IONIC EQUILLIBRIUM

1. $pH = -\log_{10}[H^+]$, $pOH = -\log_{10}[OH]^-$.

→ $pH + pOH = 14$. [concentration should be in terms of N for calculating pH]

If $[H^+] = a \times 10^{-b}$.

$\left[pH = \left(b + \log\frac{1}{a}\right) = (b - \log a)\right]$.

[$\log 10 = 1$
$\log 1 = 0$
$\log 2 = 0.3010$
$\log 3 = 0.4771$
$\log 5 = 0.7$
$\log 7 = 0.84$]

2. Ostwald's Law of Dilution-

	$AB \rightleftharpoons$	A^+	+	B^-
$(t=0)$	C	0		0
$(t=t)$	$c - c\alpha$	$c\alpha$		$c\alpha$

→ $K = \frac{C\alpha^2}{1-\alpha}$ [If $0 \le \alpha \le 5\%$ $(1-\alpha = 1)$]

⇒ $K = C\alpha^2$

→ $\alpha = \sqrt{\frac{K}{C}}$ K depends only on temperature

At constant temp. $\alpha \propto \frac{1}{\sqrt{C}}$, $\alpha \propto \frac{1}{\sqrt{n/V}}$ ⇒ $\alpha = \sqrt{V}$.

∴ on infinite dilution $(V \to \infty)$, $\alpha \approx 100\%$

⇒ Weak electrolyte behaves as strong electrolyte.

Weak acid (HA)	Weak base (BOH)
→ $K_a = \frac{C\alpha^2}{1-\alpha} \approx C\alpha^2$	$K_b = \frac{C\alpha^2}{1-\alpha} \approx C\alpha^2$
→ $[H^+] = C\alpha = \sqrt{K_a C}$	$[OH^-] = C\alpha = \sqrt{K_b C}$.
$pH = -\frac{1}{2}[\log K_a + \log C]$	$pOH = -\frac{1}{2}[\log K_b + \log C]$
$= \frac{1}{2}pK_a - \frac{1}{2}\log C$.	$= \frac{1}{2}pK_b - \frac{1}{2}\log C$.

Ostwald's law of dilution is applicable only to weak electrolyte.

→ Factors affecting α ⇒ ① temperature ② dilution (v)
③ Nature of electrolyte
④ Dielectric constant (μ) [more μ ⇒ α ↑]
⑤ Common ion effect (α ↓)
Odd ion effect (α ↑)

one electrolyte = strong ←
other = weak.

3 **Water**-

→ No. of moles of H_2O in 1 L of water = $\frac{1000}{18}$ = 55.5 moles

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

no. of H^+ = $10^{-7} N_A$.

∴ one H^+ ion is obtained from 55.5×10^7 H_2O molecules.

→ $\alpha = \frac{10^{-7} N_A}{55.55 N_A} = 18 \times 10^{-8}$ $\quad$ % $\alpha = 1.8 \times 10^{-7}$.

→ $K = \frac{[10^{-7}][10^{-7}]}{55.55} = 1.8 \times 10^{-16}$.

→ $K_w = [H^+][OH^-]$ $\quad$ $K_{H_2O} = \frac{[H^+][OH^-]}{[H_2O]}$

∴ $K_{H_2O}[H_2O] = K_w$

→ $-\log K_w = -\log[H^+] - \log[OH^-]$ $\quad$ [water is neutral ∴ $pH = pOH = \frac{pK_w}{2}$]

⇒ $pK_w = pH + pOH = 14$.

→ If Temp. ↑, ionisation ↑ ⇒ pH ↓, pOH ↓.
⇒ K_w ↑

4. **Salts**- ① Normal / general salts ⑥ Mixed salts.
② Acid salts
③ Basic salts
④ Double salts
⑤ Complex salts

5. Strong acid / base ⇌ weak conjugate base/acid.
weak acid / base ⇌ strong conjugate base/acid.

6. $CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$ $\quad$ $CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$
(WA) $\quad$ (CSB)

$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$ $\quad$ $K_b = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$.

$K_a \times K_b = [H^+][OH^-] = K_w$

∴ $K_a \times K_b = 10^{-14}$ $\quad$ $pK_a + pK_b = pK_w = 14$.

7. **Salt Hydrolysis** – (reverse of neutralization)
↳ not shown by SA-SB salt (pH=7)

(a) Cationic Hydrolysis [SA – WB]

Step 1 K_h (hydrolysis constant)

$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$

$$K_h = \frac{[NH_4OH][H^+]}{[NH_4^+]}$$

$$\boxed{K_h = \frac{K_w}{K_b}}$$

Step 2 Degree of hydrolysis (h).

$$K_h = \frac{Ch^2}{1-h} \approx Ch^2.$$

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

Step 3 pH.

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

$$pH = -\frac{1}{2}\left[\log K_w + \log C - \log K_b\right]$$

$$pH = 7 - \frac{1}{2}pK_b - \frac{1}{2}\log C.$$

$\therefore pH < 7$

Anionic Hydrolysis [WA – SB]

K_h (hydrolysis constant)

$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$

$$K_h = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$$

$$\boxed{K_h = \frac{K_w}{K_a}}$$

Degree of hydrolysis (h)

$$K_h = \frac{Ch^2}{1-h} \approx Ch^2.$$

$$\boxed{h = \sqrt{\frac{K_w}{K_a C}}}$$

$$\boxed{[OH^-] = Ch}$$

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

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

$\therefore pH > 7$

(b) Hydrolysis of [WA – WB] Salt

K_h

$$\boxed{K_h = \frac{K_w}{K_a \times K_b}}$$

h

$K_h = h^2$ $\therefore$ $\boxed{h = \sqrt{K_h} = \sqrt{\frac{K_w}{K_a \times K_b}}}$

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

$$\boxed{[H^+] = K_a h}$$

8. **Solubility**-

$AgCl \rightleftharpoons Ag^+ + Cl^-$ $\quad K = \dfrac{[Ag^+][Cl^-]}{[AgCl]}$ ← constant.

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

$AB \rightleftharpoons$	A^+	B^-
a	0	0
a – s	s	s

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

AB_2	$\rightleftharpoons$	A^{+2}	+	$2B^-$
a		a		0
a-s		s		2s

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

→ Ionic product [IP] $IP = [Ag^+]_i [Cl^-]_i$

$K_{sp} = [Ag^+]_{eq.} [Cl^-]_{eq.}$ = constant.

$IP = K_{sp}$ = saturation solution, equilibrium exists
$IP > K_{sp}$ = supersaturated solution, precipitation occurs
$IP < K_{sp}$ = unsaturated solution, precipitation will not occur.

→ Common ion decreases solubility.

Q type Find solubility of AgCl in presence of C NaCl?

AgCl	$\rightleftharpoons$	Ag^+	+	Cl^-
s		s		s

$K_{sp} = s^2$.

In NaCl - $NaCl \rightarrow Na^+ + Cl^-$
C C C

solubility of AgCl in presence of NaCl = s'

AgCl	$\rightleftharpoons$	Ag^+	+	Cl^-
s'		s'		s'+c

$K_{sp} = s'[s'+c] = s'^2 + s'c \Rightarrow s'c = K_{sp}$.

$\Rightarrow s' = \frac{K_{sp}}{c}$.

Precipitation occurs in presence of common ion.

9. Isohydric solution - different solutions having the same pH.

→ Relative strength (RS) $= \frac{\text{strength of Acid 1}}{\text{strength of Acid 2}} = \frac{[H^+]_1}{[H^+]_2} = \frac{C_1\alpha_1}{C_2\alpha_2} = \frac{\sqrt{K_{a_1} C_1}}{\sqrt{K_{a_2} C_2}}$.

10. Buffer

→ a solution which resists change in pH on addition of small amount of SA or SB.
- pH does not change appreciably on adding SA/SB.
- pH of buffer soln. does not depend on volume of solution.
∴ solution can be diluted without change in pH.
- pH does not change even if it is kept for a long time.

ⓐ **Simple Buffer** – salt of WA – WB.

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

ⓑ **Mixed Buffer**

Acidic Buffer	Basic Buffer
$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$	$NH_4OH \rightleftharpoons NH_4^+ + OH^-$
$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$	$K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]}$
$\Rightarrow [H^+] = \frac{K_a [CH_3COOH]}{[CH_3COO^-]}$	$[OH^-] = \frac{K_b [NH_4OH]}{[NH_4^+]}$
$\Rightarrow pH = pK_a + \log \frac{[salt]}{[acid]} = pK_a + \log \frac{[conjugate\ base]}{[acid]}$	$pOH = pK_b + \log \frac{[salt]}{[base]} = pK_b + \log \frac{[conjugate\ acid]}{[base]}$

→ Buffer capacity (BC) = $\frac{\text{no. of moles of acid or base added per litre}}{\text{change in pH of buffer solution}}$

more the BC ⇒ more resistant is the solution to pH change.

II. **Indicators** – (weak organic acids or bases).

ⓐ **Acidic indicators**

Phenolphthalein (HPh) $HPh \rightleftharpoons Ph^- + H^+$

Colourless pink

ⓑ **Basic indicators**

Methyl orange (MeOH) $MeOH \rightleftharpoons Me^+ + OH^-$

yellow orange-red

pH of acidic indicator / pOH of basic indicator $= pK_I + \log \frac{[Ionised\ form]}{[Unionised\ form]}$

ACIDS => SOUR TASTE
BASES => BITTER TASTE

Indicator	Colour In Acidic Medium	Colour in Basic Medium.
Methyl orange	Orange red	yellow
Methyl red	red	yellow
Phenol red	yellow	red
Phenolphthalein	colourless	pink

12. **Arrhenius concept**

acids ⇒ produce free H^+ ions in aq. soln.
bases ⇒ produce free OH^- ions in aq. soln.

→ **Bronsted-Lowry Concept**

acids ⇒ tendency to donate H^+
bases ⇒ tendency to accept H^+.
Water = amphoteric / amphiprotic ⇒ can act on both acids and bases.

→ **Lewis Concept**

acids ⇒ tendency to accept lone pair of e^-
bases ⇒ tendency to donate lone pair of e^-.

13. $Al(OH)_3 \rightleftharpoons Al^{+3} + 3OH^- \ (K_b)$
$Al(OH)_3 \rightleftharpoons [Al(OH)_2]^{+1} + OH^- \ (K_{b_1})$
$[Al(OH)_2]^{+1} \rightleftharpoons [Al(OH)]^{+2} + OH^- \ (K_{b_2})$
$[Al(OH)]^{+2} \rightleftharpoons Al^{+3} + OH^- \ (K_{b_3})$

$K_b = K_{b_1} \times K_{b_2} \times K_{b_3}$
$K_{b_1} > K_{b_2} > K_{b_3}$

$H_3PO_4 \rightleftharpoons 3H^+ + PO_4^{3-} \ (K_a)$
$H_3PO_4 \rightleftharpoons H_2PO_4^- + H^+ \ (K_{a_1})$
$H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+ \ (K_{a_2})$
$HPO_4^{2-} \rightleftharpoons PO_4^{3-} + H^+ \ (K_{a_3})$

$K_a = K_{a_1} \times K_{a_2} \times K_{a_3}$
$K_{a_1} > K_{a_2} > K_{a_3}$

14.
- Protogenic = Acidic solvent ⇒ tendency to donate proton
- Protophilic = Basic solvent ⇒ tendency to accept proton
- Amphiprotic = Amphoteric ⇒ tendency to accept or donate proton
- Aprotic solvents ⇒ neither donate nor accept.
- Ampholyte / Zwitter ion ⇒ tendency to accept and donate proton

Eg - Sulphanilic acid, glycine.

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

acid (weak) — CH_3COO^- strong conjugate base

→ $NH_4OH \rightleftharpoons NH_4^+ + OH^-$

weak base — NH_4^+ strong conjugate acid.