concentration = $2 \times 10^{-4} M$ X Second dissociation : $H_2X^- \hat{\ddagger} \hat{\uparrow} HX^- + H^+$ H^+ ion concentration = $C\alpha = 2 \times 10^{-4} \times 0.5$ Third dissociation is negligible Θ
- $[H^+] = 2 \times 10^{-4} + 10^{-4} = 3 \times 10^{-4}$ *.*.. pH = 4 - log3 = 3.52

	BEGINNEK'S BUX-5										
1.	Which of the following is a Bronsted acid ?										
	(i) HCN	(ii) $H_2PO_4^-$	(iii) NH ⁺ ₄	(iv) HCl							
	(1) (i), (iii)	(2) (i), (ii), (iii), (iv)	(3) (ii), (iii)	(4) (i), (iii), (iv)							
2.	Which of the following	ng is a Bronsted base?									
	(i) NH ₃	(ii) CH ₃ NH ₂	(iii) HCO ₃	(iv) SO_4^{2-}							
	(1) (i), (ii), (iii), (iv)	(2) (i), (ii)	(3) (ii), (ii), (iii)	(4) (i), (iii), (iv)							
3.	The conjugate base hydroxide ion is-										
	(1) H_2O	(2) H_3O^+	$(3) O^{2-}$	(4) O_2							
4.	The conjugate acid of amide ion (NH_2^-) is-										
	(1) N_2H_4	(2) NH ₂ OH	(3) NH_4^+	(4) NH ₃							
5.	Which of the following can act both as a Bronsted acid as well as a Bronsted base ?										
	(1) H_2SO_4	(2) HCO_{3}^{-}	(3) O ²⁻	(4) NH_4^+							
6.	Which of the followi	Which of the following acid-base reactions cannot be explained by the Bronste									
	(1) $CO \rightarrow C = C = C = CO$										
	$(1) \operatorname{CO}_2 + \operatorname{CaO} \to \operatorname{Ca}$		$(2) \operatorname{BF}_3 + \operatorname{NH}_3 \to \operatorname{BF}_3 \operatorname{NH}_3$								
	(3) $Ni + 4CO \rightarrow Ni(C)$	CO) ₄	(4) All of these								

7. Which of the following Bronsted acid has the weakest conjugate base? (1) H_2O (2) HCN (3) HCOOH (4) HF

ANSWER KEY

BEGINNER'S BOX-1													
1.	(3)	2.	(1)	3.	(3)	4.	(4)	5.	(1)	6.	(1)	7.	(4)
8.	(4)	9.	(2)	10.	(1)	11.	(2)						
BEGINNER'S BOX-2													
1.	(4)	2.	(2)	3.	(1)	4.	(2)	5.	(3)	6.	(2)	7.	(1)
BEGINNER'S BOX-3													
1.	(2)	2.	(3)	3.	(2)	4.	(3)	5.	(1)	6.	(2)		
BEGINNER'S BOX-4													
1.	(3)	2.	(2)	3.	(4)	4.	(1)	5.	(4)	6.	(4)		
BEGINNER'S BOX-5													
1.	(2)	2.	(1)	3.	(3)	4.	(4)	5.	(2)	6.	(4)	7.	(4)
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