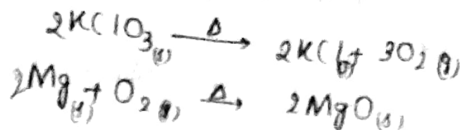# Chemical Equilibrium

Irreversible rxn –

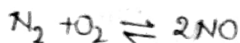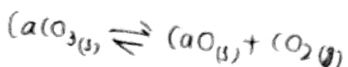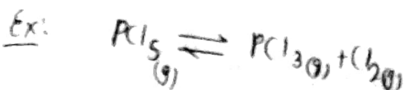Combustion rxn – $2KClO_{3(s)} \xrightarrow{\Delta} 2KCl + 3O_{2(g)}$

$2Mg_{(s)} + O_{2(g)} \xrightarrow{\Delta} 2MgO_{(s)}$

Neutralisation rxn – $NaOH + HCl \longrightarrow NaCl + H_2O$
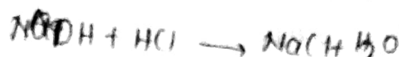
→ **Reversible rxn** – carried out in closed vessels.

Ex: $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$

$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$

$N_2 + O_2 \rightleftharpoons 2NO$

Physical eq. – Allotropic change

① $graph \rightleftharpoons dia \quad \Delta H = +ve$ endothermic
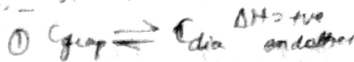
→ Pressure forward rxn is favoured & formation of diamond at high temp & pressure. $\Delta H = +ve$

② Melting of ice, $H_2O_{(s)} \rightleftharpoons H_2O_{(l)}$

$V↑, P↑ \qquad V↓, P↓$ ice melts carb
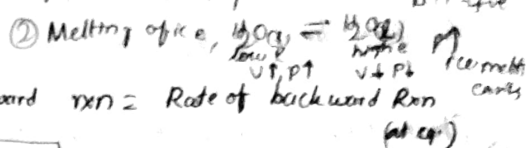
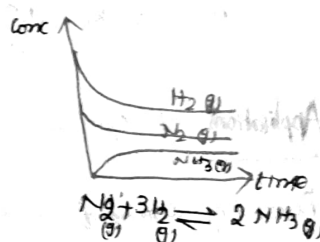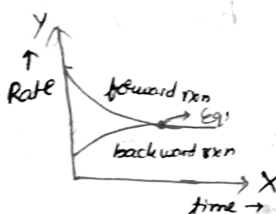→ **Concept of equilibrium:** Rate of forward rxn = Rate of backward Rxn (at eq.)
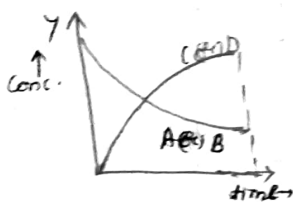
$$R_f = R_b \qquad \boxed{\Delta G = 0}$$
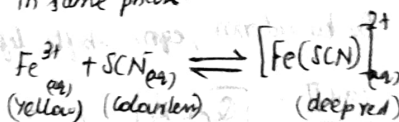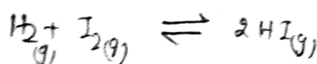
Eq. is attained for both physical & chemical rxn.

→ **Graphical representation of equilibrium:**

for a general reversible rxn – $A + B \rightleftharpoons C + D$
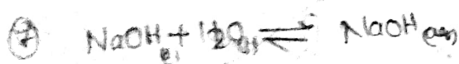

→ **Types of chemical eq:**

Homogenous eq – reactants & products are in same phase.

$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$, $Fe^{3+}_{(aq)} + SCN^-_{(aq)} \rightleftharpoons [Fe(SCN)]^{2+}_{(aq)}$
(yellow) (colourless) (deep red)

Heterogenous eq – reactants & products are in different phase

$$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$$

Equilibrium in physical process –

① $Ice_{(s)} \rightleftharpoons water_{(l)}$, ② $water \rightleftharpoons Ice_{(s)}$ ③ $S_l \rightleftharpoons S_g$ (Tr $\cdot$ s – T = 95.6°C)
(rhombic) (monoclinic)

④ $I_{2(s)} \rightleftharpoons I_{2(g)}$ ⑤ $C_{(dia)} \rightleftharpoons C_{(grap)}$ ⑥ $C_6H_{12}O_{6(s)} \rightleftharpoons C_6H_{12}O_{6(aq)} + H_2O_{(l)}$

⑦ $NaOH + H_2O \rightleftharpoons NaOH_{(aq)}$ ⑧ $S_8 \rightleftharpoons S_8$ (at 369K)
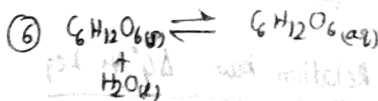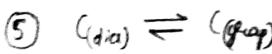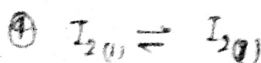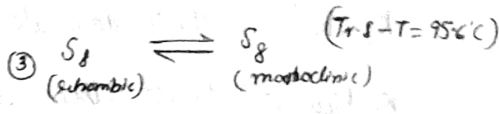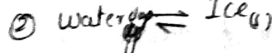
Active mass – law of mass action – eqn const (Keq)

applicable only to chemical equilibrium, for only liquids & gases.

Law of mass action $aA + bB \rightleftharpoons cC + dD$

Rate $\propto [A]^a [B]^b$

active mass = molar conc for dilute sol^n (M) = partial pressure (g)

for pure liquids, solids active mass = 1

→ **Different types of eqn. const** –

Molar conc (K_c)

$$K_c = \frac{K_f}{K_b} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

$aA + bB \rightleftharpoons cC + dD$

Units of $K_c = \left(\frac{mole}{lt}\right)^{\Delta n(g)}$

Mole fraction (K_X)

$$K_X = \frac{X_C^c \cdot X_D^d}{X_A^a \cdot X_B^b}$$

no units

Partial pressure (K_p)

$$K_p = \frac{P_C^c \cdot P_D^d}{P_A^a \cdot P_B^b}$$

Units of $K_p = (atm)^{\Delta n(g)} = (Par(a))^{\Delta n(g)}$

Relation b/w K_p, K_c & K_X — $K_p = K_X (P_{total})^{\Delta n(g)} = K_c (RT)^{\Delta n(g)}$
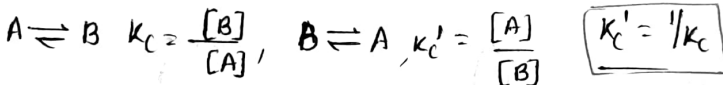
→ **Characteristic properties of chemical equilibrium :**

value of equilibrium const. is independent on initial conc of products & reactants, volume, pressure, catalysts.

K depends on ① Temp, ② Mode of writing, ③ stoichiometric coeff.

$A \rightleftharpoons B$ $K_c = \frac{[B]}{[A]}$, $B \rightleftharpoons A$, $K_c' = \frac{[A]}{[B]}$ $\boxed{K_c' = 1/K_c}$

→ **Applications of equ const (K_eq)**

Predicting direction of reaction

Case I – $\boxed{Q_c > K_c}$

Backward rxn, eqn. shifts left side

Case II – $\boxed{Q_c < K_c}$
Forward rxn

Case III – $\boxed{Q_c = K_c}$
already at eq.

→ **Q_c (reaction quotient)**

Q_c well defined at anywhere even in non eq rxn. but K_c is defined only at eq.

$Q_c = \dfrac{product\ of\ conc\ of\ products}{product\ of\ conc\ of\ reactants}$

(Alphabetical order ends is back of ⊘ so Q ↑ backward)

→ $K_c > 10^3$ products dominate, rxn is about to complete

$K_c < 10^{-3}$ reactants dominate, rxn is occurs rarely

K_c b/w 10^{-3} to 10^3 then conc of reactants = [products]

→ **Relation b/w $\Delta G°$ vs K_eq :**

$\Delta G° = -2.303\ RT\ log\ K_{eq}$

$\Delta G > 0, K < 1$
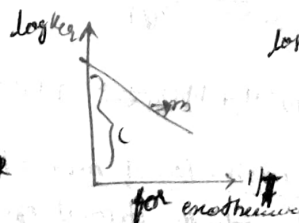
$\Delta G < 0, K > 1$

$\Delta G = 0, K = 1$

$log\ K_{eq} = \dfrac{-\Delta H°}{2.303R}\left(1/T\right) + \dfrac{\Delta S°}{2.303R}$

$y = m \quad x + c$

$log\left(\dfrac{K_2}{K_1}\right) = \dfrac{\Delta H°}{R}\left(1/T_1 - 1/T_2\right)$
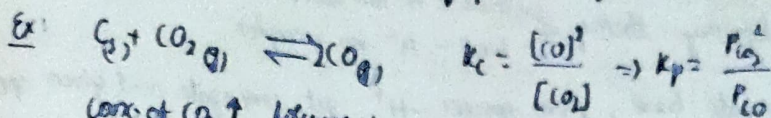
for endothermic

Le Chatelier's principle -

Factors effecting position of equilibrium -

① Effect of conc

↑ in conc of reactants (or) ↓ conc of products favours forward rxn (irreversal)

Ex: $C_{(s)} + CO_{2(g)} \rightleftharpoons 2CO_{(g)}$ $K_c = \dfrac{[CO]^2}{[CO_2]}$ ⟹ $K_p = \dfrac{P_{co}^2}{P_{co_2}}$

conc of CO_2 ↑ forward rxn favours

② Effect of pressure :-

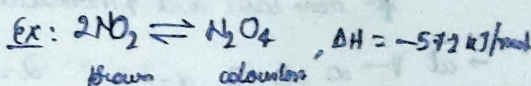i) Pressure has no effect on position of eqⁿ if $\Delta n = 0$

ii) if $\Delta n = +ve$ P↑ back ward rxn, P↓ forward rxn

iii) if $\Delta n = -ve$ P↑ back ward rxn, P↓ forward rxn.

③ Effect of temp :-

i) for endo rxn $K_{eq} \propto T$

ii) for exo rxn $K_{eq} \propto 1/T$

Ex: $2NO_2 \rightleftharpoons N_2O_4$, $\Delta H = -57.2 \, kJ/mol$
   Brown   colourless

at high T↑ Brown colour ↑ because of backward rxn. at low T forward rxn.

④ Effect of catalyst :-

→ does not appear in rxn, does not effect $K_p \& K_c$ (or) degree of dissociation.
→ But influence on $R_f, R_b \& K_f, K_b$.

⑤ Effect of addⁿ of inert gas:

① at const volume - addⁿ of inert gas no change in conc. but no of moles↑

$$X_I = \dfrac{n_I}{n_{total}} \qquad n_{total} ↑ X_I ↓ \quad P↑$$

(no of reactants, products are const).

② at const pressure - total volume↑ no of moles of reactants, products ↓ &

eq shifts in direction of more no of gaseous moles side.

Relation blw vapour pressure & degree of dissociation.

	$A_{(g)} \rightleftharpoons n B_{(g)}$	

$A_{(g)} \rightleftharpoons n B_{(g)}$ $n_{total} = 1-x + nx = 1 + x(n-1)$
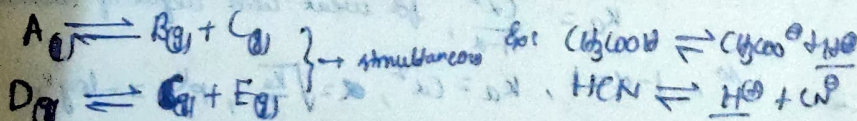
initial   1   0

after   1-x   nx

$$\dfrac{D}{d} = \dfrac{M_{theor}}{M_{mix}} = \dfrac{(V.D)_{theor}}{(V.D)_{mix}} = 1 + x(n-1)$$

$$\boxed{M_{mix} = 2 \times V.P}$$

Simultaneous eq :- two equilibria have a common reagent

$$A_{(g)} \rightleftharpoons B_{(g)} + C_{(g)} \left.\begin{array}{c} \\ \\ \end{array}\right\} \rightarrow \text{simultaneous} \quad \text{for } CH_3COOH \rightleftharpoons CH_3COO^\ominus + H^\oplus$$
$$D_{(g)} \rightleftharpoons C_{(g)} + E_{(g)} \qquad\qquad HCN \rightleftharpoons H^\oplus + CN^\ominus$$

if C is solid in both rxn not simultaneous eq.

Ionic Equilibrium

① Theories of acid-base

① Arrhenius theory —
- acids — which release H^+ ions in H_2O
- bases — which release OH^- ions in H_2O

(aqueous) (or)

② Bronsted - Lowry theory
- acid — H^+ ion donor
- base — H^+ ion acceptor

→ To get conjugate base, given species $-H^+$, get conjugate acid, given species $+H^+$

→ conjugate acid - base pair — differ by only one H^+ ion.

→ amphoteric substance — species which can donate as well as accept H^+ ion

→ aprotic substance — neither donor nor acceptor of H^+ ion

③ Lewis theory
- acid — e^- pair acceptor
- base — e^- pair donor

[all Bronsted bases are Lewis bases]

⑪ Ostwald's dilution law — applicable for weak electrolytes only (WA & WB)

for mono basic acid & monoacidic base $\alpha = \sqrt{K/c} = \sqrt{\dfrac{K \cdot v}{n}}$

→ at $V \to \infty$, $C \to 0$, $\alpha \to 1$ $\alpha = $ degree of dissociation.

⇒ **Ionic product of water (K_w)** — $K_w = [H^+][OH^-]$ (at any temp.)

as temp $\uparrow$ K_w also $\uparrow$, at $25°C$, $K_w = 1 \times 10^{-14} mol^2/lt^2$, $pH \downarrow_{H_2O}$ temp $\uparrow$ $[H^+]$

variation of K_w with temp. is given by $\log\left(\dfrac{K_{w_2}}{K_{w_1}}\right) = \dfrac{\Delta H}{2.303R}\left(\dfrac{1}{T_1} - \dfrac{1}{T_2}\right)$

⇒ **Concept of pH** — $pH = -\log_{10}[H^+] \Leftrightarrow [H^+] = 10^{-pH}$. Ully

$pOH = -\log_{10}[OH^-] \Leftrightarrow [OH^-] = 10^{-pOH}$ ①

pH scale at $25°C$ $\underset{\text{neutral}}{0 \overset{\text{acidic}}{\underset{7}{\longrightarrow}} \overset{\text{basic}}{14}}$; $pH + pOH = pK_w$

for neutral water — $[H^+] = [OH^-] = \sqrt{K_w}$

for strong acids — $[H^+] = [acid] = $ normality, for S. Bases $-[OH^-] = [Base]$

= Normality

→ Aq. soln. of SA diluted by
- i) 10 times $pH \uparrow 1$ units
- ii) 100 times $pH \uparrow 2$ units
- iii) 1000 times $pH \uparrow 3$ units.

Aq soln. of S·B diluted by
- i) 10 times $pH \downarrow 1$ unit
- ii) 100 times $pH \downarrow 2$ units
- iii) 1000 times $pH \downarrow 3$ units.

→ for weak acids $-[H^+]$

$K_a = \dfrac{C\alpha^2}{1-\alpha}$, for weak acid degree of dissociation α is very less

∴, $1 - \alpha \approx 1$, $K_a = C\alpha^2$, $\alpha = \sqrt{\dfrac{K_a}{C}}$, $pK_a = -\log K_a$

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

→ for weak bases - $[OH^-] = C\alpha = \sqrt{k_b C}$, $pOH = \frac{1}{2}(pk_b - \log C)$ ...

→ Relative strength of two weak acids - $\dfrac{[H^+]_1}{[H^+]_2} = \dfrac{C_1\alpha_1}{C_2\alpha_2} = \sqrt{\dfrac{k_{a_1}C_1}{k_{a_2}C_2}}$

Relative strength of two weak bases - $\dfrac{[OH^-]_1}{[OH^-]_2} = \dfrac{C_1\alpha_1}{C_2\alpha_2} = \sqrt{\dfrac{k_{b_1}C_1}{k_{b_2}C_2}}$

→ when 2 S·A are mixed $[H^+] = \dfrac{N_1V_1 + N_2V_2}{V_1 + V_2}$, bases - $[OH^-] = \dfrac{N_1V_1 + N_2V_2}{V_1 + V_2}$

→ when S·A is mixed with strong base - i) if $N_aV_a = N_bV_b$ (neutral)

ii) $N_aV_a > N_bV_b$ (acidic) - $[H^+]_{resultant} = \dfrac{N_aV_a - N_bV_b}{V_a + V_b}$

iii) $N_aV_a < N_bV_b$ (basic) $[OH^-]_{resultant} = \dfrac{N_bV_b - N_aV_a}{V_a + V_b}$

→ Mix. of 2 acids (weak) $[H^+] = C_1\alpha_1 + C_2\alpha_2 \Rightarrow [H^+] = \sqrt{k_{a_1}C_1 + k_{a_2}C_2}$ $\left(\begin{smallmatrix}C_1 \& C_2 \\ are \\ conc.\end{smallmatrix}\right)$

Mix. of 2 W·B $[OH^-] = C_1\alpha_1 + C_2\alpha_2 \Rightarrow [OH^-] = \sqrt{k_{b_1}C_1 + k_{b_2}C_2}$

for conjugate acid-base pair, $K_a \times K_b = K_w$; $pk_a + pk_b = pk_w$ (at any temp.)

⇒ **Buffer soln :-**

→ Buffer soln are of 2 types (i) Simple buffer (ii) Mixed buffer

→ salts of W·A & W·B act as simple buffer

→ Mixed buffer are of 2 types

i) acidic buffer = W·A + salt of SB &o: $CH_3COOH + CH_3COONa$, $H_3PO_4 + Na_2HPO_4$.

ii) basic buffer = W·B + salt of S·A Ex - $NH_4OH + NH_4Cl$, $NH_4OH + NH_4NO_3$

⇒ **Henderson's eqn** - $p^H = pk_a + \log\dfrac{[salt]}{[acid]}$, $pOH = pk_b + \log\dfrac{[salt]}{[base]}$

$[salt] = [V \times N]$, $[acid] = [V_a \times N_a]$, $[base] = [V_b \times N_b]$, $p^H + pOH = 14$

→ Buffer capacity $(\phi) = \dfrac{\text{no of moles of S·A (or) S·B added to 1 litre buffer}}{\text{Change in } p^H.}$

for max. buffer capacity of acid buffer→ $p^H = pk_a$ (or) $[salt] = [acid]$

basic buffer ⇒ $pOH = pk_b$ (or) $[salt] = [base]$

→ **Salt hydrolysis** - i) salts of S·A & S·B - don't undergo hydrolysis.

Ex: $NaCl, Na_2SO_4, CaCl_2, etc$

ii) salts of S·A & W·B = cationic hydrolysis due to presence of 1 acidic (H^+).

Ex: $NaHSO_4, NaHCO_3, etc.$

$K_B = \dfrac{k_w}{k_b}$; $pH = 7 - \dfrac{1}{2}(pk_b + \log C)$ (at 25°C) $h = \sqrt{\dfrac{k_w}{k_b \cdot C}} = \sqrt{\dfrac{k_h}{C}}$ $K_h = \dfrac{[OH^-]^2}{C}$ →Normality

→ **Double salt** ⇌ salt + salt

Ex: Mohr's salt – $FeSO_4 \cdot (NH_4)_2 SO_4 \cdot 6H_2O$

Potash alum – $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$

→ **iii) salt of WA & SB** – anionic hydrolysis, basic soln. obtained.

contain free hydroxyl gp.

Ex: $Zn(OH)Cl$, $Mg(OH)Cl$, etc..

$$K_h = \frac{K_w}{K_a} \cdot \left[\frac{[HO^-]^2}{C} = \frac{[HO^-]^2}{C} \right]$$

$$pH = 7 + \left(\frac{pK_a + \log C}{2} \right) \log C \quad , \quad h = \sqrt{\frac{K_w}{K_a \cdot C}}$$

→ **iv) salt of WA & WB** – $K_h = \frac{K_w}{K_a \times K_b} ; \quad \frac{h}{1-h} = \sqrt{K_h}, \quad pH = 7 + \left(\frac{pK_a - pK_b}{2} \right)$ (at 25°C)

1) $K_A = K_B$ (Neutral), $K_a > K_b$ (acidic), $K_b > K_a$ (basic).

→ for amphoteric salts like $NaHCO_3$, $NaHS$, NaH_2PO_4 etc.

$$pH = \frac{pK_{a_1} + pK_{a_2}}{2}, \quad \text{for } Na_2HPO_4 ; \quad pH = \frac{pK_{a_2} + pK_{a_3}}{2}$$

⇒ **Indicators** – weak organic acids & bases.

for acidic indicator $pH = pK_{In} + \log \frac{[In^-]}{[HIn]} \quad pK_{In} = pK_a$

for basic indicator $pOH = pK_{In} + \log \frac{[In^+]}{[InOH]}, \quad pK_{In} = pK_b, \quad \begin{bmatrix} pH = pK_{In} \\ \text{indicates} \\ \text{change of colour} \end{bmatrix}$

$$pH = pK_{In} \pm 1 \text{ (range of indicator)}$$

→ **Acid-base titration** – i) S·A Vs S·B ⇒ pH range 3–10 any indicator.
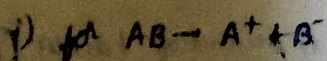
ii) W·A Vs S·B ⇒ pH range 8·3–10·0 phenolphthalein is suitable.

iii) S·A vs W·B ⇒ pH range 3·1–4·5 methyl orange is suitable.

iv) W·A vs W·B ⇒ No sharp change in pH. – No indicator

⇒ **Solubility product** – K_{sp} is generally applicable for sparingly soluble salts = molar conc. of ⊕ & molar conc. of ⊖.

i) for $AB \rightarrow A^+ + B^-$

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

$K_{sp} = S \cdot S = S^2$

ii) $A_2B_3 \rightarrow 2A^{3+} + 3B^{2-}$
        $2S \quad 3S$

$K_{sp} = [2S]^2 [3S]^3 = 4S^2 \cdot 27 S^5$

$K_{sp} = 108 S^5$

Application of solubility product.

$$A_x B_y \rightleftharpoons x A^{+}_{(aq)} + y B^{-}_{(aq)}$$
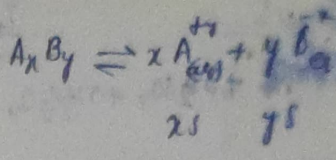
$$M_1 V_1 = M_2 V_2 \quad \textcircled{1} \text{ Ionic product } (Q)$$

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

i) $Q = k_{sp}$ for saturated soln.

$$K_{sp} = (2S)^x (yS)^y$$

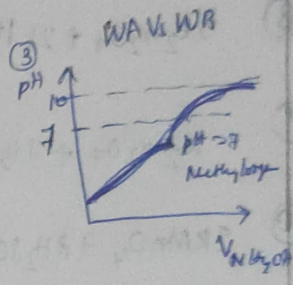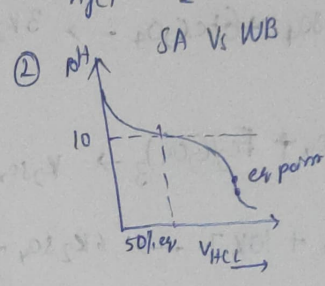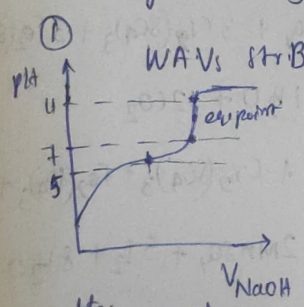ii) $Q < K_{sp}$ unsaturated soln. no formation of ppt.

$$K_{sp} = x^y y^x S^{x+y}$$

iii) $Q > K_{sp}$ super saturated soln. formation of ppt.

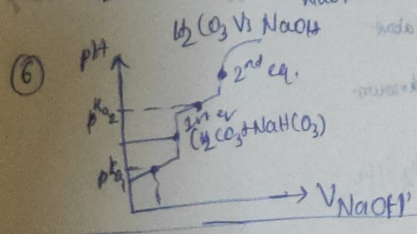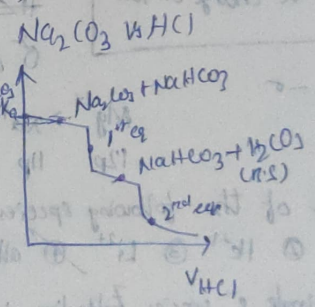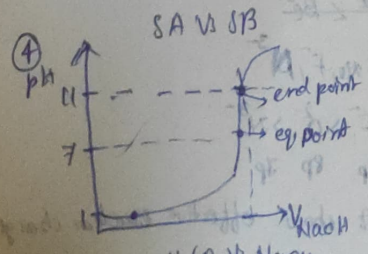→ due to common-ion effect, solubility of salts ↓

Ex: S_{AgCl} in $NaCl < S_{AgCl}$ in H_2O.

→ due to formation of complex, solubility of sparingly soluble salts ↑

Ex: S_{AgCl} in $NH_3 > S_{AgCl}$ in H_2O

① WA Vs StrB   ② pH   SA Vs WB   ③ WA Vs WB

after eq. point

$$N_R = [OH^-] = \frac{eq \cdot B - a_{WA}}{V_{total}\,(lt)} \qquad pOH = -log[OH^-]$$

SA Vs SB

Na_2CO_3 Vs HCl

④ pH   end point   eq. point

Na_2CO_3 $Na_2CO_3 + NaHCO_3$ 1st eq. $NaHCO_3 + H_2CO_3$ (r.s)

H_2CO_3 Vs NaOH

⑥ pH   2nd eq. $(H_2CO_3 + NaHCO_3)$ V_{NaOH}

for solubility
$$M = S = \frac{W_B(g)}{W_A(g)} \times 100 \quad \text{saturated soln.} \qquad S = Mole/gram$$
Poenity

$$S = M_{satur} = \left(\frac{n_B}{V}\right)_{sol} = \frac{W_B}{M_B} \times \frac{1000}{V(ml)}$$

$$\boxed{S\,(g/L) = S(mole/L) \times M_B}$$

→ Acidic or basic nature of salt of WA & WB depends on K_a and K_b value of acid and base.
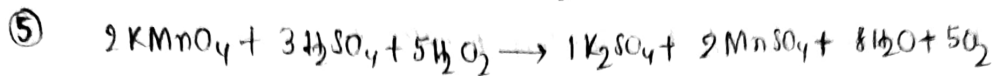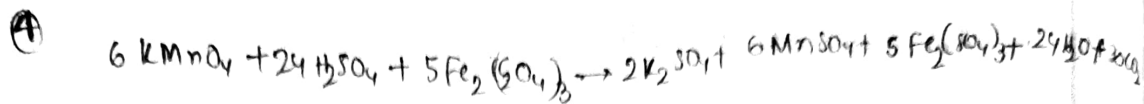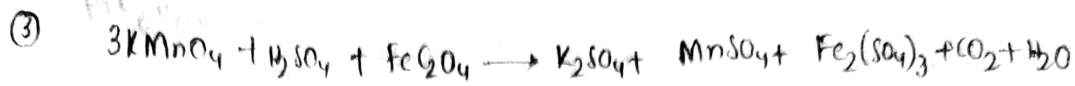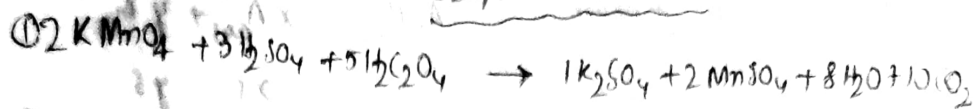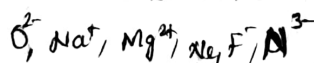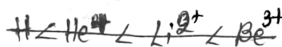
$$K_b > K_a \rightarrow basic \quad , \quad K_a > K_b \rightarrow acidic$$

Important Titrations

① $2KMnO_4 + 3H_2SO_4 + 5H_2C_2O_4 \longrightarrow 1K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2$

② $2KMnO_4 + 8H_2SO_4 + 10FeSO_4 \longrightarrow 1K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O$

③ $3KMnO_4 + H_2SO_4 + FeC_2O_4 \longrightarrow K_2SO_4 + MnSO_4 + Fe_2(SO_4)_3 + CO_2 + H_2O$

④ $6KMnO_4 + 24H_2SO_4 + 5Fe_2(SO_4)_3 \longrightarrow 2K_2SO_4 + 6MnSO_4 + 5Fe_2(SO_4)_3 + 24H_2O + 10CO_2$

⑤ $2KMnO_4 + 3H_2SO_4 + 5H_2O_2 \longrightarrow 1K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$

⑥ $K_2Cr_2O_7 + H_2SO_4 + FeSO_4 \longrightarrow 1K_2SO_4 + Cr_2(SO_4)_3 + 3Fe(SO_4)_3 + H_2O$

⑦ $K_2Cr_2O_7 + 7H_2SO_4 + 3H_2C_2O_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 3Fe(SO_4)_3 + 7H_2O + 6CO_2$

⑧ $3K_2Cr_2O_7 + 21H_2SO_4 + 6FeC_2O_4 \longrightarrow 3K_2SO_4 + 3Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 21H_2O + 12CO_2$

⑨ $K_2Cr_2O_7 + 7H_2SO_4 + Fe_2(SO_4)_3 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + Fe_2(SO_4)_3 + 7H_2O + 6CO_2$

⑩ $2KMnO_4 + 8H_2SO_4 + 10KI \longrightarrow 6K_2SO_4 + 2MnSO_4 + 5I_2 + 8H_2O$

$Z_{eff} \propto \dfrac{\text{+ve charge on ion}}{\text{-ve charge on ion}}$

$Z_{eff} = Z - \sigma$

→ Arrange $Z_{effective}$ order of isoelectronic species.

$H \leq He^+ \leq Li^{2+} \leq Be^{3+}$

$O^{2-}, Na^+, Mg^{2+}, Ne, F^-, N^{3-}$

$Mg^{2+} > Na^+ > Ne > F^- > O^{2-} > N^{3-}$
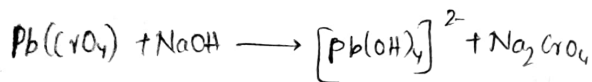$12p \quad 11p \quad 10p \quad 9p \quad 8p \quad 7p$
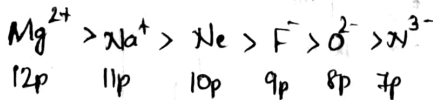
→ Which of the following species does not show effective nuclear charge.
  ① H ② He^{2+} ③ Li^{2+} ④ all of the above.

→ for single e^- species $Z_{effective}$ is not known.

$Pb(CrO_4) + NaOH \longrightarrow [Pb(OH)_4]^{2-} + Na_2CrO_4$

Logarithm values

$$\log_{10} 2 = 0.3010$$

$$\log_{10} 3 = 0.4778$$

$$\log_{10} 5 = 0.6990$$

$$\log_{10} 7 = 0.8451$$

$$\log_{10} 11 = 1.041$$

$$\log_{10} 13 = 1.1139$$