IONIC EQUILIBRIUM

Arrhenius Concept Of Acids and Bases →

Acids	Bases
Substance which give H^+ ion in water.	Substance which give OH^- ion in water.
$HX_{(aq)} \rightarrow H^+_{(aq)} + X^-_{(aq)}$	$MOH_{(aq)} \rightarrow M^+_{(aq)} + OH^-_{(aq)}$
$HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$	$NaOH \rightarrow Na^+ + OH^-$
$H_2SO_{4(aq)} \rightarrow 2H^+_{(aq)} + SO^{-2}_{4(aq)}$	$Ca(OH)_2 \rightarrow Ca^{+2} + 2OH^-$

Limitation Of Arrhenius Concept →

→ applicable only to aqueous solution.
→ Basicity of NH_3 is not explained (does not posses hydroxyl group).

Bronsted-Lowry Concept / Proton theory →

Acids → Which donate H^+ ion / proton donors.

Bases → Which accepts H^+ ion / proton acceptors.

Limitations of Bronsted, Lowry →

→ Does'nt explain about $AlCl_3$, BCl_3, ...
→ Uncertainity in reverse rx^n.

Lewis - Acids and Base →

Acid → Species which accept electron pair (lone pair)

Base → Species which donate electron pair.

Lewis Acid	Lewis Base
e^- deficient Species	e^- rich species.
$AlCl_3$, Co^{3+}, Mg^{2+}, H^+, BCl_3, BF_3, $SnCl_2$, $SnCl_4$, Ag^+, Cu^{2+}	$H_2\ddot{O}$, $\ddot{N}H_3$, OH^-, F^-, C_2H_4,

Conjugate - Acid Base Pair →

Conjugate Acid → Add H^+.
Conjugate Base → Remove H^+.

OH^- → Conjugate acid → H_2O
NH_4^+ → Conjugate base → NH_3

If Bronsted acid → strong, then it's conjugate base is weak.

Que) Conjugate Base for Bronsted Acids →

$HF \rightarrow F^-$
$H_2SO_4 \rightarrow HSO_4^-$
$HCO_3^- \rightarrow CO_3^{-2}$

Que) Conjugate Acid for Bronsted Base →

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

Amphiprotic → H^+ le bhi sakta hai, de bhi sakta hai..

Ionisation Constant

$$AB_{(aq)} \rightleftharpoons A^+_{(aq)} + B^-_{(aq)}$$

	AB	A^+	B^-
t=0	CM	0	0
t=eq^m	C - Cα	Cα	Cα

$$K_{eq} = K_i = \frac{[A^+][B^-]}{[AB]} = \frac{C^2\alpha^2}{C(1-\alpha)} = \boxed{\frac{C\alpha^2}{1-\alpha}}$$

For Weak acid = $K_i = K_a$
For Weak base = $K_i = K_b$

Neglection Theory →

$$K_i = \frac{C\alpha^2}{1-\alpha}$$

If $\frac{K_i}{C} \le 6.4 \times 10^{-3} \rightarrow 1-\alpha = 1 \Rightarrow K_i = C\alpha^2$

If $\frac{K_i}{C} > 6.4 \times 10^{-3} \rightarrow 1-\alpha \neq 1 \rightarrow$ Solve quadratic.

Que) Calculate conc. of H^+ ion, in 0.05 M CH_3COOH ($K_a = 1.25 \times 10^{-6}$)

Sol^n → $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

	CH_3COOH	CH_3COO^-	H^+
t=0	C		
t=eq^m	C - Cα	Cα	Cα

$\frac{K}{C} = \frac{1.25 \times 10^{-6}}{0.05} = 25 \times 10^{-6}$

$\boxed{K = \frac{C\alpha^2}{1-\alpha}} \rightarrow \alpha = \sqrt{\frac{K}{C}} = \sqrt{25 \times 10^{-6}} = \underline{5 \times 10^{-3}}$

$[H^+] = C\alpha = 0.05 \times 5 \times 10^{-3}$
$= \underline{\underline{25 \times 10^{-5}}}$

Quadratic eq.^{n} = $\frac{-b \pm \sqrt{b^2-4ac}}{2a}$

Ionisation Constant of Water and its Ionic Product →

→ Water acts as acid and base

$H_2O_{(l)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$

Acid Base C.A. C.B.

$K = \frac{[H_3O^+][OH^-]}{[H_2O]}$ (K = dissociation constant)

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

(K_W = Ionic product of water).

Experimentally :→

$[H^+] = [OH^-] = 10^{-7} M$ (at 298K)

$\therefore K_W = [H^+][OH^-]$

$\therefore K_W = 10^{-7} \times 10^{-7} = 10^{-14}$

↓

Ionisati^n Constant of H_2O (Temp. dependent)

Ostwald Dilution Law

$\alpha \propto \sqrt{\text{dilution (Vol}\uparrow)}$ | α = degree of ionisation

$\alpha \propto \frac{1}{\sqrt{C}}$ | C = concentration

Que) 0.2 M CH_3COOH Solution →

$V_1 = 300\, ml$, $V_2 = ?$

$\alpha_1 = \alpha$, $\alpha_2 = 2\alpha$

sol → $\alpha \propto \sqrt{V}$

$\frac{\alpha_1}{\alpha_2} \propto \sqrt{\frac{V_1}{V_2}} \Rightarrow \left(\frac{\alpha}{2\alpha}\right)^2 = \left(\sqrt{\frac{300}{V}}\right)^2$

$\Rightarrow \frac{1}{4} = \frac{300}{V}$

$\Rightarrow V = 1200$

Vol. added →
1200 − 300
= 900ml.

Common Ion Effect

(Strong electrolyte)$\xrightarrow{\text{isko add karo}}$(+)$\xrightarrow{\text{added to}}$ Weak electrolyte, having common ion then, degree of ionisation (α) of weak electrolyte ↓↓

e.g. →

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

$CH_3COONa \rightleftharpoons CH_3COO^- + Na^+$ ($\alpha\downarrow$)

→ Conc. of common ion ↑↑, So Rx.^{n} shift backwards.

Que) Conc. of H^+ at eq.^{m} of 0.1M HCl is added in an aq. sol.^{n}, containing 0.1M CHF_2COOH
$K_a = 2\times10^{-2}$

sol^n → $CHF_2COOH \rightleftharpoons CHF_2COO^- + H^+$

$0.1 - 0.1\alpha$ $\quad 0.1\alpha \quad 0.1\alpha$

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

$0.1 \quad 0.1 \quad 0.1$

$K_a = \frac{(0.1 + 0.1\alpha)0.1\alpha}{0.1 - 0.1\alpha}$

$2\times10^{-2} = \frac{0.1\alpha(1+\alpha)}{(1-\alpha)}$

$0.2 = \frac{\alpha^2 + \alpha}{1-\alpha}$

$\alpha^2 + \alpha = 0.2 - 0.2\alpha$

$\alpha^2 + 1.2\alpha - 0.2 = 0$

$\alpha = 0.148$

$H^+ = C\alpha = (0.1)\ 1\alpha$

pH-Scale

$\boxed{P = -\log}$

$p^{Ka} = -\log K_a$

$p^{Kb} = -\log K_b$

$p^{KW} = -\log K_W$

$p^{KW} = -\log 10^{-14}$

$p^{KW} = 14$ → at 25°C

Relation b/w p^H and p^{OH}.

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

$\log K_W = -(\log H^+) - (\log OH^-)$

$\boxed{pK_W = p^H + p^{OH}}$

$\boxed{14 = p^H + p^{OH}}$

p^H Scale

(acidic) | (basic)

0 (min. value) — neutral $\boxed{\frac{pK_w}{2}}$ — $14 = pK_w$ (max value)

Que) $[H^+] = 3.8 \times 10^{-3}$, $pH = ?$ $(\log 3.8 = 0.58)$

Sol^n → $[H^+] = 3.8 \times 10^{-3}$

$p^H = -\log H^+$

$\boxed{-\log = (x \times y^b) = b - \log x}$

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

$= -\log(3.8 \times 10^{-3})$

$= 3 - \log 3.8$

$= 3 - 0.58$

$= 2.42$

Que) $[HCl] = 1 \times 10^{-8} M$, $pH = ?$

$\cancel{-\log(1 \times 10^{-8})}$

$\cancel{-\log(10^{-8}) = 8}$

major Mistake

$\begin{bmatrix} 10^{-6} \\ 10^{-7} \\ 10^{-8} \end{bmatrix}$ $[H^+]$ consider H_2O

$[H^+] = 10^{-8} + 10^{-7} = 10^{-7}(10^{-1} + 1)$

$= 10^{-7}\left(\frac{11}{10}\right)$

$p^H = -\log\left(10^{-7} \times \frac{11}{10}\right)$

$= 7 - \log\left(\frac{11}{10}\right) \Rightarrow 7 - (\log 11 - \log 10)$

$\Rightarrow 7 - (1.04 - 1)$

$\Rightarrow 6.96$

Que) Determine p^H at $[H^+] = \frac{a}{b} \times 10^{-x} M$

Sol^n → $-\log(H^+)$

$\Rightarrow -\log\left(\frac{a}{b} \times 10^{-x}\right)$

$\Rightarrow x - \log\left(\frac{a}{b}\right)$

$\Rightarrow x - \log a + \log b$

Que) Find $[H^+]$ if $p^H = 5.7$.

→ $10^{0.3} = 2$ / anti $\log(0.3) = 2$

Sol^n → $[H^+] = 10^{-pH}$

$= 10^{-5.7} = 10^{-(6+0.3)}$

$= 10^{-6} \cdot 10^{0.3}$

$= 2 \times 10^{-6}$

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p^H Calculation Cases →

1. Strong Acid / Strong Base.
2. Mixture of strong acid and Base
3. Salt Hydrolysis.
4. Buffer Solution.

→ Strong monoprotic acid and base →

eg → HCl, HNO_3, $NaOH$, KOH

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

$p^{OH} = -\log[OH^-]$

$10^{-6} + 10^{-7}$

$10^{-7} + 10^{-7}$

$10^{-8} + 10^{-7}$

$[H^+] / [OH^-] < 10^{-6} M$, then, we can't calculate p^H directly by this formula, we have to consider H^+ ion conc. from water also.

Calculate p^H of strong diprotic acid, and Base →

Que) $[H^+]$ concn. of $10^{-8} M$ HCl aq. Sol.^{n} at 298 K $(K_w = 10^{-14})$ is : →

Sol.^{n} → $10^{-8} + 10^{-7}$

$\Rightarrow 10^{-7}(10^{-1} + 1) \Rightarrow 10^{-7}(1.1)$

$\Rightarrow 1.0525 \times 10^{-7} M$

Que) $0.1 M$ H_2SO_4.

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

$0.1M$ $\quad$ $0.2M$

$p^H = -\log(2 \times 10^{-1})$

$= 1 - \log 2$

$= 1 - 0.3 \Rightarrow 0.7$

Que) $10^{-3} M$ $Ba(OH)_2$.

Sol^n → $pOH = 2 \times 10^{-3}$

$= 3 - \log 2$

$= 3 - 0.3$

$pOH = 2.7$

$p^H = 14 - 2.7 = 11.3$

Mixing of Solution

Case 1 → pH of mixture of two or more strong acid solution.

$\boxed{\begin{matrix}\text{Acid 1} \\ N_1V_1\end{matrix}} + \boxed{\begin{matrix}\text{Acid 2} \\ N_2V_2\end{matrix}} = \boxed{\begin{matrix}\text{Acidic final} \\ N_mV_m\end{matrix}}$ $\quad V_m = V_1 + V_2 \ldots$

$N_1V_1 + N_2V_2 + \dots = N_mV_m$

$$N_m = \frac{V_1N_1 + V_2N_2 + \dots}{V_m}$$

$$N_m = [H^+]$$

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

Case-2 p^H of mixture of two or more strong base solution.

| Base | + | Base | = | Basic | $V_m = V_1 + V_2 + \dots$

$N_1V_1 + N_2V_2 + \dots = N_mV_m$

$$N_m = \frac{V_1N_1 + V_2N_2 + \dots}{V_m}$$

$$N_m = [OH^-]$$

$POH =$ $(14 - POH = p^H)$

Case-3 → pH of mixture of strong acid and strong base Sol.^{n}

$(N_1V_1 + N_2V_2 + \dots)_{acid} - (N_1V_1 + N_2V_2 + \dots)_{Base}$
$= V_mN_m$,

case1 → $N_m = +ve$ (acidic solution)
⇒ $N_m = [H^+]$

case2 → $N_m = -ve$ (basic solution)
$N_m = [OH^-]$

Case 3 → $N_m = 0$ (pH=7)

Que) 100 ml each of 2 solutions having pH=2 and pH=4 are mixed. Find pH of resultant Solution →

→ $H^+ = 10^{-2} = N_1$
→ $H^+ = 10^{-4} = N_2$ | ⇒ $\frac{10^{-2} \times 100 + 10^{-4} \times 100}{200}$

$$\Rightarrow \frac{1 + 0.01}{200}$$

$$H^+ \Rightarrow \frac{1.01}{200}$$

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

Que) equal vol. of pH=8 and pH=11 are mixed then find out pH of resultant Sol.^{n}

Sol.^{n} → $PH = 8 \rightarrow POH = 6 \rightarrow [OH^-] = 10^{-6} \rightarrow N_1$
$PH = 11 \rightarrow pOH = 3 \rightarrow [OH^-] 10^{-3} \rightarrow N_2$

$$\frac{10^{-6} \times \cancel{V} + 10^{-3} \times \cancel{V}}{2\cancel{V}} = \frac{10^{-3}(10^{-3} + 1)}{2}$$

$$= 10^{-3} \times \frac{1}{2} = 0.5 \times 10^{-3}$$

→ $3(-\log 0.5)$ → pOH → $p^H = 14 - POH$

Hydrolysis of Salts and pH of their Solution →

Anion → from acid	Cation → from base.
$ClO_4^-, SO_4^{2-}, NO_3^-, Br^-, Cl^-$	$Na^+, K^+, Ca^{2+}, Ba^{2+}$ → Basicity increase

Salt →
→ Salt of weak acid and strong base.
→ Salt of strong acid and weak base.
→ Salt of weak acid and weak base.
→ Salt of strong acid and strong base.

	SA and SB Salt	SA and WB Salt	WA and SB Salt	WA and WB Salt
Hydrolysis	—	Cationic	Anionic	Cationic and anionic
Nature of Solution	Neutral solution	Acidic solution	Basic solution	Almost neutral sol.
$K_h = \frac{K_W}{K_{weak}}$ ↓ Hydrolysis constant	7	$K_h = \frac{K_W}{K_b}$	$K_h = \frac{K_W}{K_a}$	$K_h = \frac{K_W}{K_aK_b}$
h, degree of hydrolysis	—	$h = \sqrt{\frac{K_h}{C}}$ ↓ $h = \sqrt{\frac{K_W}{K_b \cdot C}}$	$h = \sqrt{\frac{K_h}{C}}$ $h = \sqrt{\frac{K_W}{K_a \cdot C}}$	$h = \sqrt{K_h}$ $h = \sqrt{\frac{K_W}{K_aK_b}}$
pH	7	$pH = 7 - \frac{1}{2}pK_b - \frac{1}{2}\log C$	$pH = 7 + \frac{1}{2}pK_a + \frac{1}{2}\log C$	$pH = 7 + \frac{1}{2}pK_a - \frac{1}{2}pK_b$

Buffer Solution

Solution which resist change in pH on dilution / with addition of small amount of acids or alkali.

Buffer Solution

- Simple Buffer Sol.^{n} — Salt of W.A. and W.B.
- Mixed Buffer Sol.^{n}
  - Acidic Buffer Sol.^{n}
  - Basic Buffer Sol.^{n}

Mixed Buffer Solution

Acidic Buffer Sol.^{n}	Basic Buffer Sol.^{n}
Sol.^{n} of weak acid and salt of its conjugate ion.	Sol.^{n} of weak base and salt of it's conjugate ion.
e.g. – ($CH_3COOH + CH_3COONa$) $HCN + KCN$. $H_2CO_3 + NaHCO_3$: Blood	e.g. – ($NH_4OH + NH_4Cl$)
$pH = pKa + \log\frac{(\text{conjugate Base})}{(\text{Acid})}$	$pOH = pK_b + \log\frac{(\text{conjugate acid})}{(\text{Base})}$
$pH = pKa + \log\frac{[\text{salt}]}{[\text{acid}]}$	$pOH = pK_b + \log\frac{[\text{Salt}]}{[\text{Base}]}$

Solubility product Constant

$$BaSO_4(s) \xrightarrow[\text{Sol.}^n \text{ in water}]{\text{saturated}} Ba^{2+}_{(aq)} + SO_4^{2-}{}_{(aq.)}$$

$$K = \frac{[Ba^{2+}][SO_4^{2-}]}{[BaSO_4]}$$

$$K[BaSO_4] = [Ba^{2+}][SO_4^{2-}]$$

$$K_{sp} = [Ba^{2+}][SO_4^{2-}]$$

↓

Solubility product constant, Simply solubility product

e.g. — $Zr_3(PO_4)_4 \rightleftharpoons 3Zr + 4PO_4$

$(S) \quad (3s) \quad (4s)$

$$K_{sp} = [Zr]^3[PO_4]^4$$
$$= (3s)^3 (4s)^4$$
$$= 6912(s^7)$$

Que) Calculate the solubility of A_2X_3 in pure water assuming that neither kind of ion reacts with water the solubility product of A_2X_3, $K_{sp} = 1.1 \times 10^{-23}$?

Sol.^{n} ⟶ $A_2X_3 \longrightarrow 2A + 3X$

$S \quad 2s \quad 3s$

$$K_{sp} = (2s)^2(3s)^3$$
$$1.1 \times 10^{-23} = 108\, s^5$$
$$s = \left(\frac{1.1 \times 10^{-23}}{108}\right)^{1/5}$$

Que) Solubility of M_2S Salt is 3.5×10^{-6} then find out its solubility product?

Sol.^{n} ⟶ $4s^3 \Rightarrow 4(3.5 \times 10^{-6})^3$

$\Rightarrow 1.7 \times 10^{-16}$

Condition for precipitation Ionic product (Q_{sp}) ⟶

Q_{sp}: Contains conc of ions at any time.

K_{sp}: Contains only eq.^{m} concentration.

$Q_{sp} < K_{sp}$: Unsaturated sol.^{n} and precipitation will not occur.

$Q_{sp} = K_{sp}$: Saturated sol.^{n} and solubility eq.^{m} exist.

$Q_{sp} > K_{sp}$: Super saturated and hence, precipitation will occur.