BEHAVIOUR OF GASES

1. Gas law

(i) Boyle's law : $V \propto \frac{1}{P}(n, T = \text{const.})$ $\boxed{P_1V_1 = P_2V_2}$

(ii) Charle's law $V \propto T(n, P = \text{const.})$ $\frac{V_2}{V_1} = \frac{T_2}{T_1}$

(iii) Gay lussac's law : $P \propto T(n, V = \text{const.})$ $\frac{P_2}{P_1} = \frac{T_2}{T_1}$

(iv) Avogadro's law :

$V \propto$ moles $\propto$ number of molecules (P,T = const.)
Ideal gas equations PV = nRT
$R = 0.082$ lit atm mol^{-1} K^{-1}
$R = 8.314$ JK^{-1} mol^{-1} or 8.314 N × m K^{-1} mol^{-1}
$R = 2$ cal K^{-1} mol^{-1}
$R = 8.314 \times 10^7$ erg K^{-1} mol^{-1}

2. Graham's Diffusion law :

It is applicable for non reacting gases

$$\left.\begin{array}{l} r \propto \frac{1}{\sqrt{d}} \\ r \propto \frac{1}{\sqrt{VD}} \\ r \propto \frac{1}{\sqrt{Mw}} \end{array}\right| (P, T = \text{const.})$$

$$VD = \frac{d_{gas}}{dH_2} = \frac{Mw}{2}$$

rate of diffusion $r = \frac{\ell_{\text{diffused gas}}}{t_{\text{time take}}}$

(Where, ℓ = distance travelled by diffused gas)

$$r = \frac{V_{\text{diffused gas}}}{t_{\text{time taken}}}$$

$$r = \frac{n_{\text{diffused gas}}}{t_{\text{time taken}}}$$

3. Dalton's law of Partial Pressure

$$P_{\text{mixture}} = \underbrace{P_1 + P_2 + P_3}_{\text{Partial pressure}} \ldots\ldots\ldots\ldots\ldots(T \,\&\, V\text{const})$$

$$P_1 = P_{\text{moist gas}} = P_{\text{dry gas}} + P_{\text{water vapours}}$$

It is applicable for non reacting gases.

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Methods of determination of partial pressure (P_A & P_B are partial pressure)

(i) From ideal gas equation

$$P_AV = n_A RT \text{ and } P_BV = n_BRT$$

(ii) In the form of mole fraction.

$$P_A = X_AP_T = \frac{n_A}{n_t}P_T$$

$$P_B = X_BP_T = \frac{n_B}{n_t}P_T$$

$$X_A + X_B = 1$$

P_T = sum of partial pressure of all gases

(iii) In the form of volume fraction

$$P_A = \frac{V_A}{V}P_T \text{ and } P_B = \frac{V_B}{V}P_T$$

(iv) If individual pressure and individual volume are given

$$P_A = \frac{V_A}{V}P_1 \quad \text{and} \quad P_B = \frac{V_B}{V}P_2$$

P_1, P_2 = pressure of gases before mixing

P_A, P_B = pressure of gases after mixing

4. Kinetic gas Equation

$$PV = \frac{1}{3}mNV_{rms}^2$$

5. Average KE (KEav)

$$KEav = \frac{3}{2}nRT$$ (n moles)

$$KEav = \frac{3}{2}RT$$ (1 mol or NA molecular)

$$KEav = \frac{3}{2}kT$$ (1 molecule)

$k = 1.38 \times 10^{-23}\ JK^{-1}$

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6.

$$V_{rms} = \sqrt{\frac{v_1^2 + v_2^2 + ...v_n^2}{N}} \qquad V_{avs} = \frac{v_1 + v_2 + v_3....v_n}{N}$$

$$V_{rms} = \sqrt{\frac{3RT}{Mw}} \qquad V_{avs} = \sqrt{\frac{8RT}{\pi Mw}} \qquad V_{mps} = \sqrt{\frac{2RT}{Mw}}$$

$$V_{rms} = \sqrt{\frac{3PV}{Mw}} \qquad V_{avs} = \sqrt{\frac{8PV}{\pi Mw}} \qquad V_{mps} = \sqrt{\frac{2PV}{Mw}}$$

$$V_{rms} = \sqrt{\frac{3P}{d}} \qquad V_{avs} = \sqrt{\frac{8P}{\pi d}} \qquad V_{mps} = \sqrt{\frac{2P}{d}}$$

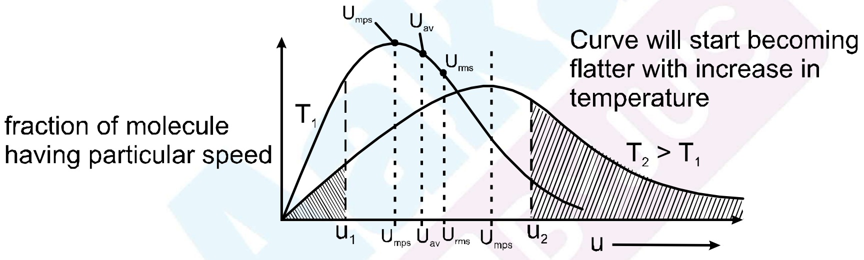
Vrms : Vavs : Vmps

$\sqrt{3}$: $\sqrt{\frac{8}{\pi}}$: $\sqrt{2}$

1.732 : 1.596 : 1.414

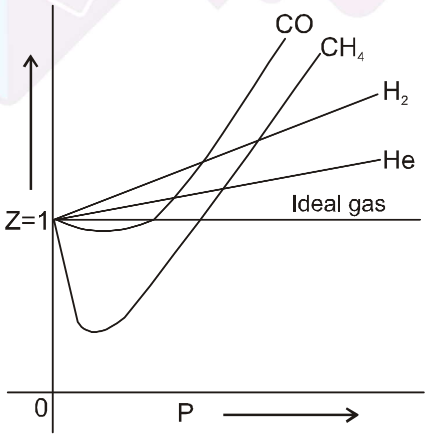
1.224 : 1.128 : 1

7. Maxwell’s distributions of molecular speeds :



8. Variation of compressibility factor (Z) :

Variation of Z with pressure at constant temperature :



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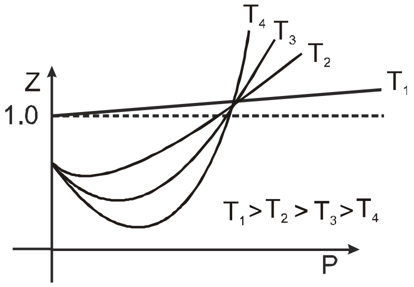
Variation of Z with pressure at different temperature (for same gas) :



Conclusions :

Z = 1 for ideal gas ; Z > 1 at all pressures for He/H_2

Z < 1 at low pressure (for all other gases) ; Z > 1 at high pressure (for all other gases)

Compressibility factor (z) = $\dfrac{P(V_m)obs}{RT}$

If z = 1. the gas show ideal gas behaviour

If z > 1, the gas show positive deviation

If z < 1, the gas show negative deviation

9. Vanderwaal's Equation

$$\left(P+\frac{an^2}{V^2}\right)(V-nb)=nRT$$

$P_1 = P_R + \dfrac{an^2}{V^2}$ $\Rightarrow$ $P_1 > P_R$

a↑ force of attraction ↑ liquification ↑

b↑ effective size of molecule ↑

incompressible vol ↑, compressible vol ↓

(i) At high pressure, Vanderwaal's equation is $\boxed{PV_m - Pb = RT}$

(ii) At low pressure, Vander waal's equation is $\boxed{PV_m + \dfrac{a}{V_m} = RT}$

Virial Equation of state :

Z is expressed in power series expansion of P or $\left(\dfrac{1}{V_m}\right)$

$$Z = 1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \frac{D}{V_m^3} + \ldots\ldots\ldots\ldots$$

Van der waal's equation in virial form :

$$Z = 1 + \frac{1}{V_m}\left(b-\frac{a}{RT}\right)$$

If $\left(b-\dfrac{a}{RT}\right) = 0 \Rightarrow$ at $T = \dfrac{a}{Rb}$; Z = 1

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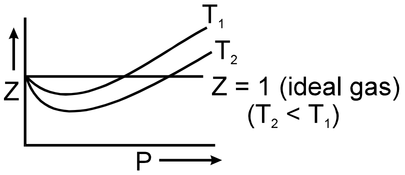
so at $T = \frac{a}{Rb}$, gas will behave as an ideal gas (or follows Boyles law)

But at constant temperature, ideal gas equation is obeying Boyles law as $T = \frac{a}{Rb}$, so the temperature is called Boyles' temperature.

$$T_B = \frac{a}{Rb}$$

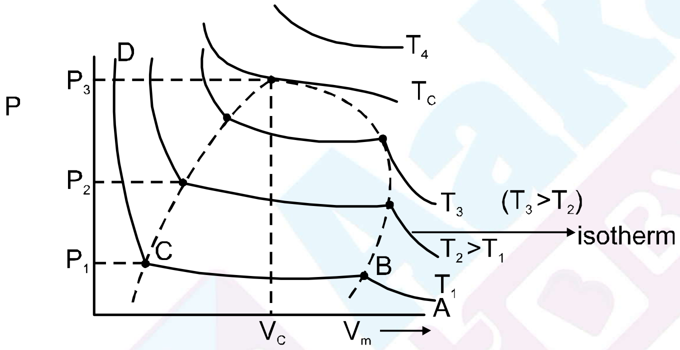
$$Z = 1 - \frac{a}{V_m RT}$$



For a single gas, if we have two graphs as above, we must conclude $T_2 < T_1$.
At Boyles' temperature 'a / RT' factor is compensated by 'b' factor, so Z = 1.

10. Critical constant of a gas (Andrews isotherm)

When pressure increases at constant temperature volume of gas decreases



$T_4 > T_c > T_3 > T_2 > T_1$

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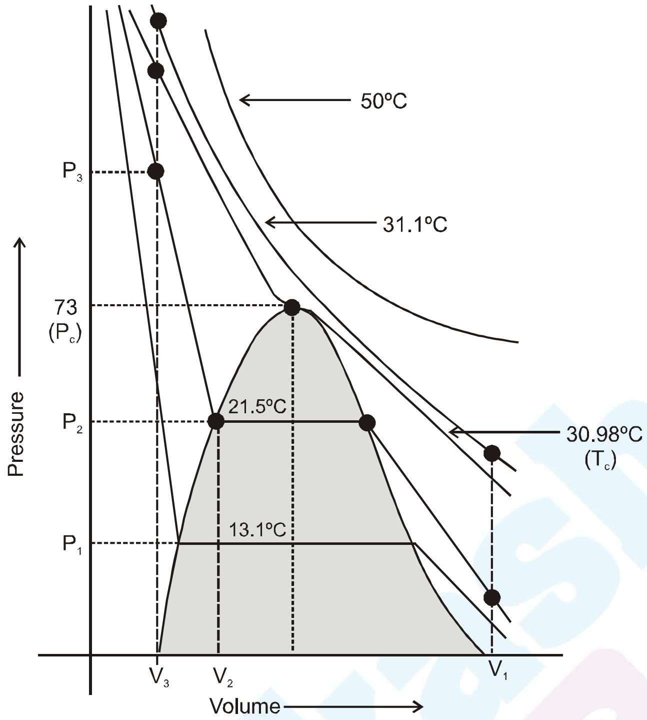

Isotherms of CO_2 at various temperatures

11. Critical point

Critical point : At this point, all the physical properties of liquid phase will be equal to physical properties in vapour such that density of liquid = density of vapour

Inversion temperature : The inversion temperature is the critical temperature below which a known ideal gas (all gases in reality) that is expanding at constant enthalpy will experience a termperature decreases, and above which will experience a temperature increases.

T_c or critical temp : Temperature above which a gas can not be liquified

Higher is the critical temperature, higher will be ease of liquification.

P_c or critical pressure : Minimum pressure which must be applied at critical temperature to convert the gas into liquid.

V_c or critical volume : Volume occupied by one mole of gas at T_C & P_C.

$$T_i = \frac{2a}{Rb}$$

$$T_C = \frac{8a}{27Rb}$$

$$V_C = 3b$$

$$P_C = \frac{a}{27b^2}$$

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CHEMICAL EQUILIBRIUM

1. Equilibrium is a Dynamic Process :

Equilibrium is established in a system when reactants combine to form products at the same rate at which products combine to form reactants.

$$\left(\frac{dx}{dt}\right)_f = \left(\frac{dx}{dt}\right)_b \text{ or } R_f = R_b$$

Chemical equilibrium can be approached from either side. A catalyst can fasten the approach of equilibrium but does not alter the state of equilibrium. System can xbe homogeneous or heterogeneous.

For a reaction in equilibrium

$$aA + bB \rightleftharpoons cC + dD$$

$$K_C = \frac{[C]^c[D]^d}{[A]^a[B]^b} \qquad \text{in terms of active mass}$$

$$K_P = \frac{[P_C]^c[P_D]^d}{[P_A]^a[P_B]^b} \quad \text{in terms of partial pressure}$$

$$K_X = \frac{[X_C]^c[X_D]^d}{[X_A]^a[X_B]^b} \qquad \text{in terms of mole fraction}$$

Partial pressure of solid is taken as unity and in calculation of partial pressure of solids their number of moles are not considered.

$K_P = K_C\ (RT)^{\Delta ng}$

(i) When $\Delta n_g = 0$ then $K_P = K_C$

(ii) When $\Delta n_g > 0$ then $K_P > K_C$

(iii) When $\Delta n_g < 0$ then $K_P < K_C$

$\Delta n_g = (c + d) - (a + b)$

Note : While determining Δn_g, take only gaseous species.

Properties of equilibrium constant :

For $A + B \rightleftharpoons C + D;\ K_C = K$

then (i) $C + D \rightleftharpoons A + B;\ K_C = \frac{1}{K}$

(ii) $2A + 2B \rightleftharpoons 2C + 2D;\ K_C = K^2$

(iii) $\frac{A}{2} + \frac{B}{2} \rightleftharpoons \frac{C}{2} + \frac{D}{2};\ K_C = \sqrt{K}$

(iv) $A \rightleftharpoons B;\ K_C = K_1$

$B \rightleftharpoons C;\ K_C = K_2$

$C \rightleftharpoons D;\ K_C = K_3$

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then $A \rightleftharpoons D$ $K_C = K_1.K_2.K_3$

(v) $A \rightleftharpoons B$ $K_C = K_1$

$C \rightleftharpoons B$ $K_C = K_2$

then $A \rightleftharpoons C$ $K_C = \frac{K_1}{K_2}$

Reaction quotient Q for the reversible reaction

$$A + B \rightleftharpoons C + D$$

$$Q = \frac{[C]\,[D]}{[A]\,[B]}$$

Q is taken at any condition of system.

⇒ If $Q = K_{eq.}$ then system is in equilibrium

⇒ If $Q > K_{eq.}$ system proceeds in backward side to attain equilibrium

⇒ If $Q < K_{eq.}$ system proceeds in forward side to attain equilibrium

For the equilibrium $A \rightleftharpoons nB$

Degree of dissociation $\alpha = \frac{D-d}{D(n-1)}$

where n is the number of moles of products from one mole of reactant, D is the theoretical vapour density (if no dissociation takes place) and d is the observed vapour density (due to dissociation or association) vapour density × 2 = molecular weight.

Vapour density × 2 = molecular weight.

Degree of dissocaition $(\alpha) = \frac{\text{Number of dissociated moles (x)}}{\text{Initial number of moles (a)}}$

Equilibrium constant (K) depends upon temperature and way of writting the reaction.

Le-Chatelier's principle : If the system at equilibrium is subjected to change of any one of the factors such as concentration, temperature or pressure, the system adjusts itself in such a way as to nullify the effect of that change.

The following conclusion have been derived from this principle.

(i) Increases in concentration of any substance favours the reaction in which it is used up.

(ii) High pressure is favourable for the reaction in which there is decreases in volume or number of moles.

(iii) A rise in temperature favours the endothermic reaction.

(iv) At constant volume : There is no effect of adding inert gas on the state of equilibrium at constant volume.

(v) At constant pressure : On adding of inert gas at constant pressure, the reaction proceeds in that direction where the sum of stoichiometric coefficient of gaseous components is greater.

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Application of Le-Chatelier's principle :

(i) Ice water system (melting of ice) :

$$\text{Ice} + \text{Heat} \rightleftharpoons \text{Water}$$

It is an endothermic process and there is decrease in volume. Thus, the favourable conditions for melting of ice are ; (a) High temperature and (b) High pressure.

(ii) Solubility of gases in liquids :

When a gas dissolves in a liquid, there is decreases in volume. Thus, increase in pressure will favour the dissolution of gas in liquid.

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IONIC EQUILIBRIUM

Acid and Base

- **Arrhenius Concept :** Acid ionises in water to give H_3O^+ ion while base ionises to give OH^- ion. Ex HCl, NaOH

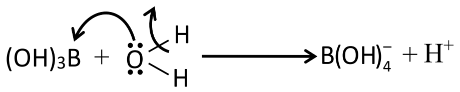
- **Bronsted-Lowry's Protonic Concept :** Acid is H^+ ion donor and base is H^+ ion acceptor. HCl and Cl^- is a conjugate acid - base pair. If acid is weak, its conjugate base is strong and vice-versa. A substance that can accept H^+ ion as well as can donate H^+ ion is called amphiprotic or amphoteric.

$$H_3O^+ \xleftarrow{H^+} \underset{\text{amphoteric}}{H_2O} \longrightarrow H^+ + OH^-$$

A Bronsted Lowry acid - base reaction is always favoured in the direction from the stronger to the weaker acid/base combinations.

- **Lewis concept :**

Lewis acid is an electron - pair acceptor.
Example : Electron deficient molecules : BF_3, $AlCl_3$, H_3BO_3, $BeCl_2$
Cations : H^+, Fe^{3+}, Na^+
Molecules with vacant orbitals : $SiCl_4$, SO_2
Lewis base is an electron pair donor.
Example : Molecules with donatable lone pairs : NH_3, H_2O, CH_3OH
Ion : X^-, CN^-, OH^-
Note :



$$(OH)_3B + H_2O \longrightarrow B(OH)_4^- + H^+$$

Here, Boric acid [i.e. $B(OH)_3$] acepts a lone pair. So, it is a lewis acid.
All lewis bases are bronsted Lowry bases but all the lewis acid are not bronsted acids.

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Dissociation of weak acid and weak base :

Weak acid	Weak base
$HA(aq.) \rightleftharpoons H^{+}(aq.) + A^{-}(aq.)$	$BOH(aq.) \rightleftharpoons B^{+}(aq.) + {}^{-}OH(aq.)$
$K_a = \frac{[H^{+}][A^{-}]}{[HA]}$	$Kb = \frac{[B^{+}][OH^{-}]}{[BOH]}$
$[H^{+}] = \sqrt{K_a.C}$	$[OH^{-}] = \sqrt{K_b.C}$
$[{}^{-}OH] = \frac{K_w}{\sqrt{K_a.C}}$	$[H^{+}] = \frac{Kw}{\sqrt{K_b \times C}}$
$pH = \frac{1}{2}(pK_a - \log C)$ $pH = -\log\sqrt{K_a.C}$	$pH = \frac{1}{2}(\log K_b - \log C)$
$pOH = 14 - \frac{1}{2}(pK_a + \log C)$	$pOH = 14 - \frac{1}{2}(\log K_b - \log C)$

Ostwald dilution law :

According to ostwald dilution low $\alpha \propto \sqrt{\text{dilution}}$

At infinite dilution , $\propto = 100\%$

For a weak acid by Ostwald dilution law

$$K_a = \frac{C\alpha^2}{(1-\alpha)} = C\alpha^2 \qquad [H^{+}] = C\alpha$$

$$\left[H^{+}\right] = \sqrt{K_aC}, pH = \frac{1}{2}\left[pK_a - \log C\right]$$

and for weak base

$$K_b = \frac{C\alpha^2}{(1-\alpha)} = C\alpha^2 \qquad [OH^{-}] = C\alpha$$

$$\left[OH^{-}\right] = \sqrt{K_bC} \qquad pOH = \frac{1}{2}\left[pK_b - \log C\right]$$

Ostwald dilution law is only applicable for weak electrolytes.

For conjugate acid-base pairs

$K_aK_b = K_w = 1 \times 10^{-14}$ at 25°C

$K_aK_b = K_w = 10^{-12}$ at 90°C

$K_w = [H_3O^{+}]\,[OH^{-}] = 1 \times 10^{-14}$ at 298 K

K_w is called ionic product of water or autoionisation or autoprotolysis constant.

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In a mixture of strong acid or bases.

$$\left[H^+\right]=\left[H_3O^+\right]=\frac{\sum NV}{\sum V},\left[OH^-\right]=\frac{\sum NV}{\sum V}$$

In a mixture of acid and base, resultant is

(a) acidic mixture if N_1V_1 (acid) > N_2V_2 (base)

$$\left[H_3O^+\right]=\frac{N_1V_1-N_2V_2}{V_1+V_2}$$

(b) basic mixture if N_2V_2 (base) > N_1V_1 (acid)

$$\left[OH^-\right]=\frac{N_2V_2-N_1V_1}{V_1+V_2}$$

(c) neutral mixture if N_1V_1 (acid) = N_2V_2 (base)

Where K_a is the ionisation constant of acid and K_b is the ionisation constant of its conjugate base.

$HA + H_2O \rightleftharpoons H_3O^+ + A^-$, K_a

$A^- + H_2O \rightleftharpoons HA + OH^-$, K_b

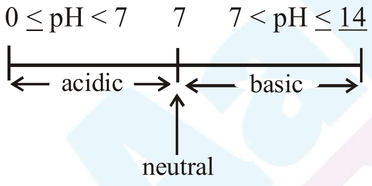
$pK_a + pK_b = 14 = pK_w$

$pH = -\log [H_3O^+]$

$pOH = -\log [OH^-]$

$pX = -\log X$

$pH + pOH = pK_w = 14$



Buffers :

Buffer solutions are which have resistive nature for pH change

(i) On dilution pH of buffer solution remains unchanged.

(ii) When small amount of SA or SB is mixed in buffer solution then pH of buffer solution remains almost unchanged.

Types of buffer solution :

(i) Simple buffer solution (Aq. solution of WAWB salts)

(ii) Mixed buffer solution :

(a) Acidic buffer solution (WA + WA-SB salts)

(b) Basic buffer solution (WB + WB-SA salt)

Henderson - Hasselbalch equation for buffer

Acidic : $pH = pK_a + \log \frac{[\text{conjugate base}] \text{ or } [\text{salt}]}{[\text{weak acid}]}$

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Basic : $pOH = pK_b + \log \dfrac{[\text{conjugate acid}]\text{or}[\text{salt}]}{[\text{weak base}]}$

Solubility product

Ionisation of weak electrolyte is decreased in the presence of common ion is called common ion effect. Solubility product of the sparingly soluble salt A_xB_y with solution (s) mol/litre in saturated solution.

$$A_xB_y \rightleftharpoons xA + yB \qquad K_{sp} = x^x\, y^y\, (s)^{x+y}$$

Salt analysis of inorganic mixture depends on common ion effect and values of solubility products. In the presence of common ion solubility of electrolyte always decreases.

Solute AB is precipitate if $[A^+][B^-] > K_{sp}$

Group Precipitation

(i) $K_{sp} > [\ ]\,[\ ] >$ Ionic product $\Rightarrow$ unsaturated

(ii) $K_{sp} = [\ ]\,[\ ] =$ Ionic product $\Rightarrow$ saturated

(iii) $K_{sp} < [\ ]\,[\ ] <$ Ionic product $\Rightarrow$ super saturated

$\Rightarrow$ precipitation occurs

Salt and Salt Hydrolysis :

$$\text{Salt + Water} \underset{\text{Neutralisation }(\Delta H = -ve)}{\overset{\text{Hydrolysis }(\Delta H + ve)}{\rightleftharpoons}} \text{Acid + base}$$

Types of Salt :

(i) General (ii) acidic (iii) basic (iv) Mixed (v) Double (vi) Complex.

Types of General Salts :

(a) SA-SB (b) SA-WB (c) WA-SB (d) WA-WB

Types of salt	Name of hydrolysis	Nature of aqueous solution and pH
SA - SB	—	Neutral, pH = 7
SA - WB	Cationic	Acidic, pH < 7
WA - SB	Anionic	Basic, pH > 7

	$K_a > K_b$	$K_b > K_a$	$K_a = K_b$
Hydrolysis	Cationic - anionic	Anionic - Cationic	Neutral hydrolysis
Nature	Acidic	Basic	Neutral
pH	pH < 7	pH > 7	pH = 7

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Summary :

Type of salt	$K_b = \frac{K_w}{\text{Ionisation constant of weak acid}}$	$h = \sqrt{\frac{K_b}{C}}$	$\left[H^+\right]$	pH
SASB	–	–	–	7
WASB	$K_h = \frac{K_w}{K_a}$	$h = \sqrt{\frac{K_w}{K_a \times C}}$	$\sqrt{\frac{K_w \times K_a}{C}}$	$7 + \frac{1}{2}pK_a + \frac{1}{2}\log C$
SAWB	$K_h = \frac{K_w}{K_b}$	$h = \sqrt{\frac{K_w}{K_b \times C}}$	$\sqrt{\frac{K_w \times C}{K_b}}$	$7 - \frac{1}{2}pK_a - \frac{1}{2}\log C$
WAWB	$K_h = \frac{K_w}{K_a \times K_b}$	$h = \sqrt{\frac{K_w}{K_a \times K_b}}$	$\sqrt{\frac{K_w \times K_a}{K_b}}$	$7 + \frac{1}{2}pK_a - \frac{1}{2}pK_b$

= For precipitation of common salt (NaCl),

HCl gas is passed & for soap ($C_{17}H_{35}$ COONa), NaCl is mixed. For amphiprotic anion (as HCO_3^-)

$$pH = \frac{pK_1 + pK_2}{2}$$

For acidic indicator (HIn),

$$HIn \rightleftharpoons H^+ + In^-,$$

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

For basic indicator (InOH)

$$InOH \rightleftharpoons In^+ + OH^-$$

$$pOH = pK_{In} + \log \frac{[In^+]}{[InOH]}$$

Colour change of the indicator is explained by:

(i) Ostwald's Theory

Name of indicator	**Colour in acidic medium**	**Colour in basic medium**	**Working pH range of indicators**
Methyl orange (MeOH)	Orange red	Yellow	3.1 to 4.5
Methyl red	Red	Yellow	4.2 to 6.2
Phenol red	Yellow red	Red	6.2 to 8.2
Phenolphthalein (HPh)	Colourless	Pink	8.2 to 10.2

Acid-Base Titration

Type of Titration	**pH range of Titration**	**Suitable indicators**
SA/SB.	3 - 11	All indicators (MeOH, HPh etc.)
SA/WB	3 - 7	Methy orange (MeOH) and methyl red
WA/SB	7 - 11	Phenolphthalein (Hph)
WA/WB	6.5 – 7.5	Phenol red

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