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IMPORTANT FACTS AND FORMULAE FOR JEE IIT - CHEMISTRY

SOME BASIC CONCEPTS

- **1 mole** = N_{Avg} × number of species = 6.023×10²³ species i.e., atoms, molecules, ions, etc.
- 2. Atomic mass = Mass of one atom Gram-atomic mass = Mass of one mole of atoms

= Mass of 6.023×10^{23} atoms in gms.

e.g. Atomic mass of O is 16 amu. gm-atomic mass of O is 16 gm.

: 16 gm O-contains 6.023×10^{23} oxygen atoms.

Atomic mass = $\frac{\text{Average mass of an atom}}{1/12 \times \text{Mass of an atom of C}^{12}}$

Average atomic mass = $\frac{\text{R.A.(1)} \times \text{M.No} + \text{R.A.(2)} \times \text{M.No}}{\text{R.A.(1)} + \text{R.A.(2)}}$

Here R.A = Relative Abundance, Mass No. = Mass number.

3. 1 amu (atomic mass unit) = $\frac{1}{N_{Avg}}$ = 1 Avogram

 $=\frac{1}{6.023 \times 10^{23}}$ gm = 1.66 × 10⁻²⁴ gm = 1 Dalton

4. **Molecular weight** = Weight of one molecule

Molar mass or gm-molecular weight = weight of one mole of molecule

= wt. of 6.023×10^{23} molecules

5. **Moles** = $\frac{\text{Weight(gm)}}{\text{Molar mass (gm / mole)}} = \frac{\text{volume of gas at STP(L)}}{22.4 \text{ lit.}}$

= Molarity × Volume (in L)

Millimoles = Molarity × Volume (mL)

6. No. of equivalent
$$= \frac{\text{Weight(gm)}}{\text{gm.equivalent weight}}$$

= Normality × Volume (L) Milliequivalent = Normality × Volume (ml)

7. Equivalent Weight =
$$\frac{\text{Molar mass}}{n - \text{factor}}$$

8. For acid-base, *n*-factor : No. of replaceable H⁺ or OH⁻ ions per mole of the species.

For compounds undergoing redox reaction, *n*-factor, no. of moles of electrons gained or lost per mole of the species. Example,

For H₃PO₄, Eqv. weight = $\frac{\text{Mol. wt}}{3}n$ -factor = 3(3 replaceable H⁺ ions) For NH3, Eqv. weight = $\frac{\text{Mol. wt.}}{1}n$ -factor = 1(can replace one mole H⁺

per mole)

For Ag₃PO₄, Eqv. wt. $= \frac{\text{Mol. wt}}{3}$ n-factor = 3For Ba₃(PO₄)₂, Eqv. wt. $= \frac{\text{Mol. wt.}}{6}$ n-factor = 6For I₂ \rightarrow Γ , Eqv. wt. I₂ $= \frac{\text{Mol. wt.}}{2}$

Eq. mass of $KMnO_4$ in acidic medium

 $MnO_{4}^{-} + 8H^{+} + 5e^{-} \rightarrow Mn^{2+} + 4H_{2}O \qquad Eq. Mass of KMnO_{4} = \frac{Formula wt.}{5}$ $Eq. Mass of KMnO_{4} in neutral medium$ $MnO_{4}^{-} + 4H^{+} + 3e^{-} \rightarrow MnO_{2}^{-} + 4H_{2}O \qquad Eq. Mass if KMnO_{4} = \frac{Formula wt.}{3}$ $Eq. Mass of KMnO_{4} in basic medium$ $MnO_{4}^{-} + e^{-} \rightarrow MnO_{4}^{2-} \qquad Eq. Mass if KMnO_{4} = \frac{Formula wt.}{1}$ $Vapour density = \frac{Molar mass}{2}$

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10. **Molar volume** = volume of 1 mole of gas at NTP/STP = 22.4 L or 22400 mL 11. **Dulong and Petit's law :** Atomic mass (approx.) = $\frac{6.4}{\text{specific heat}}$ (for metals only) (cal/g) The law is applicable only to solid elements except Be, B, C and Si. Valency = $\frac{\text{Approx. Atomic mass}}{\text{Eqv. mass}}$ The exact valency is a whole number nearest to the approximate valency calculated. The exact valency is multiplied by the Eqv. mass to get Atomic mass. Exact atomic mass = Exact valency \times Eq. mass. 12. Relation between molecular and empirical formulae : Molecular formula = $n \times \text{Empirical formula}$ $\therefore n = \frac{\text{Molecular formula weight}}{-}$ Empirical formula weight **Molarity** = $\frac{\text{Moles of solute}}{\text{volume of solution (L)}}$ 13. **Molality** = $\frac{\text{mole of solute}}{\text{mass of solvent(kg)}}$ 14. **Mole fraction** = mole fraction of A in mixture of A and B = $X_A = \frac{II_A}{n_A + n_B}$ 15. mole fraction of B in mixture of A and B = $X_B = \frac{n_B}{n_A + n_B}$ **Normality** = $\frac{\text{number of gm equivalent of solute}}{\text{volume of solution(L)}}$ 16. **Atomicity** $(\gamma) = \frac{C_p}{C_r}$ (1.66 for mono-atomic, 1.4 for di-atomic, 1.33 for tri-17. atomic gas) At mass of gaseous element = $\frac{\text{mol. mass}}{\text{Atomicity}}$ (Atomicity = number of atoms present in a molecule of the element). $C_{p} - C_{v} = R = 1.98$ cal mol⁻¹ K⁻¹ Molar heat = specific heat x mol. mass

STATES OF MATTER

Boyle's law

PV = constant [at constant n, T] $\therefore P_1V_1 = P_2V_2$

Charle's

$$\frac{V}{T} = \text{constant} \quad [\text{at constant } n, P] \qquad \therefore \frac{V_1}{T_1} = \frac{V_2}{T_2};$$
$$V_t = V_0 \left(1 + \frac{t}{273}\right) \quad [T \text{ (kelvin)} = 273 + t \text{ (°C)}]$$

Gay-Lussac's law

 $\frac{P}{T}$ = constant [at constant n, V] $\therefore \frac{P_1}{T_1} = \frac{P_2}{T_2}$

Ideal gas equation

 $\frac{PV}{nT} = R = 0.0821 \ l. \ atm.K^{-1} \ mol^{-1}$ = 1.987 Cal K⁻¹ mol⁻¹ = 8.314 J K⁻¹ mol⁻¹ 1 atm = 760 mm of Hg = 76 cm of Hg = 101325 pascal ; 1 bar = 0.9862 Atm Standard Temperature and pressure (STP) or Normal Temperature and Pressure (NTP) P = 1 atm, T = 0° C or 273 K

Density and molar mass relation

Density (d) = $\frac{PM}{RT}$

Dalton's law of Partial Pressure

 $P_{Total} = P_1 + P_2 + P_3 + \dots$

Where P₁, P₂,....etc. are partial pressures of individual gases. Partial pressure = Total pressure × mole function

Relative Humidity = $\frac{\text{Partial pressure of water in air}}{\text{Vapour pressure of water}}$

Vap. Pressure of dry gas = Vap. Pressure of wet gas - Vap. pressure of water vapour (aqu. tension)

Graham's law (Diffusion and Effusion)

 $\frac{(r_{\mathbf{A}})\text{Rate of effusion of gas A}}{(r_{\mathbf{B}})\text{Rate of effusion of gas B}} = \frac{\sqrt{\rho_{\mathbf{B}}}}{\sqrt{\rho_{\mathbf{A}}}} = \frac{\sqrt{M_{\mathbf{B}}}}{\sqrt{M_{\mathbf{A}}}} \quad \text{[at constant pressure]}$ $\frac{r_{\mathbf{A}}}{r_{\mathbf{B}}} = \frac{P_{\mathbf{A}}}{P_{\mathbf{B}}}\sqrt{\frac{M_{\mathbf{B}}}{M_{\mathbf{A}}}} = \frac{P_{\mathbf{A}}}{P_{\mathbf{B}}}\sqrt{\frac{\rho_{\mathbf{B}}}{\rho_{\mathbf{A}}}} \quad \text{[at different pressure]}$

Velocity of Molecules

Root mean square velocity $(C_{RMS}) = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3P}{d}}$ Average velocity $(C_{AVG}) = \sqrt{\frac{8RT}{\pi M}}$ Most probability velocity $(C_{MP}) = \sqrt{\frac{2RT}{M}}$ $C_{MP} < C_{AVg} < C_{RMS}$ $C_{MP} : C_{AVg} : C_{RMS} ::1:1.128:1.224$

Real Gases, Compressibility factor

$$Z = \left(\frac{PV}{n RT}\right)$$

Z measures the extent of non-idealness of an ideal gas.

Z < 1, implies that gas is more compressible

Z > 1 , implies that gas is less compressible

Z = 1, implies that gas is ideal.

Gas Equation (van der Waal's)

$$\begin{pmatrix} P + \frac{n^2 a}{V^2} \end{pmatrix} (V - nb) = nRT$$

$$\Delta H_{\mathbf{vap}} = \frac{2.303 RT_1 T_2}{(T_2 - T_1)} \log \frac{P_2}{P_1}$$

 P_{1},P_{2} vapour pressure at $T_{1},\,T_{2}$

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

i) At low pressure : $\left(p + \frac{a}{v^2}\right)V = RT$ ii) At high pressure : P (V - b) = RT Units of a are atm L² mol⁻² and *b* are L mol⁻¹

Greater is the value of a means gas can be easily liquefied

Co-volume or excluded volume = $4N_0V_m$

$$m \qquad \left[V_{m} = \frac{4}{3} \pi r \right]$$

i) Collision frequency, $Z = \frac{\pi C_{Avg} \sigma^2 (N / V)^2}{\sqrt{2}}$

ii) Mean free path $(\lambda) = \frac{V}{\sqrt{2\pi\sigma^2}N}$, where σ =molecular diameter N/V = number of molecules per unit volume

Nature of Gas Constant R

 $R = \frac{P \times V}{n T} = \frac{Pressure \times Volume}{Moles \times Degree(K)} = \frac{(Force / Area) \times (Volume)}{Moles \times Degree(K)} = \frac{Force \times Length}{Moles \times Degree(K)}$ = Work done per degree per mole

Units of gas constant (R)

$$\begin{split} & \text{R} = 0.0821 \text{ atm } \text{L } \text{K}^{\text{-1}} \text{ mol}^{\text{-1}} = 0.0821 \text{ atm } \text{dm}^{3} \text{K}^{\text{-1}} \text{ mol}^{\text{-1}} \\ & (\text{Here P} = 1 \text{ atm, V} = 22.4 \text{ L}, \text{ T} = 273 \text{ K}, 1 \text{ L} = 1 \text{ dm}^{3}) \\ & \text{If P is expressed in dynes per square centimeter} \\ & (\text{P} = 76 \times 981 \times 13.6 \text{ dyne } / \text{cm}^{2}) \\ & \text{V} = 22400 \text{ dm}^{3} \text{ and } \text{T} = 273 \text{ K} \\ & \text{then R} = 8.314 \times 10^{7} \text{ ergs } \text{K}^{\text{-1}} \text{ mol}^{\text{-1}} = 8.314 \text{ J } \text{K}^{\text{-1}} \text{ mol}^{\text{-1}} \text{ and } \text{R} = 1.987 \text{ cal } \text{K}^{\text{-1}} \\ & \text{i mol}^{\text{-1}} \\ & 1 \text{ atm. Pressure} = 0.76 \text{ m} \times 13.6 \times 10^{3} \text{ kg m}^{\text{-3}} \times 9.81 \text{ ms}^{\text{-2}} = 101.325 \times 10^{3} \\ & \text{Nm}^{\text{-2}} = 101.325 \times 10^{3} \text{ Pa} \quad [\because 1 \text{ Nm}^{\text{-2}} = 1 \text{ Pa}] \\ & \text{Thus, the gas constant R} = \frac{(101.325 \times 10^{3} \text{ Nm}^{\text{-2}}) \times (22400 \times 10^{\text{-6}} \text{m}^{3})}{(273 \text{ K}) \times (\text{Imol})} \\ & = 8.314 \text{ Nm } \text{ K}^{\text{-1}} \text{ mol}^{\text{-1}} \\ & = 5.189 \times 10^{19} \text{ eV} \text{K}^{\text{-1}} \text{ mol}^{\text{-1}} \\ & = 5.189 \times 10^{19} \text{ eV} \text{K}^{\text{-1}} \text{ mol}^{\text{-1}} \end{split}$$

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i) Avogadro's Law
V ∝ n or V ∝ N (at constant T, P)
ii) Calculation of Kinetic Energy
According to gas equation, PV =
$$\frac{1}{3}$$
 Mu² for 1 mole of gas
or PV = $\frac{2}{3} \times \frac{1}{2}$ Mu²
or $\frac{1}{2}$ Mu² = $\frac{3}{2}$ PV = $\frac{3}{2}$ RT = K.E.
For 1 molecule, the K.E.
= $\frac{3}{2} \frac{\text{RT}}{\text{N}_0} = \frac{3}{2}$ KT { $\frac{\text{R}}{\text{N}_0} = \text{K}$ (Boltzmann constant)}
iii) Average molecular weight of a gaseous mixture
M_{mix} = $\frac{\sum n_t M_t}{\sum n_t}$ where n_t is the number of moles and M_t is the
molecular weight of the component.
iv) Critical Pressure (Pc) : P_c = $\frac{a}{27b^2}$
v) Critical Temperature (T_c) : T_c = $\frac{8a}{27Rb}$
vi) Critical Volume (V_c) : V_c = 3b
vii) Relationship between Pc, V_c and T_c : $\frac{P_cT_c}{\text{RT}_c} = \frac{3}{8}$
viii) Boyle's Temperature : T_B = $\frac{a}{bR}$

ATOMIC STRUCTURE

Planck's Quantum theory

 $E = hv = \frac{hc}{\lambda}$ Where, h = Planck's constant (6.023×10⁻³⁴ Js), v = Frequency ofradiation, c = Velocity of light, $\lambda =$ wavelength of radiation $c = v\lambda$ and wave number $(v) = \frac{1}{\lambda}$

Moseley's Equation, $\sqrt{v} = a (z - b)$ Heisenberg's uncertainty equation, $\Delta p \cdot \Delta x \ge \frac{h}{4\pi}$ and $\Delta E \cdot \Delta t \ge \frac{h}{4\pi}$ Kinetic energy of electron in nth quantum state $= \frac{1}{2} \frac{Zke^2}{r_n}$ Potential energy of electron in nth quantum state $= -\frac{Zke^2}{r_n}$ Total energy (E) $= -\frac{Zke^2}{2r_n} = -\frac{(13.6)Z^2}{n^2}$ eV per atom $= -\frac{313.6}{n^2} \text{ kcal/mol} = -\frac{1312}{n^2} \text{ kJ/mol}$ $= -21.8 \times 10^{-19} \frac{Z^2}{n^2} \text{ J/atom.}$

Radius of nth quantum state = $\frac{n^2 h^2}{4\pi^2 m k Z e^2} = \frac{n^2 a_0}{Z}$ (a₀ = 0.529 Å)

$$v_{n} = \frac{2\pi Z k e^{2}}{nh} = \frac{Z}{n} \times 2.188 \times 10^{6} m/s$$

No. of revolution per second in r.p.s = $\frac{v_n}{2\pi r_n} = \frac{Zv_n}{2\pi n^2 a_0}$

Wave number of spectral line,

$$\overline{v} = \frac{1}{\lambda} = R_{\rm H} Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \qquad (R_{\rm H} = 109743 \text{ cm}^{-1}$$
$$= \left(R_{\rm H} = 109743 \text{ cm}^{-1} = \frac{2\pi^2 \text{me}^4 \text{k}^2}{\text{h}^3 \text{c}} \right)$$

de Broglie equation

$$\lambda = \frac{h}{p} = \frac{h}{mv}$$

Azimuthal (or angular) Quantum number (l); $0 \le l \le n - 1$

Orbital angular momentum, L = $\sqrt{l(l+1)} \frac{h}{2\pi}$

Magnetic quantum number (m); $-l \le m \le l$, total (2*l* + 1) values.

Magnetic moment, $\mu_{\mathbf{L}} = \frac{eh}{4\pi mc} \sqrt{l(l+1)}$ Spin angular momentum $\mu_{\mathbf{s}} = \frac{eh}{2\pi mc} \sqrt{s(s+1)}$

Aufbau Principle : subshell with lowest (n + l), value us filled first, if two subshells have same (n + l) value, lower value of 'n' is filled up first.

Photoelectric effect

Maximum kinetic energy of ejected electron

$$\frac{1}{2}mv_{\max}^{2} = h\mathbf{v} - h\mathbf{v_{0}} = hc\left[\frac{1}{\lambda} - \frac{1}{\lambda_{0}}\right]$$

Stopping potential, $eV_0 = h(v - v_0)$

Binding energy = Mass defect × 931 MeV

- i) Radius of Nucleus $(r_n) = r_0 \times A^{1/3}$ where A is the mass number and r0 is proportionality constant whose value is 1.4×10^{-13} cm.
- The radius of the nucleus is approximately 10⁻⁵ times the radius of the atoms. Volume of the nucleus of an atom is about 10⁻⁵ times the volume of the atom.
- iii) Energy of an electron in nth shell of hydrogen atom $E_n \propto 1/n^2$
- iv) Although the energy of electron increases with increase in the value of n(orbit), yet the difference of energy between successive orbits decreases.

Thus, $E_2 - E_1 > E_3 - E_2 > E_4 - E_3 > E_5 - E_4$, etc.

- v) No. of spectral lines when electron comes from n^{th} level to ground level = $\frac{n(n-1)}{2}$
- vi) Number of sub-shells in a main energy level = n
- vii) Number of orbitals in a main energy level = n^2
- viii) Number of orbitals in a sub-shell = (2l + 1)
- ix) Number of electrons in each orbital = 2
- x) Maximum number of electrons in a subshell = 2(2l + 1)
- xi) Maximum number of electrons in main shell = $2n^2$

SOLUTIONS

Solubility

 $\Delta H_{\text{solution}} = \Delta H_{\text{lattice}} - \Delta H_{\text{hydration}}$

If hydration energy > lattice energy, the solute goes into solution and $\Delta H_{solution}$ comes out to be negative value i.e., the process is exothermic.

Henry's law

Mass of the gas dissolved per unit volume (n) \propto pressure (P)

Parts per million

 $ppm(A) = \frac{Mass \text{ of } A}{Total \text{ mass of the solution}} \times 10^{6}$ Weight% = wt. of solute per 100g of solution. Volume %: (a) wt. of solute per 100 ml of solution. (b) Volume of solute per 100 ml of solution. Mole % = $\frac{Moles \text{ of solute}}{Moles \text{ of solute}} \times 100$

Relationship between Molality (m) of a solution and mole fraction of the solute (X_2)

 $X_2 = \frac{mM_1}{1 + mM_1}$ where M_1 is the molecular mass of the solvent.

Relationship between Molality (m), Molarity (M) and density of the solution (d)

Molality, m = $\frac{M}{1000d - MM_2} \times 1000$

where M_2 is the molecular mass of the solute.

Relationship between mole fraction of the solute (x_2) and Molarity (M) of the solution

$$X_2 = \frac{MM_1}{M(M_1 - M_2) + d}$$

where M_1 and M_2 are the molecular masses of solvent and solute respectively. Density of solution is d. For isotonic or iso-osmotic solutions

 $\frac{\mathbf{n_1}}{\mathbf{V_1}} = \frac{\mathbf{m_2}}{\mathbf{V_2}} [:: \mathbf{\pi_1} = \mathbf{\pi_2}]$

Raoult's law (Vapour-Pressure lowering of solution)

 $\begin{aligned} p_{s} &= p_{0} \ . \ X_{solvent} \\ \frac{p_{0} - p_{s}}{p_{s}} &= \frac{n}{N} \end{aligned}$

 p_0 = pressure of pure solvent; p_s = pressure of solvent

 α during dissociation.

 $\alpha = \frac{i-1}{n-1}$, n = no. of ions after dissociation

 $\pmb{\alpha}$ during association.

$$\alpha = \frac{1-i}{1-(1/n)}$$

Variation of vapour pressure with temperature

$$\log_{10} \frac{P_2}{P_1} = \frac{\Delta H}{2.303 \, \text{R}} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

Variation of vapour pressure with external pressure

$$\log_{10}\left(\frac{P_2}{P_1}\right) = \frac{V_0}{2.303 \text{ RT}} (P_2 - P_1)$$

Osmotic Pressure

$$\pi = i \frac{n_1}{V} RT = hdg$$
 (due to association or dissociation)

Van Hoff Factor

$$i = \frac{P_{observed}}{P_{normal}} = \frac{(\Delta P)_{observed}}{(\Delta p)_{normal}} = \frac{(\Delta T_b)_{observed}}{(\Delta T_b)_{normal}} = \frac{(\Delta T_f)_{observed}}{(\Delta T_f)_{normal}}$$
$$= \frac{Normal molecular mass}{Observed molecular mass}$$

Observed molecular mass

For solution showing dissociation, the Van't Hoff factor i > 1For solution showing association, the Van't Hoff factor i < 1For solution showing no dissociation or association, the Van't Hoff factor i = 1

Raoult's Law

 $\mathbf{P} = \mathbf{P}_{\!\mathbf{A}} + \mathbf{P}_{\!\mathbf{B}} = \mathbf{P}_{\!\mathbf{A}}^{\mathbf{0}} \mathbf{X}_{\!\mathbf{A}} + \mathbf{P}_{\!\mathbf{B}}^{\mathbf{0}} \mathbf{X}_{\!\mathbf{B}} = (1 - \mathbf{X}_{\!\mathbf{B}}) \mathbf{P}_{\!\mathbf{A}}^{\mathbf{0}} + \mathbf{P}_{\!\mathbf{B}}^{\mathbf{0}} \mathbf{X}_{\!\mathbf{B}}$

Ideal Solutions

They obey Raoult's law for all range of concentration and temperature. $\Delta H_{mix} = 0$ and $\Delta V_{mix} = 0$ e.g., Hexane + Heptane. Ethyl bromide + Ethyl chloride, Chlorobenzene + Bromobenzene, etc.

Non-Ideal Solutions

The non-ideal solution do not obey Raoult's law for all concentrations. $\Delta H_{mix} \neq 0$ and $\Delta V_{mix} \neq 0$

If $V_{mix} > 0$ and $\Delta H_{mix} \neq 0$, then non-ideal solutions show positive deviations.

If $V_{mix} < 0$ and $\Delta H_{mix} < 0$, then non-ideal solutions show negative deviations.

e.g. Acetone + ethyl alcohol, water + ethyl alcohol. CCl₄ + CHCl₃ ethanol + CHCl₃.

Acetone + carbon disulphide, Acetone + Benzene, etc.

Types of Azeotropic Mixtures

(i) Minimum Boiling Azeotropes :

e.g., Ethanol (95.5%) + water (4.5%) mixture boiling.

(ii) Maximum Boiling Azcotropes :
 e.g., HNO3 (68%) + water (32%) mixture boiling at 393.5 K.

Elevation in boiling point

$$\begin{split} &\Delta T_{b} = T_{b} - T_{0} = K_{b} m \\ &= \frac{K_{b} \times W_{B} \times 1000}{M_{B} \times W_{A}} \text{ where } W_{A} = \text{mass of solvent (g) and } W_{B} = \text{mass of solute (g)} \\ &\text{ solute (g)} \\ &\text{Molal elevation constant (K_{b})} \\ & \text{PT}^{2} \end{split}$$

 $K_{\mathbf{b}} = \frac{RT_{\mathbf{b}}^{2}}{1000L_{\mathbf{v}}} \quad [L_{\mathbf{v}} = latent heat of vapourisation]$

Depression in freezing point

$$\Delta \mathbf{H}_{\mathbf{r}} = \mathbf{T}_{\mathbf{0}} - \mathbf{T}_{\mathbf{p}} = \mathbf{k}_{\mathbf{f}} \times \mathbf{m} = \frac{\mathbf{k}_{\mathbf{F}} \times \mathbf{W}_{\mathbf{B}} \times 1000}{\mathbf{M}_{\mathbf{B}} \times \mathbf{W}_{\mathbf{A}}}$$

Molal depression constant (K_f)

$$K_{f} = \frac{RT_{f}^{2}}{1000L_{f}} \quad [L_{f} = latent heat of fusion]$$

It is interesting to note that all the above relations hold good. Only when K_f and K_b are expressed in Kelvin m⁻¹.

CHEMICAL ENERGETICS AND THERMODYNAMICS

Mechanical work

 $W = -P_{ext} (\Delta V)$ [during expansion]

First law of Thermodynamics

 $\Delta V = 0$ $W = P \Delta V = 0$ $\Delta E = q + W$ $\Delta E = q - P \Delta V$

Cyclic change (reversible)

$$\begin{split} & \mathbf{\Delta} \mathbf{E} = \mathbf{0} \\ & \mathbf{q} = -\mathbf{W} = \mathbf{P} \mathbf{\Delta} \mathbf{V} \\ & \mathbf{q} = -\mathbf{W}_{\text{max}} = \mathbf{P} \int d\mathbf{V} \end{split}$$

Isothermal reversible expansion

 $\Delta H = \Delta E = 0$ (:: internal energy is function of temperature)

q = - W_{max} = 2.303 nRT log
$$\frac{V_2}{V_1}$$
 = 2.303 nRT log $\frac{P_1}{P_2}$

Joule – Thomson coefficient

$$\mu_{\mathbf{JT}} = \left(\frac{\partial \mathbf{T}}{\partial \mathbf{P}}\right)_{\mathbf{H}} = \left(\frac{\partial \mathbf{H}}{\partial \mathbf{P}}\right)_{\mathbf{T}} / \mathbf{C}_{\mathbf{p}}$$

(i) For cooling,
$$u > 0$$
 (-ve sign)

(ii) For heating, u < 0 (+ve sign)

Second Law of Thermodynamics

Efficiency of the Carnot engine = $\eta = \frac{q_2 - q_1}{q_2} = \frac{T_2 - T_1}{T_2} = 1 - \frac{T_1}{T_2}$ q₂ = heat absorbed by engine

 q_1 = heat lost to sink

Entropy Change

 $\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}}$ $\Delta S_{\text{fusion}} = \frac{\Delta H_{\text{fus}}}{T_{\text{fus}}}; \Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T_{\text{van}}}$

 $\Delta G = G_2 - G_1$

 $\Delta G = \Delta H T \Delta S \text{ (Gibb's Helmholtz equation)}$ $\Delta G < 0 \text{ (means spontaneous process),}$

 $\Delta G > 0$ (means non-spontaneous process)

 $\Delta G = 0$ (means system is at equilibrium)

Kirchoff's equation

 $\begin{aligned} \frac{\Delta H_{2} - \Delta H_{1}}{T_{2} - T_{1}} &= \Delta C_{p} \text{ and } \frac{\Delta E_{2} - \Delta E_{1}}{T_{2} - T_{1}} = \Delta C_{v} \end{aligned}$ Where, $\Delta C_{p} = \sum C_{p} \text{ (products)} - \sum C_{p} \text{ (reactants) and} \\ \Delta C_{v} &= \sum C_{v} \text{ (products)} - \sum C_{v} \text{ (reactants)} \end{aligned}$

Degree of dissociation (x)

 $\mathbf{x} = \frac{\mathbf{D} - \mathbf{d}}{\mathbf{d}} = \frac{\mathbf{M}_1 - \mathbf{M}_0}{\mathbf{M}_0}$

where D = theoretical vapour density and d = observed vapour density.

pH of a solution

 $pH = -\log [H_3O^+]$ $pOH = -\log [OH^-]$ $pH + pOH = pK_w = 14$ For neutral solution ; pH = pOH = 7 at 298 K For acidic solution; pH < 7. But pOH > 7 at 298 K

For basic solution; pH>7, But pOH<7 at 298 K

Isothermal (reversible)

 $\Delta S = 2.303 \text{ nR} \log \frac{V_2}{V_1}$ At constant pressure, $\Delta S = 2.303 \text{ C}_p \log_{10} \frac{T_2}{T_1}$ For vaporization, $\Delta S = \frac{\Delta H_{vap}}{T_{bp}}$ $\Delta G^0 = -nFE_{cell}^0$

Sign Convention

If work is done on the system, W is positive.

If work is done by the system, W is negative.

If heat is absorbed by the system, q or Δ H is positive.

If heat is given out by the system, q or ΔH is negative.

If energy is absorbed by the system, i.e. internal energy increases. ΔE is positive.

If energy is released i.e., internal energy of the system decreases. ΔE is negative.

Heat capacity

- (i) Heat capacity at constant volume, $C_{\mathbf{v}} = \left[\frac{\partial E}{\partial T}\right]_{\mathbf{v}}$
- (ii) Heat capacity at constant pressure, $C_{\mathbf{p}} = \left[\frac{\partial H}{\partial T}\right]_{\mathbf{p}}$

For an ideal gas, $C_p - C_v = R$

Heat of Reaction

 $\Delta H = \sum H_{(p)} - \sum H_{(R)}$ For exothermic reactions : $\sum H_p < \sum H_R \quad \therefore \Delta H \text{ is - ve}$ For endothermic reaction : $\sum H_p > \sum H_R \quad \therefore \Delta H \text{ is + ve}$ Heat change at constant pressure = $q_p = \Delta H$ Heat change at constant volume = $q_v = \Delta E$

$$\begin{split} \Delta H &= \Delta U + P \Delta V \\ \Delta H &= \Delta U + \Delta n_{(g)RT} \end{split}$$
 If $\Delta n_{(g)} &= 0$, $\Delta H = \Delta U \\ \Delta n_{(g)} &> 0$, $\Delta H > \Delta U \\ \Delta n_{(g)} &< 0$, $\Delta H < \Delta U \end{split}$

Clausis - Clapeyron equation :

2.303 log
$$\frac{p_2}{p_1} = \frac{\Delta H_v}{R} \left(\frac{T_1 - T_2}{T_1 T_2} \right)$$
 where, $\Delta H_v =$ molar heat of vapourisation.

- i) **Calorific value** is the amount of heat evolved when one gram of fuel as food is burnt in the presence of air or excess of oxygen.
- ii) Joule's relationship between work done (w) and heat produced (H) $W \propto H$ or W = JHWhere, J is called mechanical equivalent of heat. Its value is $J = 4.184 \times 10^{7}$ erg Cal⁻¹ 4.184 J Cal⁻¹.

$$\operatorname{Log} \frac{S_{1}}{S_{2}} = \frac{\Delta H}{2.303 R} \left(\frac{1}{T_{1}} - \frac{1}{T_{2}} \right)$$

Where S_1 and S_2 are solubility at temperature T_1 and T_2 respectively.



CHEMICAL AND IONIC EQUILIBRIUM

Equilibrium in water = $\left(\frac{dx}{dt}\right)_{\text{forward}} = \left(\frac{dx}{dt}\right)_{\text{backward}}$ $aA + bB \rightleftharpoons cC + dD$ $\left(\frac{dx}{dt}\right)_{\text{forward}} \propto K_{\text{forward}} \left[A\right]^{a} \left[B\right]^{b}$ $\left(\frac{dx}{dt}\right)_{\text{backward}} \propto \mathbf{K}_{\text{backward}} \left[\mathbf{C}\right]^{\mathbf{c}} \left[\mathbf{D}\right]^{\mathbf{d}}$ Equilibrium constant, $K = \frac{[C]^{c}}{[A]^{a}} \frac{[D]^{d}}{[B]^{b}} = \frac{K_{forward}}{K_{backward}} = K_{c}$ In terms of partial pressure Equilibrium constant, $K_{\mathbf{p}} = \frac{p_{\mathbf{C}}^{\mathbf{c}}}{p_{\mathbf{a}}^{\mathbf{a}}} \frac{p_{\mathbf{b}}^{\mathbf{a}}}{p_{\mathbf{b}}^{\mathbf{b}}}$ $\mathbf{K}_{\mathbf{p}} = \mathbf{K}_{\mathbf{c}} (\mathbf{RT})^{\Delta n_{\mathbf{g}}} \qquad \left[\Delta n_{\mathbf{g}} = \mathbf{n}_{\mathbf{p}} - \mathbf{n}_{\mathbf{r}} \right]$ Van't Hoff equation $\log_{10} \frac{k_2}{k_1} = \frac{\Delta H^o}{2.303 R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$ Gibb's Free energy $\Delta G = \Delta H - T \Delta S$ $\Delta G^{o} = -2.303 RT \log_{10} K$ **Buffer:** $pH = pK_a + log \frac{[conjugate base]}{[acid]}$ $pOH = pK_{b} + log \frac{[conjugate acid]}{[base]}$ Mixture of weak acids = $\sqrt{k_1c_1 + k_2c_2}$ $\alpha = \frac{\% \text{ conjugation}}{100}$ $A_{\mathbf{x}}B_{\mathbf{v}} \rightleftharpoons_{\mathbf{x}} A^{\mathbf{y}+} +_{\mathbf{v}} B^{\mathbf{x}-}$

 $\therefore \qquad \mathbf{K_{sp}} = \left[\mathbf{A^{y+}} \right]^{x} \left[\mathbf{B^{x-}} \right]^{y}, \text{ when } \mathbf{A_{x}B_{y}}$ $\mathbf{K_{sp}} = \text{Solubility product.}$

Arrhenius concept : Substances which give H^+ ions when dissolved in water, while which gives OH^- ion are called bases.

Bronsted Lowry concept : Acid donates proton, base accepts proton.

Ostwald's dilution law, $\alpha = \sqrt{\frac{K}{C}}$,

- K = dissociation constant of weak electrolyte
- C = Concentration
- α = degree of dissociation
- $K_{\mathbf{w}} = [H^+][OH^-]$ [ionic product of water]

Hydrolysis constant

$$k_{h} = \frac{h^{2}C}{1-h}$$

$$h = \frac{\text{Amount of salt hydrolysed}}{\text{Total salt taken}}$$

$$\frac{\sqrt{K_{h}}}{\sqrt{K_{m}}} = \frac{K_{m}}{K_{m}}$$

$$h = \sqrt{\frac{K_{\mathbf{h}}}{C}} = \sqrt{\frac{K_{\mathbf{w}}}{K_{\mathbf{b}} \times C}}$$

Strong acid + weak base, Degree of hydrolysis (h) = $\sqrt{\frac{K_{w}}{CK_{b}}}$ $pH = \frac{1}{2} [pK_{w} - K_{b} - logC]$ Strong base + weak base, Degree of hydrolysis (h) = $\sqrt{\frac{K_{w}}{CK_{a}}}$ $pH = \frac{1}{2} [pK_{w} + pK_{a} + logC]$

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Weak acid + weak base, Degree of hydrolysis (h) = $\sqrt{\frac{K_{\mathbf{w}}}{K_{\mathbf{a}} \times K_{\mathbf{b}}}}$ pH = $\frac{1}{2} [pK_{\mathbf{a}} + pK_{\mathbf{w}} - pK_{\mathbf{b}}]$

REDOX REACTIONS AND ELECTROCHEMISTRY

 $E_{cell} = E^{o}_{cell} - \frac{0.059}{n} \log \frac{[Product]}{[Practant]}$ $-\Delta G = nFE_{cell}; -\Delta G^{o} = nFE^{o}_{cell}$ $E^{o}_{cell} = \frac{2.303RT}{nF} \log K_{eq} = \frac{0.591}{n} \log K_{eq} \qquad [At = 25^{o}C]$ $\Delta G^{o} = -2.303 \text{ RT} \log K$

Gibb's –Helmholtz equation

$$\Delta \mathbf{G} = \Delta \mathbf{H} + \mathbf{T} \left(\frac{\mathrm{d}\Delta \mathbf{G}}{\mathrm{d}t} \right)_{\mathbf{p}}$$
$$\Delta \mathbf{H} = \mathbf{n} \mathbf{F} \left[\mathbf{T} \left(\frac{\mathrm{d}\mathbf{E}}{\mathrm{d}\mathbf{T}} \right)_{\mathbf{p}} - \mathbf{E} \right]$$

Faraday's second law

w = Zit, 1 Faraday is the quantity of charge carried by 1 mol of electrons.

 $Z = \frac{\text{equivalent mass}}{96500}$; Z = weight deposited when 1A passed for 1 sec.

Faraday's second law

$$\frac{\mathbf{m_1}}{\mathbf{m_2}} = \frac{\mathbf{E_1}}{\mathbf{E_2}}$$

 m_1 , m_2 are masses deposited and E_1 and E_2 are their equivalent weights; for same amount of passed charge.

% current efficiency = $\frac{\text{Actual current}}{\text{Ammeter current}} \times 100$

Ohm's law = I = E/R

Ions are always discharged / produced in equivalent amounts whatever their speeds of deposition are,

Specific conductance = $k = \frac{1}{\rho}$, ρ = specific resistance

$$k = \frac{l}{a} \times C$$
 $\frac{l}{a} = cell constant, C = conductance = \frac{1}{R}$

Conductivity = cell constant \times observed conductance

$$\pi_{eq} = \frac{k}{C_{eq}} = \frac{k \times 1000 \text{ cm}^3 \text{L}^1}{\text{Normality}}$$

Equivalent conductance, (Λ)

 $\Lambda = \mathbf{k} \times \mathbf{V}$

V = volume in mL containing 1g equivalent of the electrolyte. Molar conductance (μ) = [Equivalent conductance]

 $(\mu) = n\Lambda$ $n = \frac{\text{Molecular mass}}{\text{Equivalent mass}}$ $\mu = k \times V \qquad V(\text{mL}) \text{ containing 1g mole of an electrolyte}$

At infinite dilution, $\Lambda_0 = \lambda_a + \lambda_c$

 $\lambda_{c} = ku_{c}$ $\lambda_{a} = ku_{a}$

 λ_a, λ_c ionic conductance of anion and cation

k = 96500C

 u_a = mobility of anions and u_c = mobility of cations

degree of dissociation, $\alpha = \frac{\Lambda}{\Lambda_{\infty}}$

Relation between equivalent and molar conductance at infinite dilution

$$\Lambda_{\infty} = \frac{1}{z^+} \lambda_+^{\infty} + \frac{1}{z^-} \lambda_-^{\infty}$$

Units of molar conductance are $\lambda^{\text{-1}}\text{cm}^2\text{mol}^{\text{-1}}$

Units of equivalent conductance are $\lambda^{\text{-1}}\text{cm}^2$ (g. eq.)-1 For weak electrolytes,

$$\alpha = \sqrt{\frac{K}{C}} = \frac{\lambda_{e}^{C}}{\lambda_{e}^{\infty}} = \frac{\lambda_{m}^{C}}{\lambda_{\mu}^{\infty}} \qquad \lambda_{e}^{C}, \lambda_{m}^{C} = \text{equivalent and molar conductance}$$

Ostwald's equation

$$\mathbf{K} = \frac{\mathbf{C} \left(\boldsymbol{\lambda}_{\mathbf{m}}^{\mathbf{C}} \right)^{2}}{\boldsymbol{\lambda}_{\mathbf{m}}^{\infty} \left(\boldsymbol{\lambda}_{\mathbf{m}}^{\infty} - \boldsymbol{\lambda}_{\mathbf{m}}^{\mathbf{C}} \right)}$$

Oxidation state of Cr in Cr₂O₃ and CrO5 is +3. The oxidation number of Ni(CO)₄ and Fe(CO)₅ is zero. The strength of oxy-acids of chlorine decreases in the order. $HClO_4 > HClO_3 > HCLO_2 > HClO$

The maximum oxidation number of an element = no. of valence electron present.

The minimum oxidation number of an element = (8 - n), where n is the no. of valence electrons.

Cell notation



Total current carried

Transport number of cation + Transport number of anion =1 n_c + n_a = 1

RATES OF CHEMICAL REACTIONS AND CHEMICAL KINETICS

$$aA + bB + cC + dD$$
Rate of reaction = $\frac{dx}{dt}$

$$= -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[B]}{dt}$$

$$-\frac{d[A]}{dt} \alpha [A]^{n_1} . \quad n_1 \text{ order of reaction with to } A$$

$$-\frac{d[B]}{dt} \alpha [B]^{n_2} \quad n_2 \text{ order of reaction with to } B \dots \text{ etc}$$

$$\frac{dx}{dt} = k[A]^{n_1} [B]^{n_2} \quad n_1 + n_2 \text{ overall order of reaction.}$$

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Rate Laws Zero-Order reaction

 $\frac{dx}{dt} = k_0 [A]^0 \qquad \therefore \quad x = k_0, t$ First-Order reaction $\frac{dx}{dt} = k_1 [A]^1 \qquad k_1 = \frac{2.303}{t} \log_{10} \left(\frac{a}{a-x}\right) \Rightarrow [A] = [A]_0 e^{-kt}$ nth Order reaction $\frac{dx}{dt} = k_n [A]^n \qquad k_n = \frac{1}{(n-1)t} \left[\frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}}\right]; \qquad n \ge 2$

Half Life Period

$$\begin{split} & T_{1/2} = \frac{0.693}{k_1}, \text{ for } n = 1 \\ & T_{1/2} = \frac{2^{n-1} - 1}{(n-1)k_n a^{n-1}}; \text{ for } n \geq 2 \\ & t_{1/2} \propto a^{n-1}; t_{3/4} = 2 \times t_{1/2}; t_{87.5\%} = 3 \times t_{1/2} \end{split}$$

Arrhenius equation

 $k = Ae^{-Ea/RT}$ $\Rightarrow \quad \log k = \log A - \frac{E_a}{2.303RT}$ $\log_{10} \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[\frac{T_2}{T} + \frac{d \ln k}{dT} \right]$

 $\log_{10} \frac{\mathbf{k_2}}{\mathbf{k_1}} = \frac{\mathbf{E_a}}{2.303 \,\mathrm{R}} \left[\frac{\mathbf{T_2} - \mathbf{T_1}}{\mathbf{T_2} \mathbf{T_1}} \right] \qquad \mathbf{k_1} \& \mathbf{k_2} \text{ at } \mathbf{T_1} \text{ and } \mathbf{T_2} \text{ temperature}$

Rates of chemical reactions and chemical kinetics Units of rate and rate constant

- (i) Rate of reaction: mol L⁻¹ S⁻¹
- (ii) Rate constant (K)

Order of reaction	Units
Zero order	mol litre-1 time-1
1 st order	time-1
2 nd order	mol-1 L time -1
n th order	(mol L-1)1-n time-1

Quantum yield or quantum efficiency of a photochemical reaction





SURFACE CHEMISTY

The isothermal variation of extent of adsorption with pressure is

$$\frac{\mathbf{x}}{\mathbf{m}} = \mathrm{Kp}^{1/\mathbf{n}}$$
 or $\log\left(\frac{\mathbf{x}}{\mathbf{m}}\right) = \log\mathrm{K} + \left(\frac{1}{\mathbf{n}}\right)\log\mathrm{P}$

where x = mass of gas adsorbed by the mass m of adsorbent at the pressure P. K and n are constant for a given pair of adsorbent and adsorbate.

Colloidal state

- True solution (size <1nm)
- Colloidal solution (size 1 nm 100 nm) and
- Suspensions (size > 100 nm)

Flocculation value $\propto \frac{1}{\text{coagulating power}}$

Hardy Schulze Rule

- (i) The ion having opposite charge to sol particles cause coagulation and
- (ii) Coagulating power of an electrolyte depends on the valency of ion i. e., greater the valency more is the coagulating power.

To coagulate **negative sol of As_2S_3**, the coagulating power of different cations has been found the decrease in the order as:

$$\operatorname{Al}^{3^+} > \operatorname{Mg}^{2^+} > \operatorname{Na}^+$$

Similarly, to coagulate a **positive sol** such as Fe(OH)₃, the coagulating power of different anions has been found to **decrease in the order:**

$$\left[\operatorname{Fe}(\operatorname{CN})_{6}^{4^{-}} > \operatorname{PO}_{4}^{3^{-}} > \operatorname{SO}_{4}^{2^{-}} > \operatorname{Cl}^{-}\right]$$

Thus, larger the charge on the coagulation ion, larger the coagulation.

Gold Number

The no. of milligrams of the protective collide required to just present the coagulation of 10 mL of red gold sol when 1 mL of 10% solution of sodium chloride is added to it.

Lower is the value of gold number greater is the protective power.

CHEMICAL FAMILIES – PERIODIC PROPERTIES

Modern Periodic law: The properties of elements are periodic functions of their atomic numbers.

Ionisaton Energy: Ionisation energy (IE) of an element is defined as the amount of energy required to remove an electron from an isolated gaseous atom of that element resulting in the formation of postitive ion.

$$M(g) \xrightarrow{(IE)} M^+(g) + e^{-igg}$$

Electron Affinity: Electron Affinity (EA) of an element is defined as the amount of energy associated with the gain of electrons by the gaseous atom.

$$F(g) + e^{-} \xrightarrow{EA} F^{-}(g)$$

Electronegativity: It is a measure of the tendency of an element to attract electrons to itself.

$$(A)^{\bullet}_{\mathsf{x}}(B) \to (\overset{\delta^{+}}{A}) - (\overset{\delta^{-}}{B})$$

B is said to be more electronegative than A as it pulls bonding pair towards itself.

Shielding or Screening Effect : A valence electron in a multi electron atom is attracted by the nucleus, and repelled by the electrons of inner shells. The combined effect of this attractive and repulsive force acting on

the valence electron is that the valence electron experiences less attraction from the nucleus. This is called Shielding or Screening Effect.

Lanthanides

General Electronic Configuration :

4F²⁻¹⁴5d^{0.1}6s²

Actinides

General Electronic Configuration : 5f

5f²⁻¹⁴5d^{0,1}7s²

CHEMICAL BONDING AND MOLECULAR STRUCTURES

Table gives an idea regarding the effect if bonding and loan pairs on geometry and bond angles of molecules.

Example	Number of orbitals on	Theoretical geometry	Number Of		Number Of		Number Of		VSEPR Notation	Bond angle	Distorted geometry due to
	central atom		Bond pairs	Lone pairs			repulsion				
BeF ₂	2	Linear	2	0	AX ₂	180•	Linear				
BF₃	3	Triangular	3	0	AX3	120 °	Plane triangle				
SO ₂	3	Plane triangle	2	1	AX2E	119•	Angular				
CH4	4	Tetrahedral	4	0	AX4	109• 28'	Tetrahedral				
NH3	4	Tetrahedral	3	1	AX3E	107• 48'	Trigonal pyramidal				
NF3	4	Tetrahedral	3	1	AX₃E	102• 35'	Pyramidal				
H ₂ O	4	Tetrahedral	2	2	AX ₂ E ₂	104• 27'	Angular				
F ₂ O	4	Tetrahedral	2	2	AX ₂ E ₂	102•	Angular				
H_2S	4	Tetrahedral	2	2	AX ₂ E ₂	90•	Angular Trigonal				
PC15	5	Triogonal pyramidal	5	0	AX5	120• and 90•	Bipyramidal Irregular tetrahedral				
SF4	5	Triogonal pyramidal	4	1	AX₄E	101• 36'	(See-saw)				

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CIF ₃	5	Triogonal pyramidal	3	2	AX3E2	87 • 40'	T-shaped
I3-	5	Triogonal pyramidal	2	3	AX ₂ E ₃	180•	Linear
SF6	6	Octahedral	6	0	AX ₆	90•	Octahedral
BrF₅	6	Octahedral	5	1	AX₅E	84 • 30'	Square pyramidal
XeF4	6	Octahedral	4	2	AX4E2	90•	Square planar

CHEMISTRY OF NON- METALS – I

- Heavy hydrogen is also called deuterium.
- **Occlusion of Hydrogen :** Metals like Pd, Pt, etc. have the property of absorbing large quantity of hydrogen at normal or higher temperature. This phenomenon is known as Occlusion of Hydrogen.
- Oxidation and reduction by $H_2 O_2$ in acidic medium is generally slow while it its rapid in alkaline medium.
- Polyoxides
- (i) *Peroxides :* In Perioxides, the two oxygen atoms are linked to each other by a single covalent bond and each oxygen has oxidation state of -1, e.g., BaO₂, H₂O₂.
- (ii) **Superoxides :** These oxides contain $(O O)^{-1}$ unit pertaining to oxidation state of each O atom as +1/2, e.g., KO₂, RbO₂.
- (iii) **Suboxides :** These oxides contain low content of oxygen than expected, e.g., Na₂O and C₃O₂.
- (iv) *Mixed Oxides:* These oxides are made up of two simpler oxides, e.g., Pb₃ (PbO₂.2PbO).
 - Liquid oxygen mixed with finely divided carbon is used in place of dynamite in Coal mining.
 - Nitric acid is also called aqua fortis (meaning Strong water)
 - Oxides of Nitrogen



CHEMISTRY OF NON – METALS- II

- Boron trihalides are Lewis acids and acid strength decreases as ${\rm BBr}_3>{\rm BCl}_3>{\rm BF}_3$.
- Hydrides of borons are known as boranes having general formula B_nH_{n+7} and B_nH_{n+6}
- Diborone is the simplest borne and borazene is known as the inorganic benzene.



Borazene

- Boron Carbide (B_4C_3) is the hardest artificial substance and is called **Norbide.**
- Acidic nature of hydrides of halides follows the order HI > HBr > HCI > HF .
- Acidic nature increase with increase in oxidation number of halogen. HCIO < HCLO₂ < HCIO₃ < HCIO₄
- In any given series of acids, the acidic character decreases with decrease in the electronegativity of central halogen atom. HCIO₄ > HBrO₄ > HIO₄
- Species which behave in the chemical behavior are called Pseudo halogens, e.g. (CN)₂ Cyanogen; thiocyanate (SCN)₂; Selenocyanogen (ScCN)₂, etc.
- Compounds contaming C, Cl, Br, F elements are called Halons, e.g., Halon 1211 (CF₂ClBr), Halon 1301 (CF₃Br) and Halon 2402 (C₂F₄Br).
- B(OH)₃ is known as Boric Acid.
- CO combines with Cl₂ in the presence of sunlight to form another poisonous gas phosgene

$$\operatorname{CO} + \operatorname{Cl}_2 \xrightarrow{\text{Sunligth}} \operatorname{COCl}_2$$

Phosgene

- CO+H₂ is known as **water gas**.
- Acetyl ides: The Carbides which on hydrolysis give acetylene are called acetylides. e.g., $MgC_2 + H_2O \rightarrow Mg(OH)_2 + HC \equiv CH$

$$MgC_2 + H_2O \rightarrow Mg(OH)_2 + HC \equiv CH$$

• Allylides: The carbides which on hydrolysis give allylene or propyne are called allylides. e.g., $Mg_2C_3 + 4H_2O \rightarrow 2Mg(OH)_2 + CH_3C \equiv CH$

Allylen or Propynes

CHEMISTRY OF LIGHTER METALS

- Sodium teraborate decarbohydrate (Na₂B₄O₇, 10H₂O) is commonly known as Borax.
- A mixture of Al(C₂H₅)₃ and TiCl₄ is known as **Ziegler Natta catalyst** which is used for polymerization of ethylene.
- Extent of hydration of alkali metal ions is of the order

$$Li^{+} > Na^{+} > K^{+} > Rb^{+} + Cs^{+}$$

- A mixture of Na₂Cl₃ and K₂CO₃ is known as **fusion mixture**.
- K₂CO₃ is known as **Pearl ash.**
- Aqueous solution of sodium chloride is known as Brine.
- CaH₂ is known as **Hydrolith**.
- **Sorel cement** is a mixture of MgO and MgCl₂. 6H₂O.
- Aluminiun chloride exists as diamers (Al₂Cl₆).

$$\begin{array}{c|c} Cl & \swarrow Cl & \checkmark Cl \\ Al & Al \\ Cl & \frown Cl & \frown Cl \end{array}$$

dimeric structure of aluminium chloride.

CHEMISTRY OF HEAVY METALS

- The two elements with the highest densities are **osmium** (22.57 g cm⁻³) and **Iridium** (22.61 g cm⁻³)
- Alums are double sulphates having general formula $X_2SO_4.M_2(SO_4)_8.24 H_2O$

X = Monovalent cations such as $NA^+, K^+, NH_{\mathbf{a}}^+$, etc. where,

M = Trivalent cations such as $Al^{3+}, Cr^{3+}, Fe^{3+}, etc.$

KMnO₄, K₂Cr₂O₇ and CrO₃ are coloured due to charge transfer and not • due to d-d transition.

- Titanium has been called **'The wonder metal'** because of useful properties.
- Among transition metals, mercury has the lowest melting point and is liquid at room temperature and Tungsten has the highest melting point among all the metals.

CHEMISTRY OF REPRESENT ATIVE ELEMENTS

- **Oxides:** The binary compounds of oxygen with various elements are called oxides. They can be classified into different categories depending upon their acid-base characteristics.
- **Acidic Oxides:** Theses are formed by combination of non metals and oxygen.

Examples: P₄O₁₀, SO₃, CO₂, N₂O₅ etc.

- **Basic Oxides:** These are formed by combination of oxygen with highly electropositive elements.
 - Examples: MgO, K₂O, CaO, BaO, Na₂O etc.
- **Amphoteric Oxides:** These are formed by combination of oxygen with borderline elements between metals and non metals. Examples: Al₂O₃, SiO₂, Zn, PbO etc.
- **Neutral Oxides:** they are neutral to litmus and do not react with acid or base.

Examples: CO, NO, N₂O etc.

- Air contains about 1% of noble gases.
- Argon is the most abundant noble gas.
- Radon is produced by radioactive decay of (Ra-226). $^{226}_{88}$ Ra \rightarrow^{222}_{86} Rn $+^{4}_{2}$ He
- Silicones: These are polymeric organsilicon compounds containing Si - O - Si bonds and having general formula (R₂SiO)_n; R have may be CH₃ or C₆H₅ group.
- **Solvay Process:** Sodium carbonate is generally prepared by this process. It can not be employed for the manufacture of potassium carbonate because potassium bicarbonate is fairly soluble in water and hence does not precipitate easily (in carbonation tower).

TRANSITION METALS INCLUDING LANTHANIDES & ACTINIDES

• The magnetic moment μ_{eff} is given by the expression $\mu_{eff} = \sqrt{n(n+2)}$, B.M. where n is the number of unpaired electrons.

- **Colour:** The colour of the compounds of the transition metals is related to the existence of the incomplete s shell and the easy excitation of an electron from one energy level to another.
- **Catalytic Properties:** The catalytic behavior of transition elements is due to their variable oxidation states.
- **Ability to form complexes:** Transition elements because of their smaller sizes of the ions and high ionic charges are well suited to attracted ligands which are usually negative or neutral molecules.

CO- ORDINATION CHEMISTRY AND ORGANO METALLICS

- Ligands containing π bonds and capable of accepting appreciable electron density form metal atom into empty π antibonding orbital of their own are called π acid ligands. e.g., CO, CH₂ = CH₂, etc.
- The compounds containing complex cation are cationic complexes.
- The compounds containing complex anion are anionic complexes.
- The compounds which do not ionize in aqueous solutions are neutral or molecular complexes.

$K^{+}[Ag(CN)_{2}]$	$\left[\operatorname{Ag}\left(\operatorname{NH}_{3}\right)_{2}\right]^{T}\operatorname{Cl}^{T}$	$\left[\text{CoCl}_{3} \left(\text{NH}_{3} \right)_{3} \right]$
Anionic complex	Cationic complex	Neutral complex

- Compounds containing very stable complex part i.e., the part which does not dissociate in solution are also called perfect complexes or penetration complexes.
- Compounds containing the complex part which has tendency to ionize reversibly in aqueous solution are called imperfect or normal complexes.

$$\mathbb{K}_{4} \left[\operatorname{Fe}(CN)_{6} \right] \rightarrow 4\mathbb{K}^{+} + \operatorname{Fe}(CN)_{6} \right]^{4}$$
Perfect complex

 $\left[\operatorname{Fe}(\operatorname{CN})_{\mathbf{6}}\right]^{\mathbf{4}}$ has least tendency to dissociate in solution

$$\left[\operatorname{Co}(\operatorname{NH}_3)_6 \right] \operatorname{Cl}_3 \to \operatorname{3Cl}^- + \left[\operatorname{Co}(\operatorname{NH}_3)_6 \right]^{3+}$$

Imperfect complex

- Monodentate ligands capable of coordinating with metal atom by two different sites are called ambidentate ligands. Examples are: nitro (← NO₂) and nitrite (← ONO).
- Ligands containing π bonds are capable of accepting appreciable

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electron density from metal atom into empty antibonding orbital \pi^* of their own are called \pi acid ligands.
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Examples are: $CO, CH_2 = CH_2, C_2H_5 - (cyclopentadienly ion), etc.$

 The number of coordinate bonds formed by the ligands surrounding the metal atom is called coordination number (CN) of the metal.
 C.N. of metal = 1 x No. of monodentate ligands or

= $2 \times No.$ of bidentate ligands or

- $= 3 \times No.$ of tridentate ligands
- Charge on the complex = O.N. of metal atom + O.N. of various ligands

NUCLEAR CHEMISTRY

Rate of disintegration

 $-\frac{dN}{dt} = \lambda . N \qquad \lambda = \text{disintegration constant}$ Amount left after n half life $N = \left(\frac{1}{2}\right)^n N_0$ $= \frac{2.303}{\lambda} \log_{10} \left(\frac{N_0}{N}\right) \text{ and } N = N_0 e^{-\lambda t}$

Half Life Period

$$t_{1/2} = \frac{0.693}{2}$$

^{$\sim_{1/2}$} λ 1 Average Life

$$\begin{split} &\frac{1}{\lambda} = 1.44 \ t_{1/2} \\ &\text{For radioactive equilibrium, } A \rightarrow B \rightarrow C \,. \\ &\text{If no. of atoms A, B, C etc, at equilibrium are N_A, N_B, N_C etc, then} \\ &-\frac{dN_A}{dt} = -\frac{dN_B}{dt} = -\frac{dN_C}{dt} \quad \text{or} \quad \lambda_A N_A = \lambda_B N_B = \lambda_C N_C \\ &\text{Or} \quad \frac{N_A}{N_B} = \frac{\lambda_B}{\lambda_A} = \frac{\left(t_{1/2}\right)_A}{\left(t_{1/2}\right)_B} \\ &\text{Mass defect = M'-M, where M = actual isotopic mass and} \\ &M' = Z \times m_p + Z \times m_e + (A - Z)m_n \\ &= Zm_H + (A - Z)m_n \quad \left(\because m_p + m_c = m_H\right) \\ &\text{Binding energy per nucleon} \\ &= \frac{Binding energy calculated from mass defect}{mass number} \end{split}$$

Packing function = $\frac{\text{Isotopic mass - Mass number}}{\text{Mass number}} \times 10^4$ Energy released by loss of 1 amu mass = 931.5 MeV

$$(1 \text{ amu} = 1.66 \times 10^{-24} \text{ g}, 1 \text{ MeV} = 10^{6} \text{ eV}, 1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}, 1 \text{ J} = 10^{7} \text{ ergs}, 1 \text{ cal} = 4.184 \text{ J})$$

PURIFICATION & CHARACTERIZATION OF ORGANIC COMPOUNDS

• Percentage of carbon in organic substance =
$$\left(\frac{12}{44}\right) \times \left(\frac{m_{cop}}{m_{compound}}\right) \times 100$$
• Percentage of hydrogen in organic substance = $\left(\frac{2}{18}\right) \times \left(\frac{m_{H_2O}}{m_{compound}}\right) \times 100$
• Percentage of nitrogen in the compound = $\frac{m_{N_2}}{m_{compound}} \times 100$
• Percentage of nitrogen in the compound = $\frac{(Volume of N_2)_{STP} \times 28}{(22.4) \times (m_{compound})} \times 100$
• Percentage of nitrogen = $\frac{1.4 \times N \times vol.of acid used}{Mass of the substance taken}$
• Percentage of nitrogen = $\frac{1.4 \times Molarity of the acid \times vol. \times Basicity}{Mass of the substance taken}$
• of X = $\frac{wt.of silver halide ppt.}{mol.mass of silver halide} \times \frac{35.5 \times 100}{wt.of org. chloro comp.}$
• Percentage of Chlorine = $\frac{35.5}{143.5} \times \frac{m_{AgCI}}{m_{compound}} \times 100$
• Percentage of Bromine = $\frac{80}{188} \times \frac{m_{AgBr}}{m_{compound}} \times 100$
• Percentage of Iodine = $\frac{127}{235} \times \frac{m_{AgI}}{m_{compound}} \times 100$

• Percentage of sulphur = $\frac{\text{wt. of BaSO_4 precipitate}}{\text{Molecular mass of BaSO_4}} \times \frac{32 \times 100}{\text{weight of organic compound containing sulphur}}$

• Percentage of Sulphur =
$$\frac{32}{233} \times \frac{m_{BaSO_4}}{m_{compound}} \times 100$$

• Percentage of phosphorus = $\frac{62}{222} \times \frac{m_{Mg_2P_2O_7}}{m_{compound}} \times 100$

Determination of Molecular mass

• Victor Meyer's method:

Molecular mass =
$$\frac{\text{Mass of liquid or solid } (w) \times 22400}{\text{Volume of air displaced at STP}}$$

• Volumetric method:

Molecular mass of the acid = $\frac{1000 \times W}{V \times x} \times n$

• By silver salt method: $\frac{\text{Mass of silver salt}}{\text{Mass of silver residue}} = \frac{\text{chemcial equivalent of silver salt}}{\text{chemical equivalent of silver}} = \frac{\text{E} + 108}{108}$

• From the platinichloride method for organic bases:

1 equivalent of salt = 1 equivalent of H_2PtCl_6

= 1 equivalent of base =
$$\frac{1}{2}$$
 (molar mass of Pt)
= $\frac{195}{2}$ g eq⁻¹

_

Equivalent mass of platinum salt

$$(M_{salt})_{eq} = \frac{\text{mass of platinum salt}}{\text{mass of platinum}} \times \frac{195}{2} \text{g eq}^{-1}$$

Equivalent mass of base

$$(M_{base})_{eq} = (M_{salt})_{eq} - (M_{H_2PtCl_6})_{eq} = \left\lfloor (M_{salt})_{eq} - \frac{410}{2} g eq^{-1} \right\rfloor$$

$$M_{base} = (acidity)(M_{base})_{eq}$$

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- A few more expressions to compute molar mass of a compound are as follows.
 - From relative lowering of vapour pressure

$$\mathbf{M_2} = \frac{\mathbf{m_2}}{\left(\mathbf{m_1}/\mathbf{M_1}\right) \left(-\frac{\Delta \mathbf{P_1}}{\mathbf{P_1^o}}\right)}$$

• From elevation of boiling point

$$M_2 = \frac{K_b}{\Delta T_b} \cdot \frac{m_2}{m_1}$$

• From depression of freezing point

$$M_{2} = \frac{K_{f}}{(-\Delta T_{f})} \cdot \frac{m_{2}}{m_{1}} \qquad [m_{1} = wt. of solvent]$$

• From osmotic pressure

$$M_{2} = \left(\frac{m_{2}}{V}\right) \frac{RT}{\pi} \qquad [where, m_{2} = wt of solute, M_{2} = mol. Wt of solute]$$

ORGANIC CHEMISTRY

• Aldol Condensation

Aldehydes having α - hydrogen (s) undergo self- condensation on warming with dilute or mild base to give β - hydroxyl aldehydes, called aldols.

e.g.,
$$CH_3CHO + CH_3CHO \xrightarrow{OH} CH_3CH(OH)CH_2CHO$$

• Beckmann Rearrangement



• Benzilic acid rearrangement

Benzil on treatment with a strong base froms benzillic acid (salt), whence the name benzilic acid rearrangement.



Benzil

Sodium salt of benzilic acid

• Mechanism

• Crossed aldol condensation

When condensation is between two different carbonyl compound, it is called Crossed aldol condensation.

(a) $R_3C - CHO + Ch_3CHO \xrightarrow{OH^{\Theta}} R_3C - CH(OH) - CH_2 - CHO$ Crossed product

(b)
$$CH_3CHO + CH_3COCH_3 \xrightarrow{OHO} CH_3 - CH(OH) - CH_2COCH_3$$

Crossed product

• Birch Reduction

When aromatic rings are reduced with sodium, potassium or lithium in liquid ammonia or amine in the presence of alcohol, addition of hydrogen takes place at position 1 and 4 to give an unconjugated diene. e.g.



• Cannizzaro Reaction

In the presence of a strong base, aldehydes without α – hydrogens, i.e. nonaldolizable aldehydes undergo self oxidation reduction, i.e., disproportions reaction.

e.g. $2C_6H_5CHO + NaOH \xrightarrow{\Delta} C_6H_5CH_2OH + C_6H_5COONa$

 $2HCHO + NaOH \longrightarrow CH_3OH + HCOONa$

• Claisen Rearreangement

Claisen rearrangement involves the shift of a group from oxygen to carbon. Thus, when aryl allyl ethers are heated (200°C) they rearrange to o-allylphenols.

e.g.



• Clemmenson Reduction

The reduction of carbonyl group of aldehydes and ketones to methylene groups with amalgamated zinc and concentrated hydrochloric acid.

e.g. $C_6H_5COCH_3 \xrightarrow{Zn-Hg.HCl} C_6H_5CH_2CH_3$

• Diels - Alder Reduction

Diels – alder reaction involves the 1, 4- addition of an alkene to a conjugated diene to form an adduct of six-membered ring.



Cyclohexene (20%)

Electron – withdrawing substituents in the dienophile, such as > C = O, –CHO, –COOR, – CN, – NO₂, etc. promote the reaction.



The reaction rate is also accelerated by the presence by the presence of electron-releasing groups in the dienes.



• Fridel – Crafts Reaction

Alkylation and acylation of the aromatic compounds with alkyl halides and acid halides or anhydrides in the presence of a metal halide (Lewis acid) is known as Fridel –Crafts reaction.

Catalyst, usually aluminium chloride is used.

e.g.
$$C_6H_6 + CH_3CH_2Cl \xrightarrow{Anhydrous,AlCl_3} C_6H_5CH_2CH_3 + HCl$$

 $C_6H_6 + CH_3COCl \xrightarrow{Anhy.AlCl_3} C_6H_5COCH_3 + HCl$
 $C_6H_5 + (CH_3CO)_2 O \xrightarrow{Anhy.AlCl_3} C_6H_5COCH_3 + CH_3COOH$

The order of reactivity of some of the catalysts is

 $\mathrm{AlBr}_3 > \mathrm{AlCl}_3 > \mathrm{FeCl}_3 > \mathrm{SbCl}_5 > \mathrm{SnCl}_4 > \mathrm{BCl}_3 > \mathrm{BF}_3$

• Fries Rearrangement

Phenolic esters on heating with aluminium trichloride (lewis acid) give o – and p – aryl phenol.



In general, low temperature favours the Para–product and high temperature favours the ortho–product.

• Gabriel Synthesis

The reaction involves the preparation of primary amines free from secondary or tertiary amines by reacting alkyl halides with alkali phthalimide and subsequent hydrolysis.



• Hell - Volhard -Zelinsky Reaction

Aliphatic carboxylic react with bromine or chlorine (but not iodine and fluorine) in the presence of small amount of red phosphorus to give exclusively mono α –halogenated acids. [Only by aliphatic acids having α –hydrogen].

e.g. $CH_3CH_2COOH + Br_2 \xrightarrow{\text{Red P}} CH_3CHBrCOOH + HBr$

Hoffmann Rearrangement or Hofmann Bromamide reaction

The reaction involves the conversion of an amide into a primary amine with one carbon loss, by the action of alkaline hypohalite (NAOH solution + Br_2 or Cl_2).

e.g. $\text{RCONH}_2 + \text{Br}_2 + 4\text{NaOH} \rightarrow \text{RNH}_2 + 2\text{NaBr} + \text{Na}_2\text{CO}_3 + 2\text{H}_2\text{O}$

• Houben – Hoesch reaction

Polyhydroxy phenols, phenolic ethers and some reactive heterocyclic compounds (e.g. pyrrole) undergo acylation with nitrile in the presence of a lewis acid.

e.g.



Knoevenagel reaction •

Condensation of aldehydes and Ketones with compounds having active methylene group in the presence of basic catalyst to form α,β – unsaturated compounds.

$$C_{6}H_{5}CHO + H_{2}C(COOR)_{2} \xrightarrow{\text{Pyridine}} C_{6}H_{5}CH = C(COOR)_{2}$$
$$C_{6}H_{4} - CH = CH - COOH \xleftarrow{1. H_{2}O}$$

Michael Reaction ٠

The base-catalysed addition of compounds having active methylene group (or relatively acidic hydrogens) to an activated olefinic bond of the type -C = C - Z (Z = electron – withdrawing) is classified as Michael

reaction.

$$C_{6}H_{5} - CH = CH - COOC_{2}H_{5} + H_{2}C(COOC_{2}H_{5})_{2} \xrightarrow{(C_{2}H_{5})ONa} C_{6}H_{5} - CH - COOC_{2}H_{5}$$

Ethylcinnamate Malonic ester $C_{6}H_{5} - CH - COOC_{2}H_{5}$
 $CH(COOC_{2}H_{5})_{2}$

$$H_{2}C(COOC_{2}H_{5}) + C_{2}H_{5}ONa \rightleftharpoons HC^{\Theta}(COOC_{2}H_{5})_{2} + C_{2}H_{5}OH$$

$$C_{6}H_{5} - CH = C + OC_{2}H_{5} \iff C_{6}H_{5} - CH - CH = C - OC_{2}H_{5} \xleftarrow{C_{2}H_{2}OH}_{(I)}$$

$$HC(COOC_{2}H_{5})_{2} \iff C_{6}H_{5} - CH - CH = C - OC_{2}H_{5} \xleftarrow{C_{2}H_{5}O}_{(I)}$$

$$C_{6}H_{5} - C H - CH = C - OH_{2}H_{5} \iff C_{6}H_{5} - C H - CH_{2} - C - OC_{2}H_{5}$$

$$(1, 4 - Addition) \qquad (\alpha,\beta - Addition)$$

• Oppenauer Oxidation

The oxidation of a secondary alcohol with a ketone and a base to the corresponding ketone of the alcohol.

e.g.,
$$R_2$$
CHOH + $(CH_3)_2$ CO $\xrightarrow{Al(OCMe_3)2}$ R_2 CO + CH_2 CHOHCH₃
 R_2 CHOH + \longrightarrow O $\xrightarrow{Al(OCMe_3)_2}$ R_2 CO + \bigwedge $\stackrel{H}{OH}$

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OH

• Perkin Reaction

In Perkin reaction, condensation has been effected between aromatic aldehydes and aliphatic acid anhydrides in the presence of sodium or potassium salt of the acid corresponding to the anhydride, to yield α,β -unsaturated aromatic acids. The acid reaction should have at least two α -hydrogens.

e.g.

$$C_6H_5CHO + (CH_3CO)_2 O \xrightarrow{AcONa} C_6H_5 - CH = CH - COOH + CH_3COOH$$

• Pinacol - Pinacolone Rearrangenent

The acid catalyzed rearrangement of diols (1, 2-diols) to ketones or aldehydes with elimination of water is known as pinacal or pinacol – pinacalone rearrangement.



Pinacol

Pinacolone (Methyl – t- butyl ketone)



2, 2- Diphenyl-1, 2- glycol

2, 2- Diphenyl acetaldehyde

• Reformasky Reaction

Reaction of an α - halo ester, usually an α - bromoester with an aldehyde or ketone in the presence of zinc metal to produce a β - hydroxyester. e.g.,



Reimer Tiemann Reaction

Formylation of phenols with chloroform in alkaline solution. e.g.,



• Schmidt Reaction

Carboxylic acids and hydrazoic acid react in the presence of sulphuric acid to give amines RCOOH + $N_3H \xrightarrow{H_2SO_4} RNH_2 + CO_2 + N_2$

• Ullmann reaction

The synthesis of diphenyl amines, diphenyl amines, diphenyl ethers and diphenyls is known as Ullmann reaction. e.g.,

 $C_{6}H_{5}NHCOCH_{3} + C_{6}H_{5}BR + K_{2}CO_{3} \xrightarrow{Cu} (C_{6}H_{5})_{2} NH + CO_{2} + CH_{3}COOK + KBr$ $C_{6}H_{5}OH + C_{6}H_{5}BR + KOH \xrightarrow{Cu} (C_{6}H_{5})_{2} O + KBr + H_{2}O$ $2C_{6}H_{5}I + Cu \xrightarrow{C_{6}H_{5}NO_{2}} C_{6}H_{5} - C_{6}H_{5} + CuI_{2}$

• Witting reaction

Synthesis of alkenes by the treatment of aldehydes or ketones with alkylidenetriphenylphosphorane $(Ph_3P = CR_2)$ or simply known as phophorane.

$Ph_3P = CH_2 + Ph_2C = O$	\rightarrow Ph ₂ C = CH ₂ +		+ $Ph_3P = O$	
	1, 1–Diphenyl		Triphenyl	
	ethylene		phosphonium oxide	

• Wolff Kishner reduction

Involves the conversion of carbonyl groups of aldehydes and ketons to methylene groups by heating their hydrozones, semicarbazones or azines in the presence of strong base such as C_2H_5ONa or NaOH. e.g.,

$$c = 0 + H_2 NNH_2 \longrightarrow c = NNH_2 \xrightarrow{C_2H_5ONa \text{ or}} cH_2 + N_2$$

Addition Reactions

(i) Electrophilic addition reaction: $CH_2 = CH_2 + Br_2 \xrightarrow{CCL_4} CH_2Br - CH_2BR$ Mechanism:







S_N 1 mechanism Rate $\infty [R_3CX]$ First – order Reaction

The rate of hydrolysis of alkyl halides by $S_N 1$ path is Allyl, Benzyl > $3^\circ > 2^\circ > 1^\circ > CH_3X$



$S_N 2$ mechanism

Rate ∝[Rx][Nu] Second under Reaction

The rate of hydrolysis of alkyl halides by $S_N 2$ path is $CH_3X > 1^{\circ} > 2^{\circ} > 3^{\circ}$



Transition state

Walden Inversion

Elimination reactions

(a) **E1 mechanism** Kinetically of the first order.

$$CH_{3} \xrightarrow{CH_{3}}_{C} \xrightarrow{C}_{Br} \xrightarrow{slow}_{CH_{3}} CH_{3} \xrightarrow{C}_{C} \xrightarrow{H}_{Br} \Theta \dots \dots (i)$$

$$CH_{3} \xrightarrow{CH_{3}}_{CH_{3}} \xrightarrow{CH_{3}}_{CH_{3}} \xrightarrow{CH_{3}}_{CH_{3}} \dots \dots (i)$$

$$CH_{3} \xrightarrow{CH_{3}}_{H_{2}C} \xrightarrow{CH_{3}}_{H_{2}C} \xrightarrow{CH_{3}}_{H_{2}C} \xrightarrow{CH_{3}}_{H_{2}C} \dots \dots (ii)$$

E1 reaction is facilitated by

- (i) branching at the α and β carbons of the substrate for stability of the olefin,
- (ii) strong polar solvent to aid ionization,
- (iii) low concentration of base the greater stability of the alkene over the carbocation makes the extraction of proton easy.

E2 mechanism

Rate α [substrate] [reagent]



2 reaction is facilitated by

E2 reaction is facilitated by

- (i) branching at α and β carbons since more stable olefin is formed,
- (ii) strong base of high concentration since a strong C H bond has to break,
- (iii) solvent of low polarity polar solvents form a strong solvent wall around the base restricting the attack. Hence DMF or DMSO are usually used as solvents.

E1cB mechanism (Elimination, Unimolecular from conjugate base)



Difference between $S_N 1$ and $S_N 2$ reaction.

	$S_N 1$ reaction	$S_N 2$ reaction	
1.	It is two step reaction.	It is one step reaction.	
2.	Rate depend only on concentration	Rate depend on concentration of	
	of substrate.	substrate and nucleophile.	
3.	It is unimolecular reaction.	It is bimolecular reaction.	
4.	The nucleophile can attack on the	The nucleophile can attack on the	
	carbon of substrate from front side	carbon of substrate from backside	
	and backside.	only.	

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5.	Reactivity order alkyl halides are	Reactivity order of alkyl halides are
	3° > 2° > 1° > methyl halide.	methyl halide > 1° > 2° > 3° .
6.	Rearrangement product is	Rearrangement product is not
	possible.	possible.
7.	Favoured by mild and low	Favoured by strong and high
	concentractionof nucleophile.	concentration of nucleophile.
8.	Favoured by solvents of high	Favoured by solvents of low polarity.
	polarity.	

Difference between $S_N 2$ and E_2 :

	Points	S _N 2	E ₂
1.	Step	One step $\overbrace{Nu}^{\overline{U}}$ $C \xrightarrow{f}_{G} \longrightarrow Nu - C + \overline{G}$:	One step B H $-C$ $-C$ $-C$ $-C$ $-C$ $-C$ $-C$ $-C$
2.	Reagent	Strong Nucleophile	strong base.
3.	Solvent	Non- hydroxylic solvents of high polarity increase the rate.	Non-hydroxylic solvents & high polarity increase the rate.
4.	Structure and reactivity nature of alkyl group	1° > 2° > 3°	3° > 2° > 1°
5.	Trasition State	-δ _δ NuC G	$B_{i}^{i} H^{+\delta}_{i} C^{+\delta}_{} C^{\delta}_{i}^{-}_{G}$
6.	Kinetics	The rate = K [substrate] [Nu]	The rate = K[substrate] [Base]
7.	Stereo specificity	Stereospecific, inversion of configuration occurs.	Stereospecific, usually trans- elimination takes place.

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Difference between $S_N 1$ and E_1

	Points	E ₁	S _N 1
1.	Step	2 steps	2steps
		$ \begin{array}{c} E \\ -C \\ $	$ \begin{array}{c} - \overset{ }{\mathbf{C}} - \overset{ }{\mathbf{G}} \longleftrightarrow \overset{ }{\mathbf{C}} \overset{ }{\mathbf{N}} \overset{ }{\mathbf{D}} \overset{ }{\mathbf{C}} \overset{ }{\mathbf{C}} \overset{ }{\mathbf{C}} \overset{ }{\mathbf{N}} \overset{ }{\mathbf{D}} \overset{ }{\mathbf{C}} \overset{ }{\mathbf{C}} \overset{ }{\mathbf{N}} \overset{ }{\mathbf{D}} \overset{ }{\mathbf{C}} \overset{ }{\mathbf{C}} \overset{ }{\mathbf{N}} \overset{ }{\mathbf{D}} \overset{ }{\mathbf{C}} \overset{ }{\mathbf{C}} \overset{ }{\mathbf{D}} \overset{ }{\mathbf{C}} \overset{ }{\mathbf{D}} \overset{ }{\mathbf{C}} \overset{ }{\mathbf{C}} \overset{ }{\mathbf{D}} \overset{ }{\mathbf{D}} \overset{ }{\mathbf{C}} \overset{ }{\mathbf{D}} \overset{ }{\mathbf{C}} \overset{ }{\mathbf{D}} \overset{ }{D$
2.	Reagent	Solvent plays the	Solvents and weakly
		role of the reagent	basic reagents of low
			concentration
3.	Solvent	Polar solvents	Polar solvents
4.	Structure and reactivity nature of alkyl group	$3^{0} > 2^{0} > 1^{0}$	$3^{0} > 2^{0} > 1^{0}$
5.	Kinetics	The second step is	The first step is rate
		rate determining	determining step. It
		step. It follows the	follows first order
		first order kinetics.	kinetics.
6.	Transition State	$ \begin{array}{c c} E \\ -C \\ -C \\ -C \\ -C^{*\delta} \\ -C^{*\delta} \end{array} $	$-C^{+\delta}G^{-\delta}$
7.	Stereochemistry	Non-stercospecific	Racemisation and partial
			inversion occur.

Prediction of number of Optical Isomers

, unsymmetrical
ners (A) = 2^n
s(m) = 0
ical isomers = $(a + m) = 2^n$
r of chiral carbon atom (s).
H3 . CHBr . CHBr . COOH
s symmetrical and has even number of chiral

Number of d and ℓ isomers (A) = $2^{(n-1)}$ Number of meso forms (m) = $2^{(n/2-1)}$

: Total number of optical isomers = (a + m)

Common example is tartaric acid, HOOC . CHoH . CHOH . COOH

iii) When the molecule is symmetrical and has an odd number of chiral carbon atoms

Number of d and ℓ forms (A) = $2^{(n-1)} - 2^{\left(\frac{n}{2} - \frac{1}{2}\right)}$

Number of meso forms (m) = $2^{\left(\frac{n}{2}, \frac{1}{2}\right)}$ \therefore Total number of optical isomers = (a + m) = $2^{(n-1)}$.

Halogenation

The order of case of substitution is Tertiary hydrogen > Secondary hydrogen > Primary hydrogen $RH + X_2 \xrightarrow{UV \text{ light}} RX + HX$ Reactivity of X_2 ; $F_2 > Cl_2 > Br_2 > I_2$

SYNTHETIC AND NATURAL POLUMERS

HOMOPOLYMERS				
Common name of the	Monomer	Uses		
homopolymer				
Polyethylene	$CH_2 = CH_2$	In the manufacture of pipes,		
	Ethylene	toys, bags, wire insulators,		
		bottles etc.		
Polyvinyl Chloride	$CH_2 = CHCl$	In the manufacture of sheets,		
(PVC)	Vinyl chloride	water pipes, hoses, hand		
		bags etc.		
Polystyrene	$C_6H_5CH = CH_2$	In the manufacture of combs,		
	Styrene	toys and radio and television		
		cabinets etc.		
Polyacrylonitrile (PAN)	$CH_2 = CH - CN$	In the manufacture of orlon		
	Acrylonitrile	(fiber) and acrilon films.		
Teflon (Polytetrafluoro	$CF_2 = CF_2$	In the manufacture of		
ethane)	Tetrafluoro	insulars, gaskets etc.		
	ethylene			

CHEMISTRY

Buna rubber	CH 2 = CH–	In the manufacture of tyres
	CH=CH ₂	etc.
	1, 3- Butadiene	

COPOLYMERS				
Common name of the copolymer	Monomer	Uses		
Dacron or Terylene	 (i) HOCH₂-CH₂OH Ethylene glycol (ii) H₃COOC(C₆H₄) COOCH₃ 	In the manufacture of fabrics and magnetic recording		
Nylon-66	 (i) H₂N(CH₂)₆NH₂ Hexamethylene diamine (ii) HOOC(CH₂)₄COOH Adipic acid 	In the manufacture of fabrics, tyre cords, ropes, carpets etc.		
Bakelite	(i) HCHO Formaldehyde (ii) C ₆ H ₅ OH Phenol	In the manufacture of electrical goods, phonograph records, fountain pen etc.		

Classification of Polymers

Classification based upon origin :

- (i) Natural Polymer : Examples silk, wool, starch, cellulose, enzymes, natural rubber, heamoglobin etc.
- (ii) Semi-synthetic polymer : Examples-Nitrocellulose, cellulose acetate, cellulose xanthate etc.
- (iii) Synthetic Polymer : These are man made polymers. Examples : Polyethylene, Polystyrene, Teflon

Classification based upon synthesis :-

- i) Addition polymers: Examples-Ethene, vinyl chloride and vinyl cynide
- ii) **Condensation polymers :** Examples-Proteins, starch, cellulose etc.

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Classification based upon molecular forces :

- i) **Elastomers :** These are the polymers having very weak intermolecular forces of attraction between the polymer chains. Examples-Vulcanised rubber.
- **ii) Fibers :** These polymers can be used for making fibers as their molecules are long and thread like. Example-Nylon-66.
- **iii)** Thermoplastics : These can be easily moulded by heating. Example-Polyethylene, Polypropylene.
- **iv)** Thermosetting polymers : A thermosetting polymer becomes hard on heating. Example-Bakelite.