# IMPORTANT FACTS AND FORMULAE FOR JEE
# IIT – CHEMISTRY

## SOME BASIC CONCEPTS

**1.** **1 mole** = $N_{Avg} \times$ number of species = $6.023 \times 10^{23}$ 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 $6.023 \times 10^{23}$ atoms in gms.

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

$\therefore$ 16 gm O-contains $6.023 \times 10^{23}$ oxygen atoms.

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

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

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

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

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

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

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

= wt. of $6.023 \times 10^{23}$ molecules

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

= Molarity × Volume (in L)

Millimoles = Molarity × Volume (mL)

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

= Normality × Volume (L)

Milliequivalent = Normality × Volume (ml)

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

**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 $H_3PO_4$, Eqv. weight $= \dfrac{\text{Mol. wt}}{3}$ *n*-factor = 3(3 replaceable $H^+$ ions)

For NH3, Eqv. weight $= \dfrac{\text{Mol. wt.}}{1}$ *n*-factor = 1(can replace one mole $H^+$ per mole)

For $Ag_3PO_4$, Eqv. wt. $= \dfrac{\text{Mol. wt}}{3}$ n-factor = 3

For $Ba_3(PO_4)_2$, Eqv. wt. $= \dfrac{\text{Mol. wt.}}{6}$ n-factor = 6

For $I_2 \rightarrow I^-$, Eqv. wt. $I_2 = \dfrac{\text{Mol. wt.}}{2}$

**Eq. mass of $KMnO_4$ in acidic medium**

$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ Eq. Mass of $KMnO_4 = \dfrac{\text{Formula wt.}}{5}$

**Eq. Mass of $KMnO_4$ in neutral medium**

$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 4H_2O$ Eq. Mass if $KMnO_4 = \dfrac{\text{Formula wt.}}{3}$

**Eq. Mass of $KMnO_4$ in basic medium**

$MnO_4^- + e^- \rightarrow MnO_4^{2-}$ Eq. Mass if $KMnO_4 = \dfrac{\text{Formula wt.}}{1}$

**9.** **Vapour density** $= \dfrac{\text{Molar mass}}{2}$

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.) $= \dfrac{6.4}{\text{specific heat}}$ (for metals only) (cal/g)

The law is applicable only to solid elements except Be, B, C and Si.

Valency $= \dfrac{\text{Approx. Atomic mass}}{\text{Eqv. mass}}$

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 = $n \times$ Empirical formula

$$\therefore n = \frac{\text{Molecular formula weight}}{\text{Empirical formula weight}}$$

13. **Molarity** $= \dfrac{\text{Moles of solute}}{\text{volume of solution (L)}}$

14. **Molality** $= \dfrac{\text{mole of solute}}{\text{mass of solvent(kg)}}$

15. **Mole fraction** = mole fraction of A in mixture of A and B = $X_A = \dfrac{n_A}{n_A + n_B}$

mole fraction of B in mixture of A and B = $X_B = \dfrac{n_B}{n_A + n_B}$

16. **Normality** $= \dfrac{\text{number of gm equivalent of solute}}{\text{volume of solution(L)}}$

17. **Atomicity** $(\gamma) = \dfrac{C_p}{C_v}$ (1.66 for mono-atomic, 1.4 for di-atomic, 1.33 for tri-atomic gas)

At mass of gaseous element $= \dfrac{\text{mol. mass}}{\text{Atomicity}}$

(Atomicity = number of atoms present in a molecule of the element).

$C_p - C_v = R = 1.98$ cal $\text{mol}^{-1}$ $\text{K}^{-1}$

Molar heat = specific heat $\times$ mol. mass

## STATES OF MATTER

### Boyle's law

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

### Charle's

$\frac{V}{T}$ = constant [at constant $n$, P] $\therefore \frac{V_1}{T_1} = \frac{V_2}{T_2}$;

$V_t = V_0\left(1 + \frac{t}{273}\right)$ [T (kelvin) = 273 + $t$ ($^0$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 = $0^0$ C or 273 K

### Density and molar mass relation

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

### Dalton's law of Partial Pressure

$P_{Total} = P_1 + P_2 + P_3 + \ldots\ldots..$

Where $P_1$, $P_2$,.....etc. are partial pressures of individual gases.

Partial pressure = Total pressure × mole function

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

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

**Graham's law (Diffusion and Effusion)**

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

$$\frac{r_{\mathbf{A}}}{r_{\mathbf{B}}} = \frac{\mathrm{P}_{\mathbf{A}}}{\mathrm{P}_{\mathbf{B}}}\sqrt{\frac{\mathrm{M}_{\mathbf{B}}}{\mathrm{M}_{\mathbf{A}}}} = \frac{\mathrm{P}_{\mathbf{A}}}{\mathrm{P}_{\mathbf{B}}}\sqrt{\frac{\rho_{\mathbf{B}}}{\rho_{\mathbf{A}}}} \quad \text{[at different pressure]}$$

**Velocity of Molecules**

Root mean square velocity $(\mathrm{C}_{\mathbf{RMS}}) = \sqrt{\frac{3\mathrm{RT}}{\mathrm{M}}} = \sqrt{\frac{3\mathrm{P}}{d}}$

Average velocity $(\mathrm{C}_{\mathbf{AVG}}) = \sqrt{\frac{8\mathrm{RT}}{\pi\mathrm{M}}}$

Most probability velocity $(\mathrm{C}_{\mathbf{MP}}) = \sqrt{\frac{2\mathrm{RT}}{\mathrm{M}}}$

$\mathrm{C}_{\mathbf{MP}} < \mathrm{C}_{\mathbf{Avg}} < \mathrm{C}_{\mathbf{RMS}}$

$\mathrm{C}_{\mathbf{MP}} : \mathrm{C}_{\mathbf{Avg}} : \mathrm{C}_{\mathbf{RMS}} :: 1 : 1.128 : 1.224$

**Real Gases, Compressibility factor**

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

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

$\mathrm{Z} < 1$, implies that gas is more compressible

$\mathrm{Z} > 1$, implies that gas is less compressible

$\mathrm{Z} = 1$, implies that gas is ideal.

**Gas Equation (van der Waal's)**

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

$$\Delta\mathrm{H}_{\mathbf{vap}} = \frac{2.303\,\mathrm{RT}_{\mathbf{1}}\mathrm{T}_{\mathbf{2}}}{(\mathrm{T}_{\mathbf{2}} - \mathrm{T}_{\mathbf{1}})}\log\frac{\mathrm{P}_{\mathbf{2}}}{\mathrm{P}_{\mathbf{1}}}$$

$\mathrm{P}_1,\mathrm{P}_2$ vapour pressure at $\mathrm{T}_1$, $\mathrm{T}_2$

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

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 $L^2$ $mol^{-2}$ and *b* are L $mol^{-1}$

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

Co-volume or excluded volume = $4N_0V_m$ $\left[V_m = \frac{4}{3}\pi r^3\right]$

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 $\sigma$ =molecular diameter

N/V = number of molecules per unit volume

**Nature of Gas Constant R**

$$R = \frac{P \times V}{nT} = \frac{\text{Pressure} \times \text{Volume}}{\text{Moles} \times \text{Degree(K)}} = \frac{(\text{Force / Area}) \times (\text{Volume})}{\text{Moles} \times \text{Degree(K)}} = \frac{\text{Force} \times \text{Length}}{\text{Moles} \times \text{Degree(K)}}$$

= Work done per degree per mole

**Units of gas constant (R)**

R = 0.0821 atm L $K^{-1}$ $mol^{-1}$ = 0.0821 atm $dm^3$ $K^{-1}$ $mol^{-1}$

(Here P = 1 atm, V = 22.4 L, T = 273 K, 1 L = 1 $dm^3$)

If P is expressed in dynes per square centimeter

$(P = 76 \times 981 \times 13.6\,\text{dyne}/\text{cm}^2)$

V = 22400 $dm^3$ and T = 273 K

then R = $8.314 \times 10^7$ ergs $K^{-1}$ $mol^{-1}$ = 8.314 J $K^{-1}$ $mol^{-1}$ and R = 1.987cal $K^{-1}$ $mol^{-1}$

1 atm. Pressure = $0.76\,m \times 13.6 \times 10^3\,kg\,m^{-3} \times 9.81\,ms^{-2}$ = $101.325 \times 10^3$ $Nm^{-2}$ = $101.325 \times 10^3$ Pa [∵ 1 $Nm^{-2}$ = 1 Pa]

Thus, the gas constant R = $\frac{(101.325 \times 10^3\,Nm^{-2}) \times (22400 \times 10^{-6}\,m^3)}{(273K) \times (1mol)}$

= 8.314 Nm $K^{-1}$ $mol^{-1}$

= $5.189 \times 10^{19}$ e$VK^{-1}$ $mol^{-1}$

[∵ 1 eV = $1.602 \times 10^{-19}$ volts coulomb (Joule)]

**i)** **Avogadro's Law**

$V \propto n$ or $V \propto N$ (at constant T, P)

**ii)** **Calculation of Kinetic Energy**

According to gas equation, $PV = \frac{1}{3} Mu^2$ for 1 mole of gas

or $PV = \frac{2}{3} \times \frac{1}{2} Mu^2$

or $\frac{1}{2} Mu^2 = \frac{3}{2} PV = \frac{3}{2} RT$ = K.E.

For 1 molecule, the K.E.

$= \frac{3\ RT}{2\ N_0} = \frac{3}{2} KT \left\{ \frac{R}{N_0} = K \text{ (Boltzmann constant)} \right\}$

**iii)** **Average molecular weight of a gaseous mixture**

$M_{mix} = \frac{\Sigma n_i M_i}{\Sigma n_i}$ where $n_i$ is the number of moles and $M_i$ is the molecular weight of the component.

**iv)** **Critical Pressure ($P_C$) :** $P_C = \frac{a}{27b^2}$

**v)** **Critical Temperature ($T_C$) :** $T_C = \frac{8a}{27Rb}$

**vi)** **Critical Volume ($V_C$) :** $V_C = 3b$

**vii)** **Relationship between $P_C$, $V_C$ and $T_C$ :** $\frac{P_C T_C}{RT_C} = \frac{3}{8}$

**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 ($6.023 \times 10^{-34}$ Js), $v$ = Frequency of radiation, $c$ = Velocity of light, $\lambda$ = wavelength of radiation

$c = v\lambda$ and wave number $(\bar{v}) = \frac{1}{\lambda}$

**Moseley's Equation,** $\sqrt{v} = a\,(z - b)$

**Heisenberg's uncertainty equation,**

$$\Delta p.\Delta x \geq \frac{h}{4\pi} \text{ and } \Delta E.\Delta t \geq \frac{h}{4\pi}$$

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 $= \frac{n^2h^2}{4\pi^2 mkZe^2} = \frac{n^2a_0}{Z}$ $(a_0 = 0.529\,\overset{0}{\mathrm{A}})$

Velocity of electron,

$$v_n = \frac{2\pi Zke^2}{nh} = \frac{Z}{n} \times 2.188 \times 10^6 \text{ m/s}$$

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,

$$\bar{v} = \frac{1}{\lambda} = R_H Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \qquad (R_H = 109743 \text{ cm}^{-1}$$

$$= \left(R_H = 109743\text{cm}^{-1} = \frac{2\pi^2 me^4k^2}{h^3c}\right)$$

**de Broglie equation**

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

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

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

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

Magnetic moment, $\mu_L = \frac{eh}{4\pi mc}\sqrt{l(l+1)}$

Spin angular momentum $\mu = \frac{eh}{\pi}\sqrt{s(s+1)}$

**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

$$\frac{1}{2}mv_{\mathbf{max}}^{\mathbf{2}} = h\nu - h\nu_0 = hc\left[\frac{1}{\lambda} - \frac{1}{\lambda_0}\right]$$

Stopping potential, $eV_0 = h(\nu - \nu_0)$

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 $1.4 \times 10^{-13}$cm.

ii) 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

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

If hydration energy > lattice energy, the solute goes into solution and $\Delta H_{\mathbf{solution}}$ 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

$$\text{ppm(A)} = \frac{\text{Mass of A}}{\text{Total mass of the solution}} \times 10^{6}$$

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.

$$\text{Mole } \% = \frac{\text{Moles of solute}}{\text{Moles of solute} + \text{Moles of solvent}} \times 100$$

### 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)

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

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

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

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

$p_s = p_0 \, . \, X_{solvent}$

$$\frac{p_0 - p_s}{p_s} \qquad \begin{matrix} n \\ N \end{matrix}$$

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

$\alpha$ during dissociation.

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

$\alpha$ during association.

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

Variation of vapour pressure with temperature

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

Variation of vapour pressure with external pressure

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

### Osmotic Pressure

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

### Van Hoff Factor

$$i = \frac{P_{observed}}{P_{normal}} = \frac{(\Delta p)_{observed}}{(\Delta p)_{normal}} = \frac{(\Delta T_b)_{observed}}{(\Delta T_b)_{normal}} = \frac{(\Delta T_f)_{observed}}{(\Delta T_f)_{normal}}$$

$$= \frac{\text{Normal molecular mass}}{\text{Observed molecular mass}}$$

For solution showing dissociation, the Van't Hoff factor $i > 1$

For solution showing association, the Van't Hoff factor $i < 1$

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

**Raoult's Law**

$$P = P_A + P_B = P_A^0 X_A + P_B^0 X_B = (1 - X_B)P_A^0 + P_B^0 X_B$$

**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. $CCl_4$ + $CHCl_3$ ethanol + $CHCl_3$.

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**

$\Delta T_b = T_b - T_0 = K_b m$

$= \dfrac{K_b \times W_B \times 1000}{M_B \times W_A}$ where $W_A$ = mass of solvent (g) and $W_B$ = mass of solute (g)

Molal elevation constant ($K_b$)

$K_b = \dfrac{RT_b^2}{1000L_v}$ [$L_v$ = latent heat of vapourisation]

**Depression in freezing point**

$$\Delta H_r = T_0 - T_p = k_f \times m = \frac{k_F \times W_B \times 1000}{M_B \times W_A}$$

**Molal depression constant ($K_f$)**

$$K_f = \frac{RT_f^2}{1000L_f} \quad [L_f = \text{latent heat of fusion}]$$

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)**

$\Delta E = 0$

$q = - W = P\Delta V$

$q = - W_{max} = P\int dV$

**Isothermal reversible expansion**

$\Delta H = \Delta E = 0$ ($\because$ 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**

$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H = \left(\frac{\partial H}{\partial P}\right)_T / C_p$$

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

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

### Second Law of Thermodynamics

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

$q_2$ = heat absorbed by engine
$q_1$ = heat lost to sink

### Entropy Change

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surrounding}$$

$$\Delta S_{fusion} = \frac{\Delta H_{fus}}{T_{fus}} ; \Delta S_{vap} = \frac{\Delta H_{vap}}{T_{vap}}$$

### Gibb's free energy (G)

$\Delta G = G_2 - G_1$
$\Delta G = \Delta H \; T \Delta S$ (Gibb's Helmholtz equation)
$\Delta G < 0$ (means spontaneous process),
$\Delta G > 0$ (means non-spontaneous process)
$\Delta G = 0$ (means system is at equilibrium)

### Kirchoff's equation

$$\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = \Delta C_p \text{ and } \frac{\Delta E_2 - \Delta E_1}{T_2 - T_1} = \Delta C_v$$

Where, $\Delta C_p = \sum C_p$ (products) - $\sum C_p$ (reactants) and

$\Delta C_v = \sum C_v$ (products) - $\sum C_v$ (reactants)

### Degree of dissociation (x)

$$x = \frac{D - d}{d} = \frac{M_1 - M_0}{M_0}$$

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)**

$$\Delta S = 2.303\ nR \log \frac{V_2}{V_1}$$

At constant pressure, $\Delta S = 2.303\ C_p \log_{10} \frac{T_2}{T_1}$

For vaporization, $\Delta S = \frac{\Delta H_{vap}}{T_{bp}}$

$$\Delta G^0 = -nFE^0_{cell}$$

**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 $\Delta H$ is positive.
If heat is given out by the system, q or $\Delta H$ is negative.
If energy is absorbed by the system, i.e. internal energy increases. $\Delta E$ is positive.
If energy is released i.e., internal energy of the system decreases. $\Delta E$ is negative.

**Heat capacity**

(i) Heat capacity at constant volume, $C_v = \left[\frac{\partial E}{\partial T}\right]_v$

(ii) Heat capacity at constant pressure, $C_p = \left[\frac{\partial H}{\partial T}\right]_p$

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

**Heat of Reaction**

$$\Delta H = \sum H_{(p)} - \sum H_{(R)}$$

For exothermic reactions : $\sum H_p < \sum H_R \quad \therefore \Delta H$ is - ve

For endothermic reaction : $\sum H_p > \sum H_R \quad \therefore \Delta H$ is + ve

Heat change at constant pressure = $q_p = \Delta H$

Heat change at constant volume = $q_v = \Delta E$

$$\Delta H = \Delta U + P\Delta V$$

$$\Delta H = \Delta U + \Delta n_{(g)}RT$$

If $\Delta n_{(g)} = 0, \quad \Delta H = \Delta U$

$\Delta n_{(g)} > 0, \quad \Delta H > \Delta U$

$\Delta n_{(g)} < 0, \quad \Delta H < \Delta U$

**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.

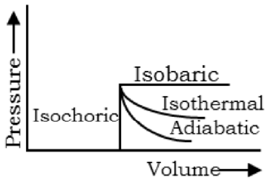
i) **Calorific value** is the amount of heat evolved when one gram of fuel as food is burnt in the presence of air or excess of oxygen.

ii) Joule's relationship between work done (w) and heat produced (H) $W \propto H$ or $W = JH$

Where, J is called mechanical equivalent of heat. Its value is $J = 4.184 \times 10^7$ erg $Cal^{-1}$ 4.184 J $Cal^{-1}$.

$$\text{Log} \frac{S_1}{S_2} = \frac{\Delta H}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

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



## CHEMICAL AND IONIC EQUILIBRIUM

Equilibrium in water $= \left(\frac{dx}{dt}\right)_{\mathbf{forward}} = \left(\frac{dx}{dt}\right)_{\mathbf{backward}}$

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

$$\left(\frac{dx}{dt}\right)_{\mathbf{forward}} \propto K_{\mathbf{forward}}[A]^{a}[B]^{b}$$

$$\left(\frac{dx}{dt}\right)_{\mathbf{backward}} \propto K_{\mathbf{backward}}[C]^{c}[D]^{d}$$

Equilibrium constant, $K = \frac{[C]^{c}[D]^{d}}{[A]^{a}[B]^{b}} = \frac{K_{\mathbf{forward}}}{K_{\mathbf{backward}}} = K_{c}$

In terms of partial pressure

Equilibrium constant, $K_{p} = \frac{p_{C}^{c}\, p_{D}^{d}}{p_{A}^{a}\, p_{B}^{b}}$

$$K_{p} = K_{c}(RT)^{\Delta n_{g}} \qquad \left[\Delta n_{g} = n_{p} - n_{r}\right]$$

**Van't Hoff equation**

$$\log_{10}\frac{k_2}{k_1} = \frac{\Delta H^{o}}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

**Gibb's Free energy**

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G^{o} = -2.303RT \log_{10} K$$

**Buffer:**

$$pH = pK_{a} + \log\frac{[\text{conjugate base}]}{[\text{acid}]}$$

$$pOH = pK_{b} + \log\frac{[\text{conjugate acid}]}{[\text{base}]}$$

Mixture of weak acids $= \sqrt{k_1c_1 + k_2c_2}$

$$\alpha = \frac{\%\ \text{conjugation}}{100}$$

$$A_{x}B_{y} \rightleftharpoons_{x} A^{y+} +_{y} B^{x-}$$

$\therefore \quad K_{sp} = \left[A^{y+}\right]^{x}\left[B^{x-}\right]^{y}$, when $A_xB_y$

$K_{sp}$ = 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
$\alpha$ = degree of dissociation
$K_w = \left[H^+\right]\left[OH^-\right]$ [ionic product of water]

**Hydrolysis constant**

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

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

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

Strong acid + weak base, Degree of hydrolysis (h) $= \sqrt{\frac{K_w}{CK_b}}$

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

Strong base + weak base, Degree of hydrolysis (h) $= \sqrt{\frac{K_w}{CK_a}}$

$$pH = \frac{1}{2}\left[pK_w + pK_a + \log C\right]$$

Weak acid + weak base, Degree of hydrolysis (h) $= \sqrt{\dfrac{K_w}{K_a \times K_b}}$

$$pH = \frac{1}{2}\left[pK_a + pK_w - pK_b\right]$$

**REDOX REACTIONS AND ELECTROCHEMISTRY**

$$E_{cell} = E^o{}_{cell} - \frac{0.059}{n} \log \frac{[\text{Product}]}{[\text{Practant}]}$$

$-\Delta G = nFE_{cell}; -\Delta G^o = nFE^o{}_{cell}$

$$E^o{}_{cell} = \frac{2.303RT}{nF} \log K_{eq} = \frac{0.591}{n} \log K_{eq} \qquad [\text{At} = 25^o\text{C}]$$

$\Delta G^o = -2.303$ RT log K

**Gibb's –Helmholtz equation**

$$\Delta G = \Delta H + T\left(\frac{d\Delta G}{dt}\right)_p$$

$$\Delta H = nF\left[T\left(\frac{dE}{dT}\right)_p - E\right]$$

**Faraday's second law**

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

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

**Faraday's second law**

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

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

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

Ohm's law = I = E/R

Ions are always discharged / produced in equivalent amounts whatever their speeds of deposition are, Specific conductance $= k = \frac{1}{\rho}, \rho =$ specific resistance

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

Conductivity = cell constant × observed conductance

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

**Equivalent conductance,** $(\Lambda)$

$$\Lambda = k \times V$$

V = volume in mL containing 1g equivalent of the electrolyte.

Molar conductance $(\mu)$ = [Equivalent conductance]

$$(\mu) = n\Lambda$$

$$n = \frac{\text{Molecular mass}}{\text{Equivalent mass}}$$

$\mu = k \times V \qquad$ V(mL) containing 1g mole of an electrolyte

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

$$\lambda_c = ku_c$$

$$\lambda_a = ku_a$$

$\lambda_a, \lambda_c$ ionic conductance of anion and cation

$$k = 96500\,C$$

$u_a =$ 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 $\lambda^{-1}\text{cm}^2\text{mol}^{-1}$

Units of equivalent conductance are $\lambda^{-1}\text{cm}^2$ (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**

$$K = \frac{C\left(\lambda_m^c\right)^2}{\lambda_m^\infty\left(\lambda_m^\infty - \lambda_m^c\right)}$$

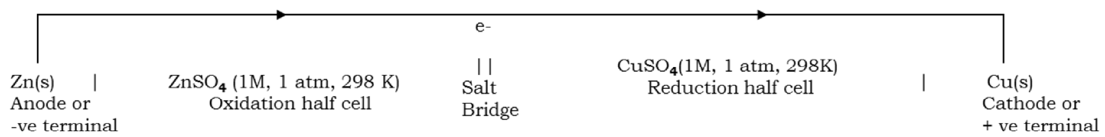
Oxidation state of Cr in $Cr_2O_3$ and CrO5 is +3 .
The oxidation number of $Ni(CO)_4$ and $Fe(CO)_5$ is zero.
The strength of oxy-acids of chlorine decreases in the order.

$HClO_4 > HClO_3 > HCLO_2 > HClO$

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**



**Transport number**

$$\text{Transport number} = \frac{\text{Current carrired by ion}}{\text{Total current carried}}$$

Transport number of cation + Transport number of anion =1

$n_c + n_a = 1$

**RATES OF CHEMICAL REACTIONS AND CHEMICAL KINETICS**

$aA + bB + cC + dD$

$$\text{Rate of reaction} = \frac{dx}{dt}$$

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

$-\frac{d[A]}{dt}\alpha[A]^{n1}$ . $n_1$ order of reaction with to A

$-\frac{d[B]}{dt}\alpha[B]^{n2}$ $n_2$ order of reaction with to B .....etc

$\frac{dx}{dt} = k[A]^{n1}[B]^{n2}$ $n_1 + n_2$ - overall order of reaction.

**Rate Laws**

**Zero-Order reaction**

$$\frac{dx}{dt} = k_0[A]^0 \qquad \therefore \quad x = k_0,t$$

**First-Order reaction**

$$\frac{dx}{dt} = k_1[A]^1 \qquad k_1 = \frac{2.303}{t}\log_{10}\left(\frac{a}{a-x}\right) \Rightarrow [A] = [A]_0\, e^{-kt}$$

**n<sup>th</sup> Order reaction**

$$\frac{dx}{dt} = k_n[A]^n \qquad k_n = \frac{1}{(n-1)t}\left[\frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}}\right]; \qquad n \geq 2$$

**Half Life Period**

$$T_{1/2} = \frac{0.693}{k_1}, \text{ for } n = 1$$

$$T_{1/2} = \frac{2^{n-1}-1}{(n-1)k_n a^{n-1}}; \text{ for } n \geq 2$$

$$t_{1/2} \propto a^{n-1};\ t_{3/4} = 2 \times t_{1/2};\ t_{87.5\%} = 3 \times t_{1/2}$$

**Arrhenius equation**

$$k = Ae^{-Ea/RT}$$

$$\Rightarrow \qquad \log k = \log A - \frac{E_a}{2.303RT}$$

$$\log_{10}\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_2T_1}\right]$$

$k_1$ & $k_2$ at $T_1$ and $T_2$ temperature

$$\frac{d\ln k}{dT} = \frac{E_a}{RT^2}$$

**Rates of chemical reactions and chemical kinetics**

**Units of rate and rate constant**

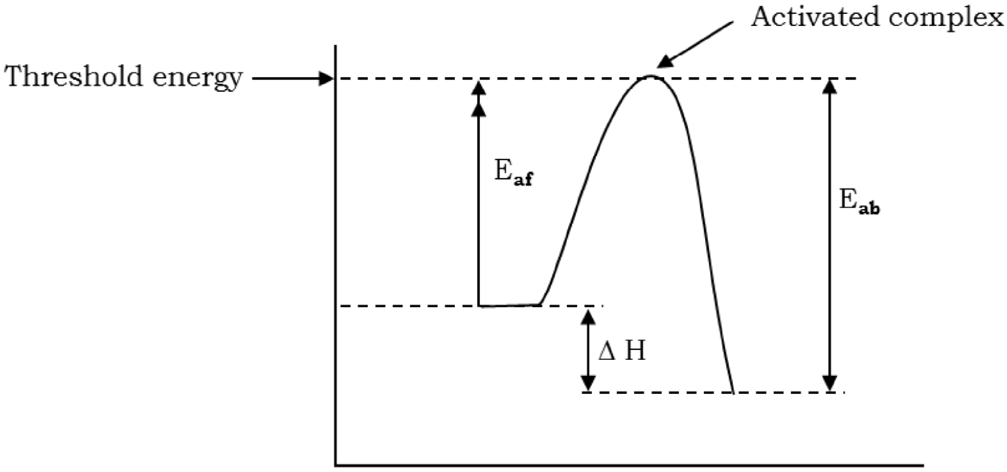
(i) Rate of reaction: mol $L^{-1}$ $S^{-1}$

(ii) Rate constant (K)

| Order of reaction | Units |
|---|---|
| Zero order | mol $\text{litre}^{-1}$ $\text{time}^{-1}$ |
| 1st order | $\text{time}^{-1}$ |
| 2nd order | $\text{mol}^{-1}$ L $\text{time}^{-1}$ |
| nth order | $(\text{mol } L^{-1})^{1-n}$ $\text{time}^{-1}$ |

**Quantum yield or quantum efficiency of a photochemical reaction**

$$\phi = \frac{\text{number of reactant molecule reacting in a given time}}{\text{number of photons (quanta) of light absorbed in the same time}}$$



## SURFACE CHEMISTY

The isothermal variation of extent of adsorption with pressure is

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

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)

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

**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:

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

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:**

$$[Fe(CN)_6]^{4-} > PO_4^{3-} > SO_4^{2-} > Cl^-$$

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.

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

**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.

$$(A)\overset{\bullet}{\underset{\times}{}}(B) \rightarrow \overset{\delta+}{(A)} - \overset{\delta-}{(B)}$$

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 : $4F^{2\text{-}14} 5d^{0.1} 6s^{2}$

**Actinides**

General Electronic Configuration : $5f^{2\text{-}14} 5d^{0,1} 7s^{2}$

## 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 central atom | Theoretical geometry | Number Of | | VSEPR Notation | Bond angle | Distorted geometry due to repulsion |
|---|---|---|---|---|---|---|---|
| | | | Bond pairs | Lone pairs | | | |
| $BeF_2$ | 2 | Linear | 2 | 0 | $AX_2$ | 180° | Linear |
| $BF_3$ | 3 | Triangular | 3 | 0 | $AX_3$ | 120° | Plane triangle |
| $SO_2$ | 3 | Plane triangle | 2 | 1 | $AX_2E$ | 119° | Angular |
| $CH_4$ | 4 | Tetrahedral | 4 | 0 | $AX_4$ | 109° 28’ | Tetrahedral |
| $NH_3$ | 4 | Tetrahedral | 3 | 1 | $AX_3E$ | 107° 48’ | Trigonal pyramidal |
| $NF_3$ | 4 | Tetrahedral | 3 | 1 | $AX_3E$ | 102° 35’ | Pyramidal |
| $H_2O$ | 4 | Tetrahedral | 2 | 2 | $AX_2E_2$ | 104° 27’ | Angular |
| $F_2O$ | 4 | Tetrahedral | 2 | 2 | $AX_2E_2$ | 102° | Angular |
| $H_2S$ | 4 | Tetrahedral | 2 | 2 | $AX_2E_2$ | 90° | Angular Trigonal |
| $PCl_5$ | 5 | Triogonal pyramidal | 5 | 0 | $AX_5$ | 120° and 90° | Bipyramidal Irregular tetrahedral |
| $SF_4$ | 5 | Triogonal pyramidal | 4 | 1 | $AX_4E$ | 101° 36’ | (See-saw) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $CIF_3$ | 5 | Triogonal pyramidal | 3 | 2 | $AX_3E_2$ | 87°40’ | T-shaped |
| $I_3^-$ | 5 | Triogonal pyramidal | 2 | 3 | $AX_2E_3$ | 180° | Linear |
| $SF_6$ | 6 | Octahedral | 6 | 0 | $AX_6$ | 90° | Octahedral |
| $BrF_5$ | 6 | Octahedral | 5 | 1 | $AX_5E$ | 84°30’ | Square pyramidal |
| $XeF_4$ | 6 | Octahedral | 4 | 2 | $AX_4E_2$ | 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 $H_2O_2$ in acidic medium is generally slow while it its rapid in alkaline medium.
- **Polyoxides**

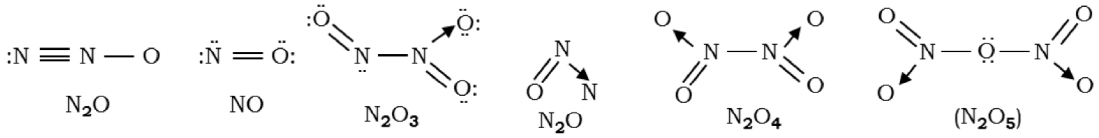
(i) *Peroxides :* In Perioxides, the two oxygen atoms are linked to each other by a single covalent bond and each oxygen has oxidation state of – 1, e.g., $BaO_2$, $H_2O_2$.

(ii) ***Superoxides :*** These oxides contain $(O-O)^-$ unit pertaining to oxidation state of each O atom as $+1/2$, e.g., $KO_2$, $RbO_2$.

(iii) ***Suboxides :*** These oxides contain low content of oxygen than expected, e.g., $Na_2O$ and $C_3O_2$.

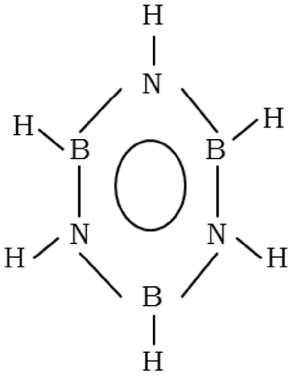
(iv) ***Mixed Oxides:*** These oxides are made up of two simpler oxides, e.g., $Pb_3(PbO_2.2PbO)$.

- 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 $BBr_3 > BCl_3 > BF_3$ .
- 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

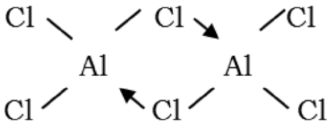
- Boron Carbide ($B_4C_3$) is the hardest artificial substance and is called **Norbide.**
- Acidic nature of hydrides of halides follows the order $HI > HBr > HCI > HF$ .
- Acidic nature increase with increase in oxidation number of halogen.
  $HCIO < HCLO_2 < HCIO_3 < HCIO_4$
- In any given series of acids, the acidic character decreases with decrease in the electronegativity of central halogen atom.
  $HCIO_4 > HBrO_4 > HIO_4$
- 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 ($CF_2ClBr$), Halon 1301 ($CF_3Br$) and Halon 2402 ($C_2F_4Br$).
- $B(OH)_3$ is known as Boric Acid.
- CO combines with $Cl_2$ in the presence of sunlight to form another poisonous gas phosgene

$$CO + Cl_2 \xrightarrow{\textbf{Sunligth}} \underset{\textbf{Phosgene}}{COCl_2}$$

- $CO + H_2$ is known as **water gas.**
- **Acetyl ides:** The Carbides which on hydrolysis give acetylene are called acetylides.
  e.g., $MgC_2 + H_2O \rightarrow Mg(OH)_2 + \underset{\textbf{acetylene}}{HC \equiv CH}$
- **Allylides:** The carbides which on hydrolysis give allylene or propyne are called allylides. e.g., $Mg_2C_3 + 4H_2O \rightarrow 2Mg(OH)_2 + \underset{\textbf{Allylen or Propynes}}{CH_3C \equiv CH}$

## CHEMISTRY OF LIGHTER METALS

- Sodium teraborate decarbohydrate ($Na_2B_4O_7 . 10H_2O$) is commonly known as Borax.
- A mixture of $Al(C_2H_5)_3$ and $TiCl_4$ 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 $Na_2Cl_3$ and $K_2CO_3$ is known as **fusion mixture.**
- $K_2CO_3$ is known as **Pearl ash.**
- Aqueous solution of sodium chloride is known as **Brine.**
- $CaH_2$ is known as **Hydrolith.**
- **Sorel cement** is a mixture of MgO and $MgCl_2 . 6H_2O$.
- Aluminiun chloride exists as diamers ($Al_2Cl_6$).



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
  $X_2SO_4.M_2(SO_4)_8.24\ H_2O$

  where, X = Monovalent cations such as $NA^+, K^+, NH_4^+$, etc.

  M = Trivalent cations such as $Al^{3+}, Cr^{3+}, Fe^{3+}$, etc.
- $KMnO_4$, $K_2Cr_2O_7$ and $CrO_3$ 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: $P_4O_{10}$, $SO_3$, $CO_2$, $N_2O_5$ etc.
- **Basic Oxides:** These are formed by combination of oxygen with highly electropositive elements.
  Examples: MgO, $K_2O$, CaO, BaO, $Na_2O$ etc.
- **Amphoteric Oxides:** These are formed by combination of oxygen with borderline elements between metals and non metals.
  Examples: $Al_2O_3$, $SiO_2$, Zn, PbO etc.
- **Neutral Oxides:** they are neutral to litmus and do not react with acid or base.
  Examples: CO, NO, $N_2O$ etc.
- Air contains about 1% of noble gases.
- Argon is the most abundant noble gas.
- Radon is produced by radioactive decay of (Ra-226). $_{88} \rightarrow ^{222}_{86} \quad ^{4}_{2}\text{He}$
- **Silicones:** These are polymeric organsilicon compounds containing $Si-O-Si$ bonds and having general formula $(R_2SiO)_n$; R have may be $CH_3$ or $C_6H_5$ 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 $\mu_{eff}$ 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 $\pi$ bonds and capable of accepting appreciable electron density form metal atom into empty $\pi$ antibonding orbital of their own are called $\pi$**- acid ligands.** e.g., CO, $CH_2 = CH_2$ , 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.

$$\underset{\textbf{Anionic complex}}{K^+\left[Ag(CN)_2\right]^-} \quad \underset{\textbf{Cationic complex}}{\left[Ag(NH_3)_2\right]^+Cl^-} \quad \underset{\textbf{Neutral complex}}{\left[CoCl_3(NH_3)_3\right]}$$

- 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.

$$\underset{\textbf{Perfect complex}}{K_4\left[Fe(CN)_6\right]} \rightarrow 4K^+ + Fe(CN)_6]^{4-}$$

$\left[Fe(CN)_6\right]^{4-}$ has least tendency to dissociate in solution

$$\underset{\textbf{Imperfect complex}}{\left[Co(NH_3)_6\right]Cl_3} \rightarrow 3Cl^- + \left[Co(NH_3)_6\right]^{3+}$$

- Monodentate ligands capable of coordinating with metal atom by two different sites are called ambidentate ligands. Examples are: nitro $(\leftarrow NO_2)$ and nitrite $(\leftarrow ONO)$.
- Ligands containing $\pi$ bonds are capable of accepting appreciable electron density from metal atom into empty antibonding orbital $\pi^*$ of their own are called $\pi$ acid ligands.
  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.
  $$\begin{aligned}\text{C.N. of metal} &= 1\times\text{No. of monodentate ligands or}\\ &= 2\times\text{No. of bidentate ligands or}\\ &= 3\times\text{No. of tridentate ligands}\end{aligned}$$
- 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

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

### 1 Average Life

$$\frac{1}{\lambda} = 1.44\ t_{1/2}$$

For radioactive equilibrium, $A \rightarrow B \rightarrow C$.

If no. of atoms A, B, C etc, at equilibrium are $N_A$, $N_B$, $N_C$ etc, then

$$-\frac{dN_A}{dt} = -\frac{dN_B}{dt} = -\frac{dN_C}{dt} \text{ or } \lambda_A N_A = \lambda_B N_B = \lambda_C N_C$$

$$\text{Or } \frac{N_A}{N_B} = \frac{\lambda_B}{\lambda_A} = \frac{\left(t_{1/2}\right)_A}{\left(t_{1/2}\right)_B}$$

Mass defect $= M' - M$, where M = actual isotopic mass and

$$M' = Z\times m_p + Z\times m_e + (A-Z)m_n$$

$$= Zm_H + (A-Z)m_n \qquad (\because m_p + m_c = m_H)$$

Binding energy per nucleon

$$= \frac{\text{Binding energy calculated from mass defect}}{\text{mass number}}$$

$$\text{Packing function} = \frac{\text{Isotopic mass} - \text{Mass number}}{\text{Mass number}} \times 10^{4}$$

Energy released by loss of 1 amu mass = 931.5 MeV

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

## PURIFICATION & CHARACTERIZATION OF ORGANIC COMPOUNDS

- Percentage of carbon in organic substance $= \left(\frac{12}{44}\right) \times \left(\frac{m_{\mathbf{co_2}}}{m_{\mathbf{compound}}}\right) \times 100$
- Percentage of hydrogen in organic substance $= \left(\frac{2}{18}\right) \times \left(\frac{m_{\mathbf{H_2O}}}{m_{\mathbf{compound}}}\right) \times 100$
- Percentage of nitrogen in the compound $= \frac{m_{\mathbf{N_2}}}{m_{\mathbf{compound}}} \times 100$

**[Duma's Method]**

$$= \frac{\left(\text{Volume of } N_2\right)_{\mathbf{STP}} \times 28}{(22.4) \times \left(m_{\mathbf{compound}}\right)} \times 100$$

- Percentage of nitrogen $= \frac{1.4 \times N \times \text{vol. of acid used}}{\text{Mass of the substance taken}}$

**[Kjeldhal's Method]**

$$= \frac{1.4 \times \text{Molarity of the acid} \times \text{vol.} \times \text{Basicity}}{\text{Mass of the substance taken}}$$

$$\%\ \text{of X} = \frac{\text{wt. of silver halide ppt.}}{\text{mol. mass of silver halide}} \times \frac{35.5 \times 100}{\text{wt. of org. chloro comp.}}$$

**[Carius Method]**

- Percentage of Chlorine $= \frac{35.5}{143.5} \times \frac{m_{\mathbf{AgCl}}}{m_{\mathbf{compound}}} \times 100$
- Percentage of Bromine $= \frac{80}{188} \times \frac{m_{\mathbf{AgBr}}}{m_{\mathbf{compound}}} \times 100$
- Percentage of Iodine $= \frac{127}{235} \times \frac{m_{\mathbf{AgI}}}{m_{\mathbf{compound}}} \times 100$

- Percentage of sulphur =
$$\frac{\text{wt. of BaSO}_4\text{ precipitate}}{\text{Molecular mass of BaSO}_4}\times\frac{32\times100}{\text{weight of organic compound containing sulphur}}$$

- Percentage of Sulphur $=\frac{32}{233}\times\frac{m_{\mathbf{BaSO_4}}}{m_{\mathbf{compound}}}\times100$

- Percentage of phosphorus $=\frac{62}{222}\times\frac{m_{\mathbf{Mg_2P_2O_7}}}{m_{\mathbf{compound}}}\times100$

**Determination of Molecular mass**

- **Victor Meyer's method:**

  Molecular mass $=\frac{\text{Mass of liqiud or solid }(w)\times22400}{\text{Volume of air displaced at STP}}$

- **Volumetric method:**

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

- **By silver salt method:**

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

- **From the platinichloride method for organic bases:**

  1 equivalent of salt $\equiv$ 1 equivalent of $H_2PtCl_6$

  $\equiv$ 1 equivalent of base $\equiv\frac{1}{2}$(molar mass of Pt)

  $\equiv\frac{195}{2}$ g eq$^{-1}$

  Equivalent mass of platinum salt

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

  Equivalent mass of base

  $$(M_{\mathbf{base}})_{\mathbf{eq}}=(M_{\mathbf{salt}})_{\mathbf{eq}}-(M_{\mathbf{H_2PtCl_6}})_{\mathbf{eq}}=\left[(M_{\mathbf{salt}})_{\mathbf{eq}}-\frac{410}{2}\text{ g eq}^{-1}\right]$$

  $$M_{\mathbf{base}}=(\text{acidity})(M_{\mathbf{base}})_{\mathbf{eq}}$$

A few more expressions to compute molar mass of a compound are as follows.

- From relative lowering of vapour pressure

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

- From elevation of boiling point

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

- From depression of freezing point

$$M_2 = \frac{K_f}{(-\Delta T_f)} \cdot \frac{m_2}{m_1}$$ [$m_1$ = wt. of solvent]

- From osmotic pressure

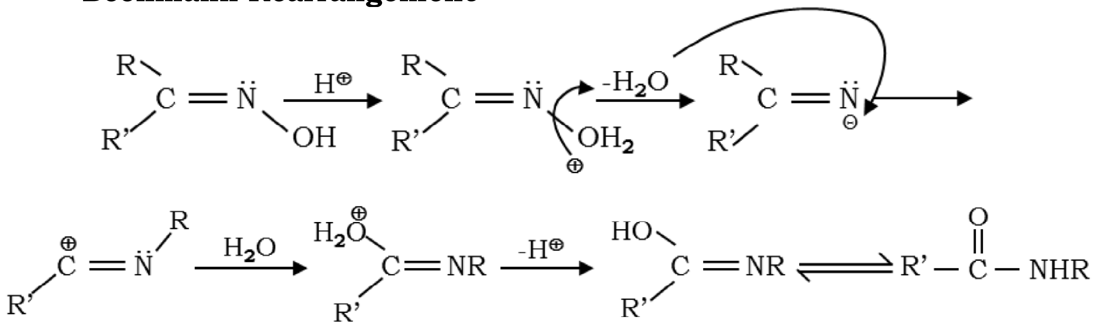
$$M_2 = \left(\frac{m_2}{V}\right)\frac{RT}{\pi}$$ [where, $m_2$ = wt of solute, $M_2$ = mol. Wt of solute]

## ORGANIC CHEMISTRY

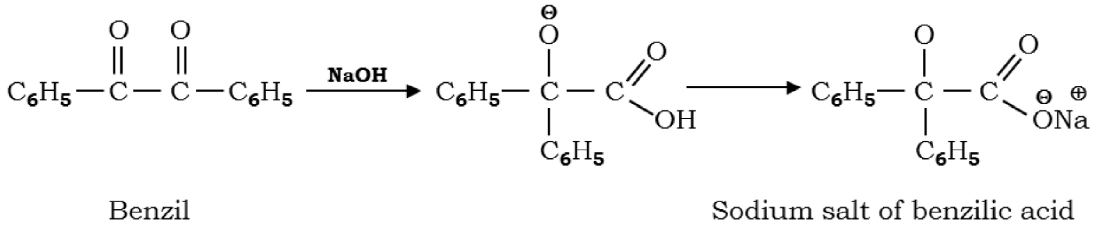
- **Aldol Condensation**
  Aldehydes having $\alpha$ - hydrogen (s) undergo self- condensation on warming with dilute or mild base to give $\beta$ - hydroxyl aldehydes, called aldols.

  e.g., $CH_3CHO + CH_3CHO \overset{OH}{\rightleftharpoons} CH_3 \overset{\ominus}{C}H(OH)CH_2CHO$

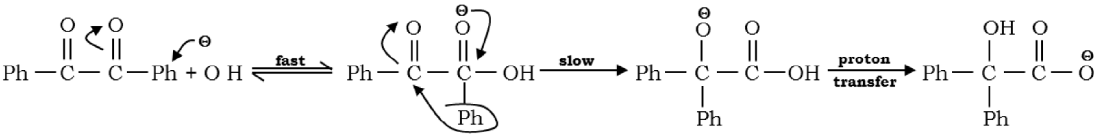
- **Beckmann Rearrangement**



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



- **Mechanism**

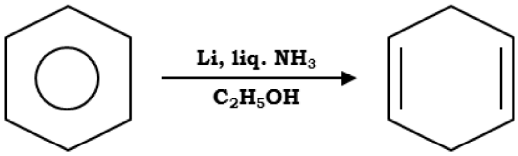


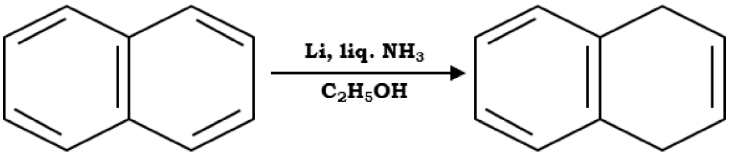
- **Crossed aldol condensation**
  When condensation is between two different carbonyl compound, it is called Crossed aldol condensation.

(a) $${}_3C - CHO + Ch_3CHO \xrightarrow{OH^{\ominus}} \underset{\textbf{Crossed product}}{R_3C - CH(OH) - CH_2 - CHO}$$

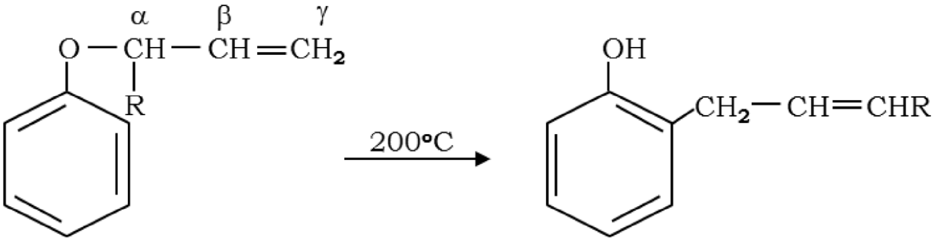
(b) $$CH_3CHO + CH_3COCH_3 \xrightleftharpoons{OH^{\ominus}} \underset{\textbf{Crossed product}}{CH_3 - CH(OH) - CH_2\,COCH_3}$$

- **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.



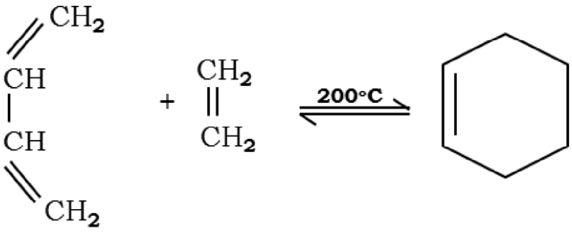


- **Cannizzaro Reaction**
  In the presence of a strong base, aldehydes without $\alpha-$hydrogens, i.e. nonaldolizable aldehydes undergo self oxidation reduction, i.e., disproportions reaction.
  e.g. $2C_6H_5CHO + NaOH \xrightarrow{\Delta} C_6H_5CH_2OH + C_6H_5COONa$
  $2HCHO + NaOH \xrightarrow{\Delta} CH_3OH + HCOONa$
- **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.



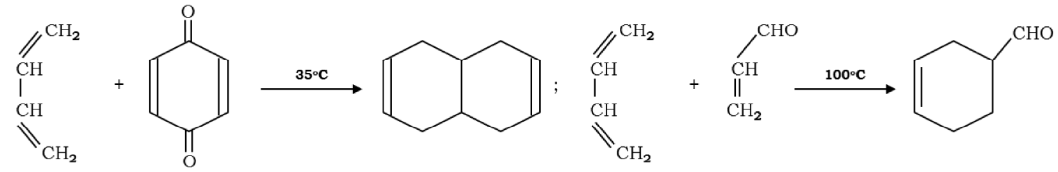
- **Clemmenson Reduction**
  The reduction of carbonyl group of aldehydes and ketones to methylene groups with amalgamated zinc and concentrated hydrochloric acid.
  e.g. $C_6H_5COCH_3 \xrightarrow[\text{Reflux}]{\text{Zn-Hg.HCl}} C_6H_5CH_2CH_3$

- **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.

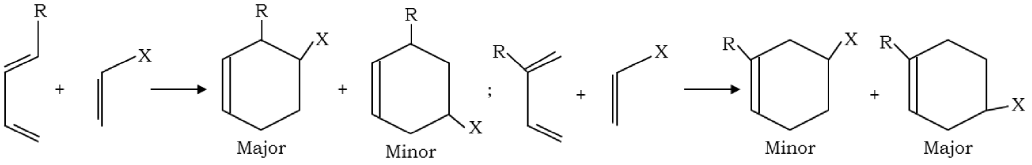


Cyclohexene (20%)

Electron – withdrawing substituents in the dienophile, such as $> C = O, –CHO, –COOR, – CN, – NO_2$, 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. $C_6H_6 + CH_3CH_2Cl \xrightarrow[80^oC]{Anhydrous,AlCl_3} C_6H_5CH_2CH_3 + HCl$

  $C_6H_6 + CH_3COCl \xrightarrow[C_6H_5NO_2]{Anhy.AlCl_3} C_6H_5COCH_3 + HCl$

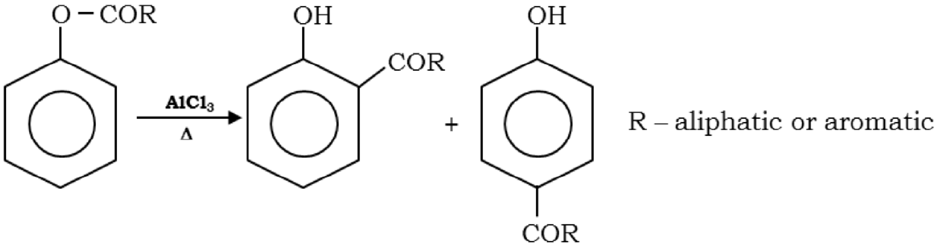
  $C_6H_5 + (CH_3CO)_2\,O \xrightarrow{Anhy.AlCl_3} C_6H_5COCH_3 + CH_3COOH$

  The order of reactivity of some of the catalysts is

  $AlBr_3 > AlCl_3 > FeCl_3 > SbCl_5 > SnCl_4 > BCl_3 > BF_3$

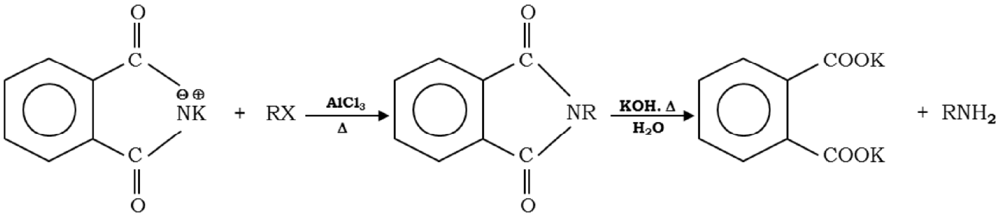
- **Fries Rearrangement**

  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.

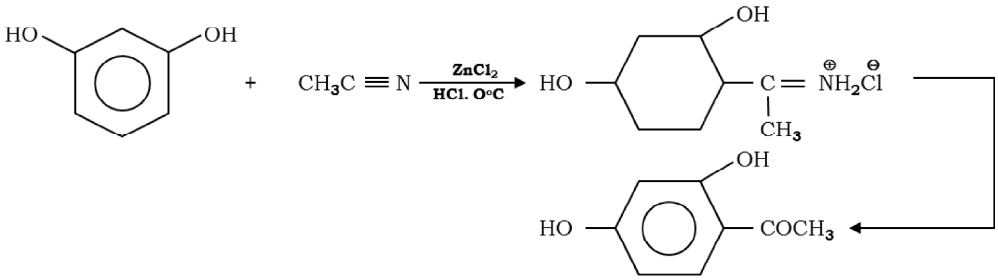
- **Gabriel Synthesis**
  The reaction involves the preparation of primary amines free from secondary or tertiary amines by reacting alkyl halides with alkali phthalimide and subsequent hydrolysis.



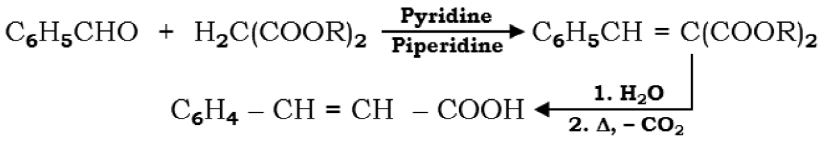
- **Hell – Volhard –Zelinsky Reaction**
  Aliphatic carboxylic react with bromine or chlorine (but not iodine and fluorine) in the presence of small amount of red phosphorus to give exclusively mono $\alpha$ – halogenated acids. [Only by aliphatic acids having $\alpha$ – hydrogen].
  e.g. $CH_3CH_2COOH + Br_2 \xrightarrow{\text{Red P}} CH_3CHBrCOOH + HBr$

- **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. $RCONH_2 + Br_2 + 4NaOH \rightarrow RNH_2 + 2NaBr + Na_2CO_3 + 2H_2O$

- **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.

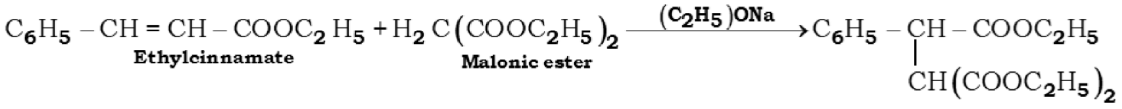


- **Knoevenagel reaction**
  Condensation of aldehydes and Ketones with compounds having active methylene group in the presence of basic catalyst to form $\alpha,\beta-$unsaturated compounds.



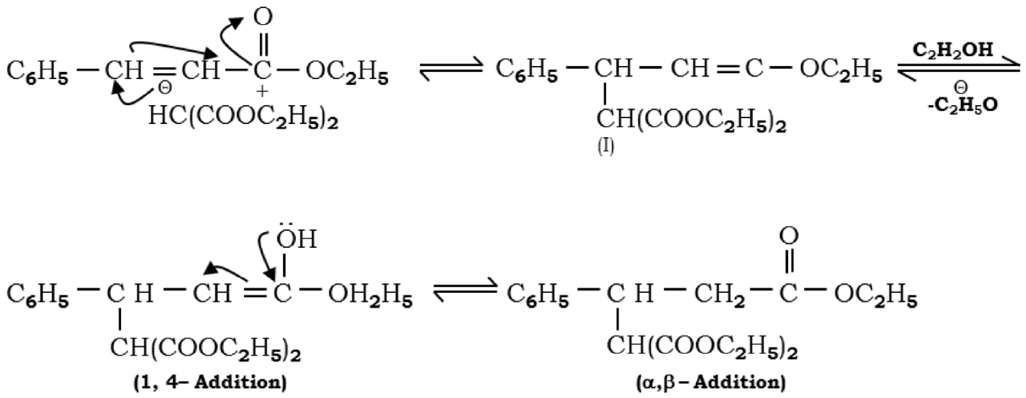
$$C_6H_5CHO + H_2C(COOR)_2 \xrightarrow[\text{Piperidine}]{\text{Pyridine}} C_6H_5CH = C(COOR)_2 \xrightarrow[2.\ \Delta,\ -CO_2]{1.\ H_2O} C_6H_4 - CH = CH - COOH$$

- **Michael Reaction**
  The base-catalysed addition of compounds having active methylene group (or relatively acidic hydrogens) to an activated olefinic bond of the type $-\underset{|}{C}=\underset{|}{C}-Z$ (Z = electron – withdrawing) is classified as Michael reaction.



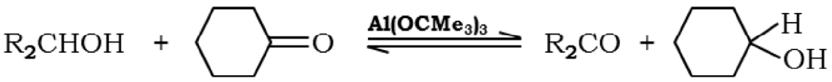
$$\underset{\text{Ethylcinnamate}}{C_6H_5-CH=CH-COOC_2H_5} + \underset{\text{Malonic ester}}{H_2C(COOC_2H_5)_2} \xrightarrow{(C_2H_5)ONa} C_6H_5-\underset{\substack{|\\ CH(COOC_2H_5)_2}}{CH}-COOC_2H_5$$

$$H_2C(COOC_2H_5) + C_2H_5ONa \rightleftharpoons H\overset{\ominus}{C}(COOC_2H_5)_2 + C_2H_5OH$$



- **Oppenauer Oxidation**
  The oxidation of a secondary alcohol with a ketone and a base to the corresponding ketone of the alcohol.

e.g., ${}_2CHOH + (CH_3)_2CO \xrightleftharpoons{Al(OCMe_3)2} {}_2CO + CH_2CHOHCH_3$



- **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 $\alpha,\beta-$unsaturated aromatic acids. The acid reaction should have at least two $\alpha-$hydrogens.

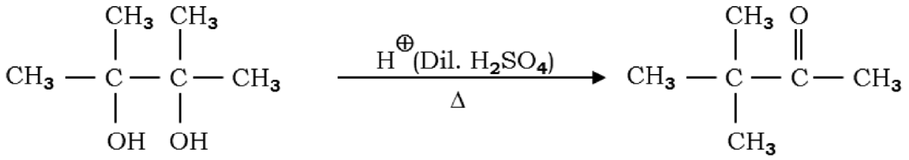
  e.g.

  $$C_6H_5CHO+(CH_3CO)_2O \xrightarrow[170-180^{o},5Hr]{AcONa} C_6H_5-CH=CH-COOH+CH_3COOH$$

- **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.

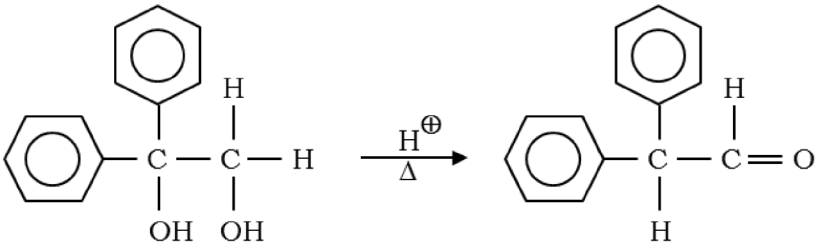
  e.g,



$$CH_3-\underset{OH}{\overset{CH_3}{C}}-\underset{OH}{\overset{CH_3}{C}}-CH_3 \xrightarrow[\Delta]{H^{\oplus}(\text{Dil. }H_2SO_4)} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\overset{O}{\overset{\|}{C}}-CH_3$$

Pinacol

Pinacolone
(Methyl – t- butyl ketone)



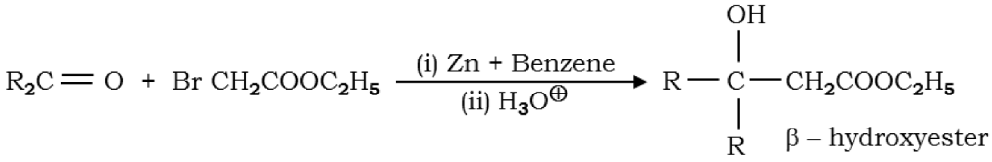
2, 2- Diphenyl-1, 2- glycol

2, 2- Diphenyl acetaldehyde

- **Reformasky Reaction**

  Reaction of an $\alpha-$halo ester, usually an $\alpha-$bromoester with an aldehyde or ketone in the presence of zinc metal to produce a $\beta-$hydroxyester.

  e.g.,



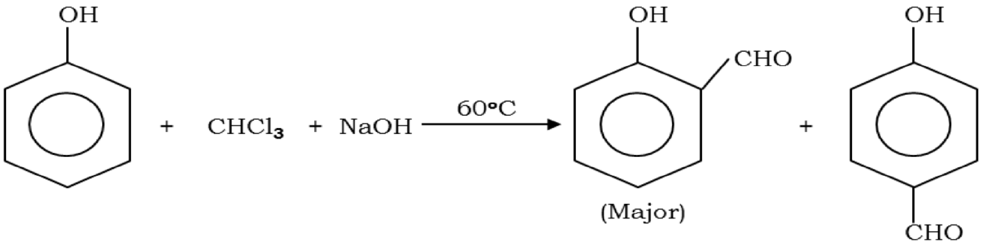
$$R_2C=O + Br\,CH_2COOC_2H_5 \xrightarrow[\text{(ii) }H_3O^{\oplus}]{\text{(i) Zn + Benzene}} R-\underset{R}{\overset{OH}{C}}-CH_2COOC_2H_5$$

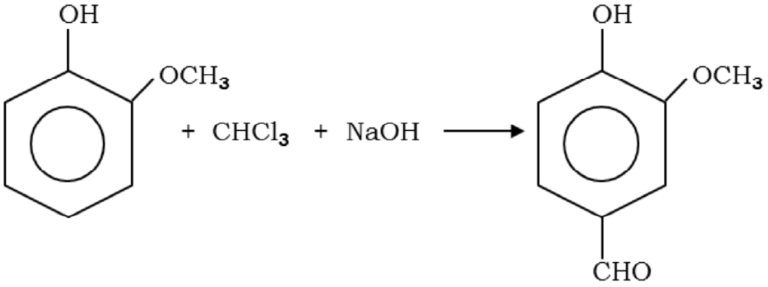
β – hydroxyester

- **Reimer Tiemann Reaction**

  Formylation of phenols with chloroform in alkaline solution.

  e.g.,





Vanillin

- **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.,

$$C_6H_5NHCOCH_3 + C_6H_5BR + K_2CO_3 \xrightarrow[reflux]{Cu} (C_6H_5)_2 NH + CO_2 + CH_3COOK + KBr$$

$$C_6H_5OH + C_6H_5BR + KOH \xrightarrow[Reflux]{Cu} (C_6H_5)_2 O + KBr + H_2O$$

$$2C_6H_5I + Cu \xrightarrow[\Delta]{C_6H_5NO_2} C_6H_5 - C_6H_5 + CuI_2$$

- **Witting reaction**

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

$$Ph_3P = CH_2 + Ph_2\,C = O \longrightarrow Ph_2C = CH_2 \quad + \quad Ph_3P = O$$

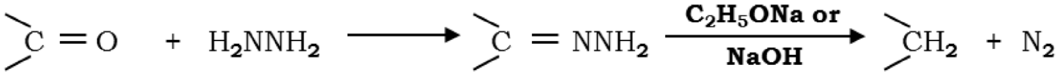
1, 1–Diphenyl ethylene

Triphenyl 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.,



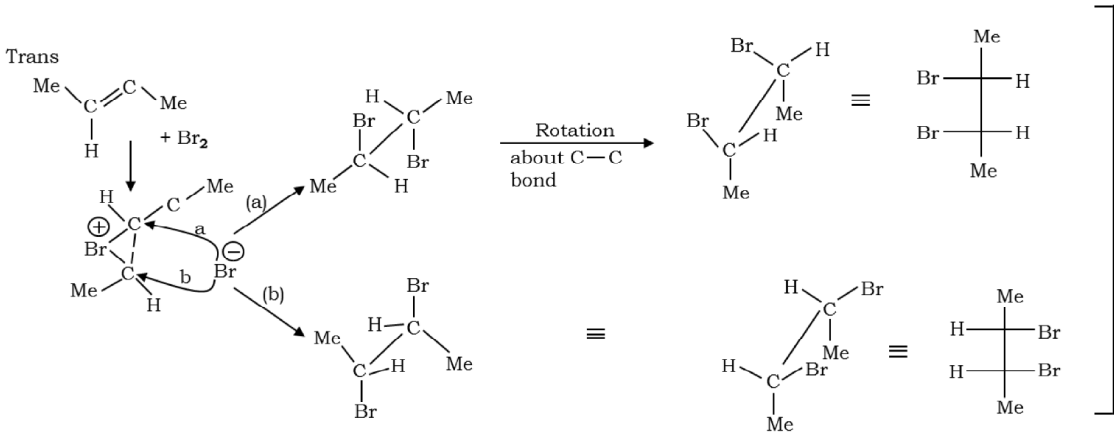
$$>C=O + H_2NNH_2 \longrightarrow >C=NNH_2 \xrightarrow[\textbf{NaOH}]{\textbf{C}_2\textbf{H}_5\textbf{ONa or}} >CH_2 + N_2$$

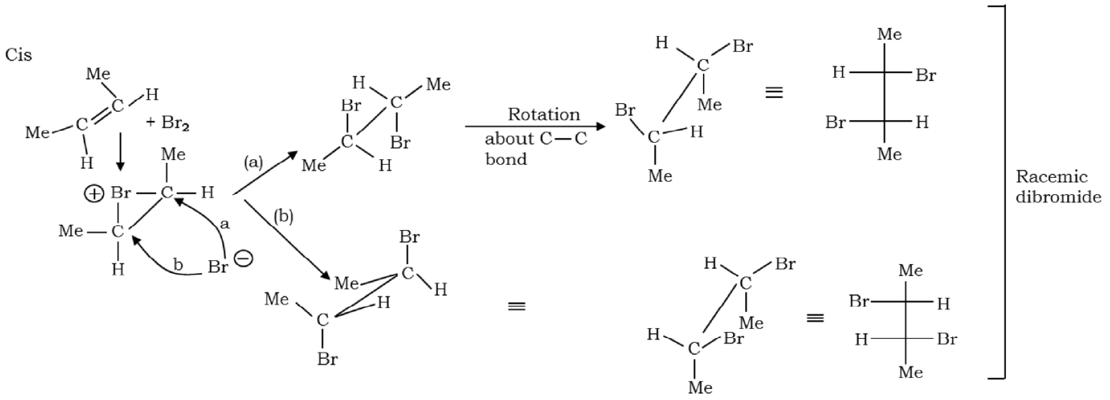
**Addition Reactions**

(i) **Electrophilic addition reaction:**

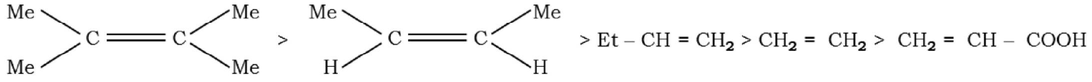
$$CH_2 = CH_2 + Br_2 \xrightarrow{\text{CCL4}} CH_2Br - CH_2BR$$

**Mechanism:**



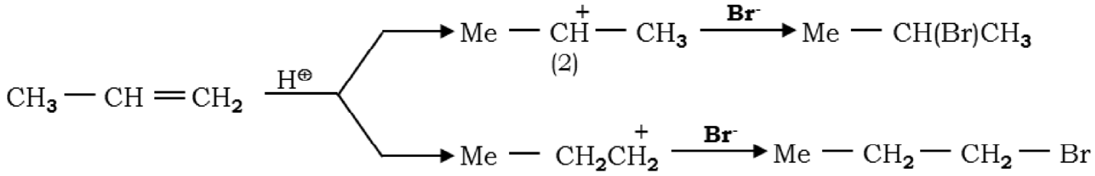


## Relative rates of addition



$Me_2C{=}CMe_2 > MeCH{=}CHMe > Et-CH=CH_2 > CH_2 = CH_2 > CH_2 = CH - COOH$

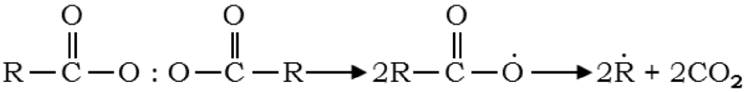
## Markovnikov Rule



$$CH_3 - CH = CH_2 \xrightarrow{H^{\oplus}} Me - \underset{(2)}{\overset{+}{C}H} - CH_3 \xrightarrow{Br^-} Me - CH(Br)CH_3$$

$$CH_3 - CH = CH_2 \xrightarrow{H^{\oplus}} Me - CH_2\overset{+}{C}H_2 \xrightarrow{Br^-} Me - CH_2 - CH_2 - Br$$

## Peroxide effect



$$R-\overset{O}{\overset{\|}{C}}-O:O-\overset{O}{\overset{\|}{C}}-R \longrightarrow 2R-\overset{O}{\overset{\|}{C}}-\dot{O} \longrightarrow 2\dot{R} + 2CO_2$$

$$\dot{R} + H : Br \rightarrow RH + \dot{B}r$$

$$CH_3 - CH - CH_2 \quad + \quad \dot{B}r \longrightarrow CH_3 - \underset{(2^o)}{\dot{C}H} - CH_2Br \text{ (not } CH_3 - \underset{(1^o)}{CHBr} - \dot{C}H_2)$$

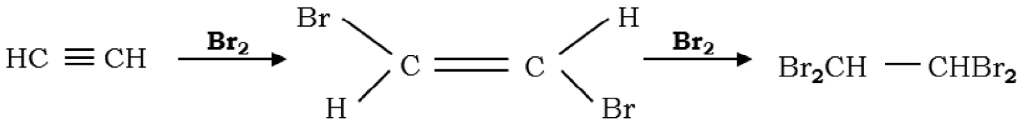
$$CH_3 - \dot{C}H - CH_2Br + H : Br \longrightarrow CH_3CH_2CH_2Br + \dot{B}r$$

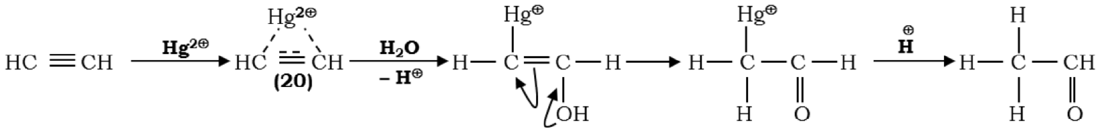
## Addition to conjugate dienes

$$CH_2 = CH - CH = CH_2 \xrightarrow[Br^-]{Br_2} CH_2Br - \overset{+}{C}H - CH_2 \longleftrightarrow CH_2Br - CH = CH_2 -$$

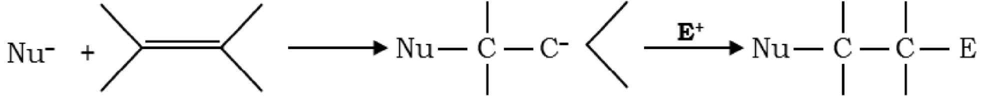
$$\overset{+}{C}H_2 \xrightarrow{Br^-} \underset{\textbf{(1, 4 - Addition)}}{CH_2Br - CH = CH - CH_2Br} + \underset{\textbf{(1, 2 - Addition)}}{CH_2Br - CHBrCH = CH_2}$$

**Addition to alkynes**

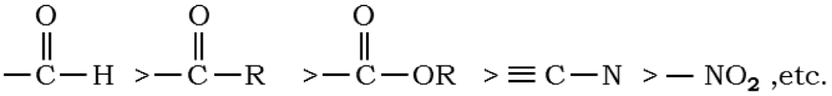




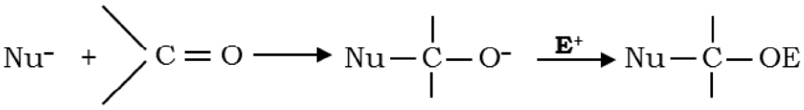
(ii) **Nucleophilic addition reaction**



**Electron withdrawing groups are**



$-\overset{O}{\overset{\|}{C}}-H > -\overset{O}{\overset{\|}{C}}-R > -\overset{O}{\overset{\|}{C}}-OR > \equiv C-N > -NO_2$ ,etc.

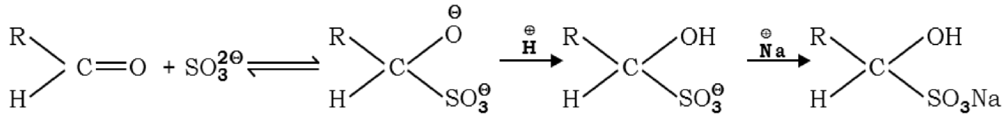


**Reactivity of the carbonyl groups decreases in the order**

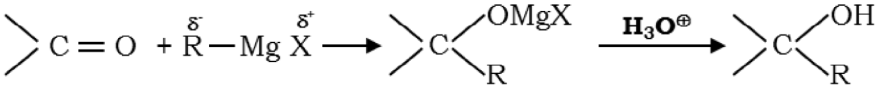
$H_2C=O > RCHO > R_2CO > ArCHO > AR_2CO$

(iii) **Bisulphite addition**

$NaHSO_3 \rightleftharpoons \overset{\oplus}{N}a + \overset{\oplus}{H} + SO_3^{2\ominus}$



(iv) **Carbanion addition**

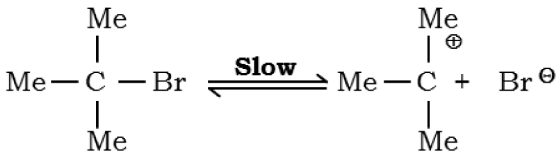


**S<sub>N</sub> 1 mechanism**

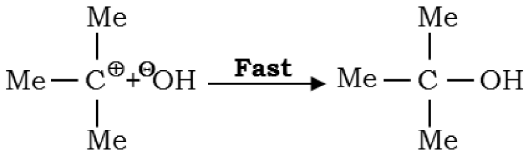
Rate $\propto[\;_{3}CX]$

First – order Reaction

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



$$\mathrm{Me-\underset{Me}{\overset{Me}{C}}-Br \overset{\textbf{Slow}}{\rightleftharpoons} Me-\underset{Me}{\overset{Me}{C}}{}^{\oplus} + Br^{\ominus}}$$ ........(i)



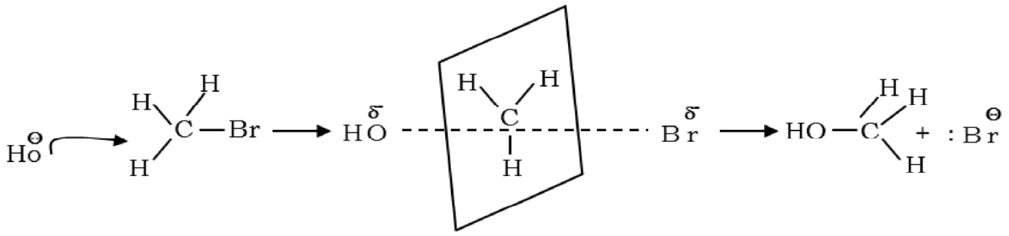
$$\mathrm{Me-\underset{Me}{\overset{Me}{C}}{}^{\oplus} + {}^{\ominus}OH \xrightarrow{\textbf{Fast}} Me-\underset{Me}{\overset{Me}{C}}-OH}$$ ........(ii)

**$S_N$ 2 mechanism**

Rate $\propto [Rx][Nu]$

Second under Reaction

The rate of hydrolysis of alkyl halides by $S_N$ 2 path is $CH_3X > 1^o > 2^o > 3^o$



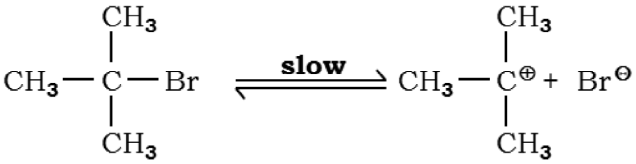
Transition state

Walden Inversion

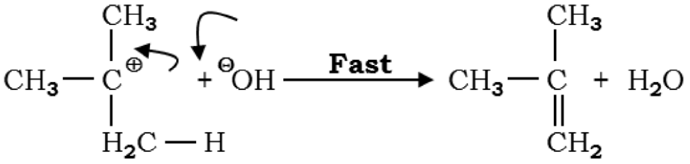
## Elimination reactions

(a) **E1 mechanism**

Kinetically of the first order.



$$\mathrm{CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Br \overset{\textbf{slow}}{\rightleftharpoons} CH_3-\underset{CH_3}{\overset{CH_3}{C}}{}^{\oplus} + Br^{\ominus}}$$ ........(i)



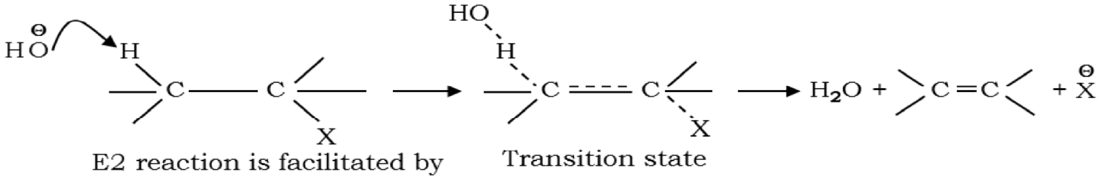
$$\mathrm{CH_3-\underset{H_2C-H}{\overset{CH_3}{C}}{}^{\oplus} + {}^{\ominus}OH \xrightarrow{\textbf{Fast}} CH_3-\underset{CH_2}{\overset{CH_3}{\underset{\|}{C}}} + H_2O}$$ ........(ii)

E1 reaction is facilitated by

(i) branching at the $\alpha$ – and $\beta$ – 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.

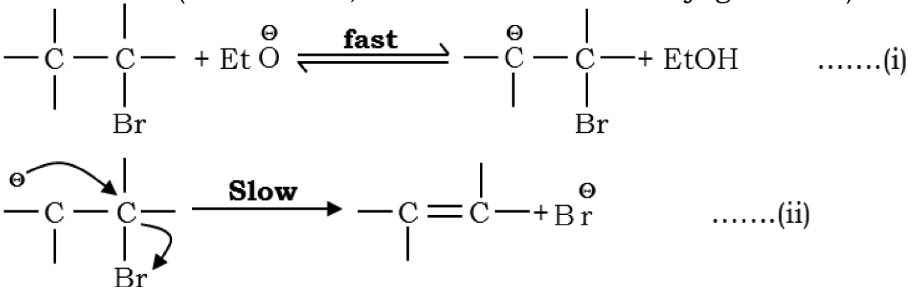
**E2 mechanism**

Rate $\alpha$ [substrate] [reagent]



E2 reaction is facilitated by
(i) branching at $\alpha$ – and $\beta$ – 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)

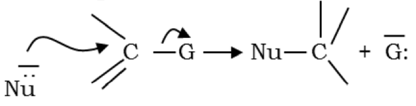
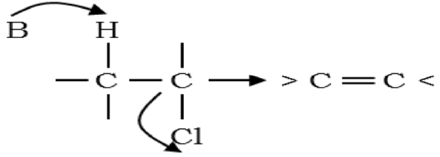
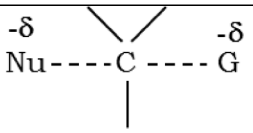
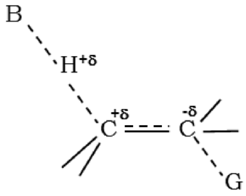


**Difference between $S_N1$ and $S_N2$ reaction.**

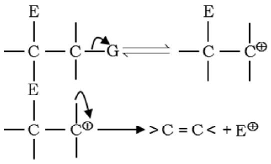
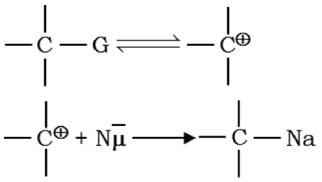
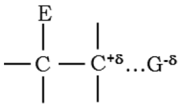
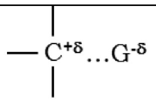
| | **$S_N1$ reaction** | **$S_N2$ reaction** |
|---|---|---|
| **1.** | It is two step reaction. | It is one step reaction. |
| **2.** | Rate depend only on concentration of substrate. | Rate depend on concentration of substrate and nucleophile. |
| **3.** | It is unimolecular reaction. | It is bimolecular reaction. |
| **4.** | The nucleophile can attack on the carbon of substrate from front side and backside. | The nucleophile can attack on the carbon of substrate from backside only. |

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

**Difference between $S_N2$ and $E_2$:**

| | **Points** | **$S_N2$** | **$E_2$** |
|---|---|---|---|
| **1.** | Step | One step  | One step  |
| **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 | $1^\circ > 2^\circ > 3^\circ$ | $3^\circ > 2^\circ > 1^\circ$ |
| **5.** | Trasition State |  |  |
| **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. |

**Difference between $S_N1$ and $E_1$**

| | **Points** | **$E_1$** | **$S_N1$** |
|---|---|---|---|
| 1. | Step | 2 steps<br> | 2steps<br> |
| 2. | Reagent | Solvent plays the role of the reagent | Solvents and weakly 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 rate determining step. It follows the first order kinetics. | The first step is rate determining step. It follows first order kinetics. |
| 6. | Transition State | <br>$C^{+\delta}\ldots G^{-\delta}$ | <br>$C^{+\delta}\ldots G^{-\delta}$ |
| 7. | Stereochemistry | Non-stercospecific | Racemisation and partial inversion occur. |

**Prediction of number of Optical Isomers**

**i) When the molecule is unsymmetrical**

Number of d and $\ell$ isomers (A) = $2^n$

Number of meso forms (m) = 0

$\therefore$ Total number of optical isomers = (a + m) = $2^n$

Where n is the number of chiral carbon atom (s).

Common example is $CH_3$ . CHBr . CHBr . COOH

**ii) When the molecule is symmetrical and has even number of chiral carbon atoms**

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

∴ Total number of optical isomers = (a + m) = $2^{(n-1)}$ .

### Halogenation

The order of case of substitution is

Tertiary hydrogen > Secondary hydrogen > Primary hydrogen

$$RH + X_2 \xrightarrow[\text{or A}]{\text{UV light}} RX + HX$$

Reactivity of $X_2$ ; $F_2 > C\ell_2 > Br_2 > I_2$

## SYNTHETIC AND NATURAL POLUMERS

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

| | | |
|---|---|---|
| Buna rubber | $CH_2 = CH–CH=CH_2$<br>1, 3- Butadiene | In the manufacture of tyres etc. |

| **COPOLYMERS** | | |
|---|---|---|
| **Common name of the copolymer** | **Monomer** | **Uses** |
| Dacron or Terylene | (i) $HOCH_2–CH_2OH$<br>Ethylene glycol<br>(ii) $H_3COOC(C_6H_4)COOCH_3$ | In the manufacture of fabrics and magnetic recording |
| Nylon-66 | (i) $H_2N(CH_2)_6NH_2$<br>Hexamethylene diamine<br>(ii) $HOOC(CH_2)_4COOH$<br>Adipic acid | In the manufacture of fabrics, tyre cords, ropes, carpets etc. |
| Bakelite | (i) HCHO<br>Formaldehyde<br>(ii) $C_6H_5OH$<br>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.

**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.