MIND MAP

FOR NEET ASPIRANTS

PHYSICAL CHEMISTRY

IONIC EQUILIBRIUM

ONE-SHOT

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Topics *to be covered*

1. Acids - Bases theory
2. p^H calculations
3. Weak acids & Bases
   - pH
   - Common ion effect
   - Buffer
   - salt hydrolysis
4. Solubility Product

Ionic Equilibrium → Reversible rxn → Closed container → for weak electrolytes

Acids, Bases & salts ← electrolyte → conduct electricity

electrolyte
- Strong electrolyte
  - $HA \rightarrow H^{\oplus} + A^{\ominus}$
  - irreversible rxn
  - ($\alpha = 1$ or 100%)
  - → no eqm
- weak electrolyte
  - $HB \rightleftharpoons H^{\oplus} + B^{\ominus}$
  - Reversible rxn
  - ($\alpha < 1$ or 100%)
  - → Ionic eqm possible

Acid	Base	Arrhenius concept
(1) Gives $H^{\oplus}$ ion in water	(1) Gives $OH^{\ominus}$ ion in water	
(2) Sour in taste.	(2) Bitter in taste	
(3) Blue litmus changes to red.	(3) Red litmus changes to Blue.	
(4) $pH < 7$	(4) $pH > 7$	→ at room temp
(5) Gives $H^{\oplus}$ ion in any medium (proton donor)	(5) accept $H^{\oplus}$ in any medium (proton acceptor)	→ Bronsted-lowry Concept
(6) $e^{\ominus}$ acceptor	(6) $e^{\ominus}$ donor	→ lewis concept.

⇒ All arrhenius acids are Bronsted acids.

⇒ All Bronsted Bases are lewis Bases.

$H^{\oplus} + H_2O \longrightarrow H_3O^{\oplus} \xrightarrow{H_2O} H_5O_2^{\oplus} \xrightarrow{H_2O} H_7O_3^{\oplus}$

$H^{\oplus}$ → exist as $H_{2n+1}O_n^{+}$

H_2O → neutral

$OH^{\ominus} + H_2O \longrightarrow H_3O_2^{\ominus} \xrightarrow{H_2O} H_5O_3^{\ominus} \xrightarrow{H_2O} H_7O_4^{\ominus}$

$OH^{\ominus}$ → exist as $H_{2n-1}O_n^{-}$

Acid $\longrightarrow H^{\oplus}$ + C·B (Conjugate Base)

Base + $H^{\oplus}$ $\longrightarrow$ Conjugate acid (C·A)

⇒ Weak acids have strong C.B

⇒ Strong acids have weak C.B

$$\underset{\text{Acid}}{H_2O} + \underset{\text{Base}}{H_2O} \rightleftharpoons \underset{\text{C.A}}{H_3O^{\oplus}} + \underset{\text{C.B}}{OH^{\ominus}}$$

Lewis acid → $e^{\ominus}$ acceptor → vacant orbitals and incomplete Octet

Lewis Base → $e^{\ominus}$ donor → Complete octet with lone pair.

Ostwald's dilution law → (for weak electrolytes)

↳ (Conc ↓ degree of dissociation ↑)

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

	AB	$A^{\oplus}$	$B^{\ominus}$
t=0	C	0	0
t=eqm	C−Cα	Cα	Cα

$$K_{eq} = \frac{C\alpha \cdot C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha}$$

If $\alpha < 5\%$ or 0.05, then $1-\alpha \simeq 1$

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

$$\alpha = \sqrt{\frac{K_{eq}}{C}}$$

α
- Conc ↓ α ↑
- Temp. ↑ α ↑
- dielectric constant ↑ α ↑
- for strong electrolytes, (α = 100% or 1)

$$\alpha\% = \alpha_{\text{fraction}} \times 100$$

for numericals, α is used in fraction.

$$\alpha = \frac{\text{no. of moles dissociated}}{\text{total moles taken}}$$

$$\alpha = \frac{M_T - M_0}{(n-1)M_0} = \frac{D-d}{(n-1)d}$$

$\boxed{p^x = -\log x}$

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

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

$p^{K_w} = -\log K_w$

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

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

$p^{K_h} = -\log K_h$

Shortcut

① if $X = 10^{-a}$, then $p^X = a$

② if $p^X = \underbrace{b}_{\text{integer}}$, then $X = 10^{-b}$

③ if $p^X = \underbrace{c}_{\text{fraction}}$, then $X = \text{antilog}(-c)$

④ if $X = a \times 10^{-b}$, then $p^X = b - \log$

pH Calculation

① Strong acid → $[H^+] = [HA] = 2[H_2A] = 3[H_3A]$

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

$[HA]$ → monobasic acid; $[H_2A]$ → dibasic acid; $[H_3A]$ → tribasic acid

② Strong Base ⇒ $[OH^\ominus] = [BOH] = 2[B(OH)_2] = 3[B(OH)_3]$

$pH = 14 - pOH$, $pOH = -\log[OH^\ominus]$

$[BOH]$ → monoacidic Base; $[B(OH)_2]$ → diacidic Base; $[B(OH)_3]$ → triacidic Base

③ $H_2O \rightleftharpoons H^{\oplus} + OH^{\ominus}$

K_w = ionic product of water $= [H^+][OH^-]$

- $pK_w = pH + pOH$
- pH scale range = 0 to pK_w.
- pH of neutral water $= \frac{pK_w}{2}$
- Pure water $\Rightarrow [H^+] = [OH^-] = \sqrt{K_w}$

at room temp $K_w = 10^{-14}$

Neutral water

$[H^+] = [OH^-] = 10^{-7}$

$pH = pOH = 7$

pH scale range = 0 to 14

$pK_w = 14 = pH + pOH$

$H_2O \rightleftharpoons H^{\oplus} + OH^{\ominus}$

55.55M $\quad 10^{-7} \quad 10^{-7}$

weak electrolyte.

Keq/dissociation constant of water $= \frac{10^{-14}}{55.55}$

α for water $= \frac{10^{-7}}{55.55}$

Temp ↑ K_w ↑ pK_w ↓ pH scale range ↓ pH of neutral water ↓

④ $[H^+] = 1M \rightarrow pH = -\log 1 = 0$

↳ Highly acidic

⑤ $[H^+] > 1M \rightarrow pH = -ve \rightarrow$ pH scale is not valid for Concentrated acid/Base

↳ Highly concentred acid

⑥ if $[H^+]$ is in b/w 10^{-6} to 10^{-9} M, then we have to consider $[H^+]$ from H_2O also during pH calculation.

⑦ if $[H^+] > 10^{-6}$ M, then we neglect $[H^+]$ from H_2O.

⑧ if $[H^+] < 10^{-9}$ M, then $pH = 7$ due to water.

⑨ effect of dilution/concentration ⇒ $M_1V_1 = M_2V_2$ → pH changes.
dilution ↑ concentration ↓ pH ↑

⑩ Mixing (a) if two strong acids are mixed,

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

$$pH_{mix} = -\log[H^+]_{mix}$$

(b) if two bases are mixed, then

$$[OH^\ominus]_{mix} = \frac{N_1V_1 + N_2V_2}{V_1 + V_2}$$ → pOH_{mix} and pH_{mix}

(c) if strong acids and strong bases are mixed.

then Case-I → $N_AV_A = N_BV_B$ (Complete neutralisation) → $pH = 7$ due to water

Case-II $N_AV_A > N_BV_B$ → acidic nature, $pH < 7$

$$[H^+]_{mix} = \frac{N_AV_A - N_BV_B}{V_{mix}}$$ → pH

Case-III $N_BV_B > N_AV_A$

$$[OH^\ominus]_{mix} = \frac{N_BV_B - N_AV_A}{V_{mix}}$$ → $pH > 7$

Weak acids

$$HA \rightleftharpoons H^{\oplus} + A^{\ominus}$$

	HA	$H^{\oplus}$	$A^{\ominus}$
t=0	C	0	0
t=eqm	C-Cα	Cα	Cα

Keq for acid $(K_a) = \frac{C\alpha^2}{1-\alpha}$

if $\alpha < 5\%$ or 0.05, $1-\alpha \simeq 1$

$$K_a = C\alpha^2 \qquad \alpha = \sqrt{\frac{K_a}{C}}$$

$$[H^+] = C\alpha = \sqrt{K_a \times C}$$

$$pH = -\log[H^+] = \frac{1}{2}(pK_a - \log C)$$

Acidic strength $\propto [H^+] \propto C\alpha \propto \sqrt{K_a \times C}$

If two weak acids are mixed,

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

Weak Bases

$$BOH \rightleftharpoons B^{\oplus} + OH^{\ominus}$$

	BOH	$B^{\oplus}$	$OH^{\ominus}$
	C	0	0
	C-Cα	Cα	Cα

Keq for Base $K_b = \frac{C\alpha^2}{1-\alpha}$

if $\alpha < 5\%$ or 0.05, $1-\alpha \simeq 1$

$$K_b = C\alpha^2 \qquad \alpha = \sqrt{\frac{K_b}{C}}$$

$$[OH^{\ominus}] = C\alpha = \sqrt{K_b \times C}$$

$$pOH = -\log[OH^{\ominus}] = \frac{1}{2}(pK_b - \log C)$$

Basic strength $\propto [OH^{\ominus}] \propto C\alpha \propto \sqrt{K_b \times C}$

If two weak Base are mixed,

$$[OH^{\ominus}]_{mix} = \sqrt{K_{b_1} \times C_1 + K_{b_2} \times C_2}$$

Weak acid + its C·B

Ka Kb

$K_a \times K_b = K_w$

$pK_a + pK_b = pK_w$

Weak Base + its C·A

Kb Ka

$K_a \times K_b = K_w$

$pK_a + pK_b \neq pK_w$

Common ion effect ⇒ Weak electrolyte + strong electrolyte with a common ion.

↳ α decreases.

W·A + S·A

$\alpha' = \frac{K_a}{(X)}$ → $[H^+]$ from S·A

W·B + S·B

$\alpha' = \frac{K_b}{(X)}$ → $[OH^\ominus]$ from S·B

Buffer Solution ⇒ resist the change in pH

↳ pH independent of volume of solution.

simple Buffer

Salt of (W·A + W·B)

Mixed Buffer

(A) Acidic Buffer : W·A + its C·B
or
W·A + its salt with S·B
or
$\underbrace{W\cdot A}_{x\,eq} + \underbrace{S\cdot B}_{y\,eq}\}\ x > y$

$$pH = pK_a + \log \frac{[Salt/C\cdot B]}{[Acid]}$$

(B) Basic Buffer → W·B + its C·A
or
W·B + its salt with S·A
or
$\underbrace{W\cdot B}_{x\,eq} + \underbrace{S\cdot A}_{y\,eq}\}\ x > y$

$$pOH = pK_b + \log \frac{[salt]}{[Base]}$$

$$\text{Buffer capacity} = \frac{\Delta n}{\Delta pH}$$

↓ max. buffer capacity ($\Delta pH = 0$)

→ Higher the Buffer capacity, more is the resistance to change pH.

Acidic Buffer ⇒ $pH = pK_a$

↳ when [salt] = [Acid]

Basic Buffer ⇒ $pOH = pK_b$

↳ when [salt] = [Base]

Buffer range

Acidic Buffer

$pH = pK_a - 1$

$\frac{[Salt]}{[Acid]} = \frac{1}{10}$

$pH = pK_a$

$[Salt] = [Acid]$

$pH = pK_a + 1$

$\frac{[Salt]}{[Acid]} = 10$

Basic Buffer

$pOH = pK_b - 1$

$\frac{[Salt]}{[Base]} = \frac{1}{10}$

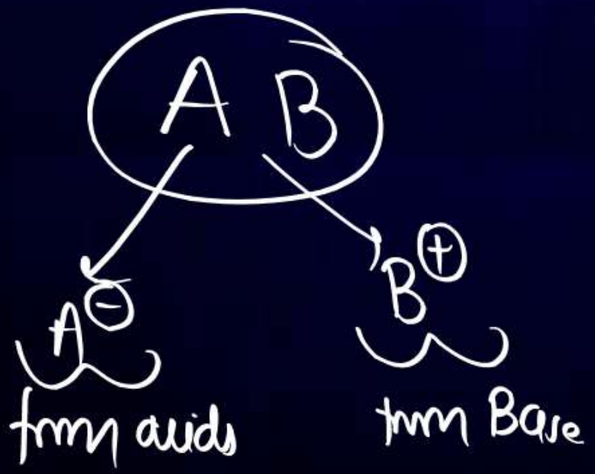
$pOH = pK_b$

$[Salt] = [Base]$

$pOH = pK_b + 1$

$\frac{[Salt]}{[Base]} = 10$

Salts



$$\text{Acid} + \text{Base} \longrightarrow \text{Salt} + H_2O$$

Salt Hydrolysis ⇒ interaction of weaker part of salt with H_2O.

- K_h = Hydrolysis constant
- h = degree of hydrolysis

Salts of (S·A + S·B) ⇒ NO weaker part
- NO hydrolysis
- pH = 7 due to H_2O

Salt of (W·B + S·A) → Cationic part = weaker
- Cationic hydrolysis.
- pH < 7

$$B^{\oplus} + H_2O \rightleftharpoons BOH + H^{\oplus}$$

Salt of (W·A + S·B) → Anionic part = weaker
- Anionic hydrolysis.
- pH > 7

$$A^{\ominus} + H_2O \rightleftharpoons HA + OH^{\ominus}$$

Salt of (W·A + W·B) → Cationic & Anionic part = weak.
- Cationic & Anionic Hydrolysis
- pH ≃ 7

$$A^{\ominus} + B^{\oplus} + H_2O \rightleftharpoons HA + BOH$$

Salts of (W·A + S·B)

$$A^{\ominus} + H_2O \rightleftharpoons HA + OH^{\ominus}$$

C		0	0
C-Ch		Ch	Ch

$$K_h = \frac{Ch^2}{1-h} = \frac{K_w}{K_a}$$

if $h < 5\%$ or 0.05, $1-h \simeq 1$

$$K_h = Ch^2$$

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

$$[OH^{\ominus}] = Ch = \sqrt{K_h \times C} = \sqrt{\frac{K_w}{K_a} \times C}$$

$$pOH = 7 - \frac{1}{2}(pK_a + \log C)$$

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

Salts of (W·B + S·A) → Cationic hydrolysis

$$B^{\oplus} + H_2O \rightleftharpoons BOH + H^{\oplus}$$

C		0	0
C-Ch		Ch	Ch

$$K_h = \frac{Ch^2}{1-h} = \frac{K_w}{K_b}$$

if $\alpha < 5\%$ or 0.05, $1-h = 1$

$$K_h = Ch^2$$

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

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

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

Salts of (W·A + W·B)

$$A^{\ominus} + B^{\oplus} + H_2O \rightleftharpoons HA + BOH$$

C	C		0	0
C-Ch	C-Ch		Ch	Ch

$$K_h = \frac{h^2}{(1-h)^2} = \frac{K_w}{K_a \times K_b}$$

if $\alpha < 5\%$ or 0.05, then $1-h \simeq 1$

$$K_h = h^2$$

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

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

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

Solubility Product (K_{sp}) ⇒ for Sparingly soluble salt

(solubility $< 10^{-2}$ mol/ℓ or M)

(always in mol/ℓ)

$$AB_{(s)} \rightleftharpoons A^{\oplus}_{aq.} + B^{\ominus}_{aq.}$$

$$\left\{ K_{sp} = [A^+][B^{\ominus}] = s \times s = s^2 \right\}$$

$$A_xB_y \rightleftharpoons xA^{+y} + yB^{-x}$$

$$xs \quad ys$$

$$K_{sp} = (xs)^x \cdot (ys)^y$$

K_{sp} → solubility product
- → defined only at eqm.
- → Value constant.
- → depends only on temp.
- → independent of Conc^n, pressure, vol.

I.P (Ionic product) → Same expression as K_{sp}.
- → defined at any moment of rxn.
- → value changes during rxn.
- → value depends on Temp., Pressure, Conc^n and volume.

I.P < Ksp → unsaturated solution.
→ only ionised part is present in solution.

I.P = Ksp → saturated solution.
→ at equilibrium.
→ $AB_{(s)} \rightleftharpoons A^{\oplus} + B^{\ominus}$
→ Ionised & non-ionised part of salt is present in solution.

I.P > Ksp → precipitate of salt will occur.

⇒ Weak salt + Strong salt having common ion → solubility of weak salt decreases.

$HB \rightarrow H^{\oplus} + B^{\ominus}$
$x \quad x \quad x$

$AB \rightleftharpoons A^{\oplus} + B^{\ominus}$
$s' \quad s'+x \simeq x$

$(K_{sp})_{AB} = [A^+][B^{\ominus}] = s' \times x$

$s' = \frac{K_{sp}}{x}$

#Simultaneous equilibrium

$$AB \rightleftharpoons A^{\oplus} + B^{\ominus}$$
$$(S_1+S_2) \quad S_1$$
$$(K_{sp})_{AB} = (S_1+S_2)S_1$$

$$AC \rightleftharpoons A^{\oplus} + C^{\ominus}$$
$$(S_2+S_1) \quad S_2$$
$$(K_{sp})_{AC} = (S_1+S_2)S_2$$

$$\frac{(K_{sp})_{AB}}{(K_{sp})_{AC}} = \frac{S_1}{S_2}$$

If $(K_{sp})_{AB} >>>> (K_{sp})_{AC}$, then $S_1 >>> S_2$
$(S_1+S_2 \simeq S_1)$

#indicators ⇒ Buffer solution
- phenolphthalein
- methyl orange

Color 1 / Colour 2

$$HIn \rightleftharpoons H^{\oplus} + In^{\ominus}$$

$$pH = pK_{In} + \log \frac{[In^{\ominus}]}{[HIn]}$$

Homework

- PYQs
- NCERT → examplar


Thank you