Chemistry

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1. SOME BASIC CONCEPTS OF CHEMISTRY

(1). Number of molecules in W(g) of substance $= \frac{W(g) \times N_A}{GMM}$

(2). Molality (m) = $\frac{\text{No. of moles of solute}}{\text{Mass of solvent in kg}}$

(3). Number of molecules in V litre of gas at S.T.P. = $\frac{VN_A}{22.4}$

(4). Number of gram atoms = $\frac{W(g)}{GAM}$ (GAM \rightarrow gram atomic mass)

(5). Number of gram molecules = $\frac{W(g)}{Gram molecular mass}$

(6). Dilution formula : $M_1V_1 = M_2V_2$

For mixing two solutions of the same substance

$$M_1V_1 + M_2V_2 = M_3(V_1 + V_2)$$

Molarity can be directly calculated from % by mass (w/w) if density is known

 $Molarity = \frac{\% \times 10 \times d}{GMM}$

(7). Mass of 1 atom of element $= \frac{GAM}{N_A}$

(8). Mass of 1 molecule of substance $= \frac{MM}{N_A}$ (MM \rightarrow Molar mass)

(9). $T(K) = T(^{\circ}C) + 273.15$

(10). Relative atomic mass =
$$\frac{\text{Mass of an atom of the element}}{\frac{1}{12} \times \text{Mass of an atom of carbon (C-12)}}$$

(11). Number of molecules in n moles of substance $= n \times N_{a}$

(12). Mass % of an element in a compound $= \frac{\text{Mass of that element in 1 mole of the compound}}{\text{Molar mass of the compount}} \times 100$

(13). Mass percent = $\frac{\text{Mass of solute}}{\text{Mass of solution}} \times 100$

(14).
$$\frac{X_{B}}{1 - X_{B}} = \frac{\text{molality} \times M_{A}}{1000} \text{ where } M_{A} \text{ - mass of solvent}$$

(15). Molarity (M) = $\frac{\text{No. of moles of solute}}{\text{Volume of solution in litres}} \text{mole / L}$
(16). Avogadro's No. N_A = 6.022×10^{23}
(17). T(°F) = $\frac{9}{5}$ T(°C) + 32
(18). Molecular mass = $2 \times \text{vapour density}$
(19). Mole fraction of A = $\frac{\text{No. of moles of A}}{\text{No. of moles of solution}}$

2. STRUCTURE OF ATOM

(1). Wavelength of matter wave

$$\lambda = \frac{h}{mv}$$
$$\lambda = \frac{h}{p}$$
$$\lambda = \frac{h}{\sqrt{2Em}}$$

Where, E = Kinetic energy

(2). Total number of nodes = n - 1

Radial nodes =
$$n - l - 1$$

Angular nodes = *I*

(3). Number of neutrons = A - Z

(4). Number of subshells in nth shell = n

Number of orbitals in n^{th} shell = n^2

Number of electrons in n^{th} shell = $2n^2$

Number of orbitals in subshell = 2l + 1

Number of electrons in subshell = 2(2l + 1)

(5). Energy of quantum of radiation according to Planck's quantum theory

$$E = hv$$

(6).
$$hv = hv_0 + \frac{1}{2}m_ev^2$$

Einstein's photoelectric equation.

(7). Line spectrum of hydrogen

$$\overline{v} = 109677 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) cm^{-1}$$
 where \overline{v} is wave number and $\overline{v} = \frac{1}{\lambda}$.

Where $n_1 = 1, 2,$

$$n_2 = n_1 + 1, n_1 + 2, \dots$$

(8). Bohr's model of hydrogen atom

(a) **Frequency** of radiation absorbed or emitted during transition ; $v = \frac{\Delta E}{h}$

$$v = \frac{E_2 - E_1}{h}$$

 E_1 = Energy of lower energy state

 E_2 = Energy of higher energy state.

(b) Orbit angular momentum of an electron,

$$m_e vr = n \cdot \frac{h}{2\pi}$$

Where, n = 1, 2, 3,....

(c) **Energy** of stationary states

$$E_{n} = -2.18 \times 10^{-18} \left(\frac{Z^{2}}{n^{2}}\right) J$$

ts
$$r_{n} = 52.9 \times \left(\frac{n^{2}}{Z}\right) pm$$

(d) Radii of the stationary states/orbits

(9). Energy gap between the two orbits

$$\Delta E = R_{H} \left(\frac{1}{n_{i}^{2}} - \frac{1}{n_{f}^{2}} \right)$$

Where $R_{H}^{}=2.18\times10^{-18}$

Where, $n_i = initial orbit$

 $n_f = final orbit$

(10). Atomic number (Z) = Number of protons in the nucleus of an atom

= Number of electrons in a neutral atom

(11). Heisenberg's uncertainty principle

$$\Delta x \times \Delta p \ge \frac{h}{4\pi}$$
; $\Delta x \times m \Delta v \ge \frac{h}{4\pi}$

(12). Speed of light is equal to the product of frequency and wavelength of light



(13). Mass Number (A) = Number of protons + Number of neutrons

3. STATE OF MATTER

(1). Van der Waals Equation :
$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

(2). Combined Gas Equation :
$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$
; (n, R constant)

(3). Dalton's Law of partial pressures : $P_{Total} = P_1 + P_2 + P_3 +$

(4) Ideal gas equation : PV = nRT

$$M = \frac{dRT}{P}$$

(5) **Charles's Law** : $\frac{V_1}{T_1} = \frac{V_2}{T_2}$ (at constant P and n)

(6). Avogadro's Law: V = kn (at constant P and T)

(7). Partial Pressure in Terms of Mole Fraction :
$$P_i = x_i P_{total}$$

(8). Boyle's Law : ${\sf P}_1{\sf V}_1\,={\sf P}_2{\sf V}_2\,$ (at constant T and n)

(9). Compressibility factor $Z = \frac{PV}{RT}$ (for 1 mole of Gas)

4. THERMODYNAMICS

- First law of thermodynamics ∆U = q + W
- Enthalpy of reaction

 $\Delta H = \sum \Delta_i H^o$ (products) $- \sum \Delta_i H^o$ (reactants)

By convention heat of formation of every element in its standard state is arbitrarily assumed to be zero.

$$\Delta_{sub} H^{o} = \Delta_{fus} H^{o} + \Delta_{vap} H^{o}$$

- Heat Capacity Specific heat capacity $c_s = \frac{q}{m\Delta T}$
 - $C = \frac{q}{\Delta T} \qquad \text{molar heat capacity } c_m = \frac{q}{n\Delta T}$
- Energy changes $q_v \rightarrow$ heat exchange at constant volume

 $\Delta U = q_v\,,~~\Delta H = q_p ~~q_p \rightarrow~$ heat exchange at constant pressure

- Enthalpy H = U + pV
- Relation between ΔH and ΔU $\Delta H = \Delta U + p\Delta V$ Or $\Delta H = \Delta U + \Delta n_g RT$

•
$$C_p - C_v = R$$

$$\Delta S = \frac{q_{rev}}{T}$$

 $\Delta \mathsf{G} = \Delta \mathsf{H} - \mathsf{T} \Delta \mathsf{S}$

 $\Delta G^{o} = -RT In K$

| Atomicity | γ | Ср | Cv |
|----------------------|-----|------|------|
| Monoatomic | 5/3 | 5R/2 | 3R/2 |
| Diatomic | 7/5 | 7R/2 | 5R/2 |
| Triatomic non linear | 4/3 | 4R | 3R |

5. EQUILIBRIUM

(1). $K_w = K_a \times K_b$

- (2). $K_i = \frac{[A^+][B^-]}{[AB]}$
- (3). $K_{sp} = [A^{y+}]^x [B^{-x}]^y$
- (4). $\Delta G^{\circ} = -2.303 \text{ RT} \log \text{ K}$

(5). $K_a = \frac{[A^-][H_3O^+]}{[HA]}$ $K_b = \frac{[B^-][OH^-]}{[BOH]}$

(6).
$$K_w = \left[H^+\right] \left[OH^-\right] = 10^{-16} \text{ at } 25^\circ \text{ C}$$

(7). $pH = -log [H^+]$

(8).
$$pK_w = pH + pOH = 14 \text{ at } 25^{\circ}C$$

(9).
$$K_p = K_c (RT)^{\Delta n}$$

(10). Hydrolysis of salts

(i) For a salt of strong acid and weak base

$$pH = \frac{1}{2}[pK_w - pK_b - \log c]$$

(ii) for a salt of weak acid and strong base

$$pH = \frac{1}{2}[pK_w + pK_a + \log c]$$

(iii) For salts of weak acid and weak base

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

(11). Equilibrium constant,
$$K_{eq} = \frac{K_a}{K_b}$$

(12). K_a or $K_b^{}=c\alpha^2$

(13). Concentration quotient,
$$Q = \frac{[C]^{c}[D]^{a}}{[A]^{a}[B]^{b}}$$

6. SOLID STATE

(1). Density of Cubic Crystal System

$$\rho$$
 (or d) = $\frac{Z \times M}{a^3 \times N_A}$ g.cm⁻³

Where, Z = number of atoms per unit cell

 $N_A = Avogadro's$ Number

M = Gram atomic weight of element (g. mol⁻¹)

a=edge-length

(2). Radius-ratio in ionic solids

| Voids | Triangular | Tetrahedral | Octahedral | Cubical |
|--------------|-------------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|
| Radius-ratio | $0.155 \le \frac{r^+}{r^-} < 0.225$ | $0.255 \le \frac{r^+}{r^-} < 0.414$ | $0.414 \le \frac{r^+}{r^-} < 0.732$ | $0.732 \le \frac{r^+}{r^-} < 0.999$ |

(3).

| Crystal | Radius of atom (r) | No. of atoms per unit cell | p.f. |
|--------------|------------------------|----------------------------|--------|
| Simple cubic | а | 1 | 52.4 % |
| | 2 | | |
| F.C.C. | а | 2 | 74 % |
| | $\overline{2\sqrt{2}}$ | | |
| B.C.C | $\sqrt{3}$ | 2 | 68 % |
| | a | | |

(4). Packing Fraction (p.f.) = Volume occupied by particles (per unit cell) Volume of unit cell

Contribution of each atom present on the corner = $\frac{1}{8}$

Contribution of each atom present on the centre of face = $\frac{1}{2}$

Contribution of each atom present on the body centre = 1

Contribution of each atom present on the edge centre = $\frac{1}{4}$

(5). Seven crystal system with dimensions :

(a) Cubic : $\alpha = \beta = \gamma = 90^{\circ}$, a = b = c

(b) Tetragonal : $\alpha = \beta = \gamma = 90^{\circ}$, $a = b \neq c$

(c) Orthorhombic : $\alpha = \beta = \gamma = 90^{\circ}$; $a \neq b \neq c$

(d) Monoclinic : $\alpha = \gamma = 90^{\circ}$; $\beta \neq 90^{\circ}$; $a \neq b \neq c$

(e) Hexagonal : $\alpha = \beta = 90^{\circ}$; $\gamma = 90^{\circ}$; $a = b \neq c$

(f) Rhombohedral or trigonal : $\alpha = \beta = \gamma \neq 90^{\circ}$; a = b = c

(g) Triclinic : $\alpha \neq \beta \neq \gamma \neq 90^{\circ}$; $a \neq b \neq c$

7. SOLUTIONS

(1). Depression in freezing point

 $\Delta T_{f} = K_{f} \times m$

$$K_{f} = \frac{RT_{0}^{2}}{1000 I_{fusion}} = \frac{M_{A}RT_{0}^{2}}{1000 \Delta H_{fusion}}$$

(2) Dissociation of solute

 $(A)_n \rightarrow nA$

 $i = \frac{1 + (n - 1)\alpha}{1}$ { a = degree of dissociation}

(3).
$$P_{sol} = \frac{P_A^o X_A + P_B^o X_B}{(P_B^o - P_A^o)X_B + P_A^o}$$
 Raoult's law

(4). Osmotic pressure

 $\pi=CRT$

For isotonic solution, $\pi_1 = \pi_2$

(5)
$$\frac{1}{P_{sol}} = \frac{Y_A}{P_A^o} + \frac{Y_B}{P_B^o}$$

(6). Relative lowering of vapour pressure

$$\frac{P_A^{o} - P}{P_A^{o}} = \chi_B \qquad \{\chi_B = \text{mole fraction of solute}\}$$
(7) $Y_A = \frac{P_A}{P_T}; Y_B = \frac{P_B}{P_T}$

Where Y_A and Y_B are mole fractions in vapour phase and $P_A = P_A^o X_A$: $P_B = P_B^o X_B$

(8). Elevation of boiling point

$$\Delta T_{b} = K_{b} \times m$$

$$K_{b} = \frac{RT_{0}^{2}}{100 I_{vapour}} = \frac{M_{A}RT_{0}^{2}}{1000 \Delta H_{vapour}}$$

Where, m = molality

M_A = molecular mass of solvent

(9).

Molality (m) =
$$\frac{\text{Number of moles of solute}}{\text{Weight of solvent (kg)}}$$
 mole / kg

Molarity (M) = $\frac{\text{Number of moles of solute}}{\text{Volume of solution (L)}}$ mole / L

Normality (N) = $\frac{\text{Number of gram equivalent of solute}}{\text{Volume of solution (L)}}$ g equiv / L

Formality (F) = $\frac{\text{Number of gram formula mass}}{\text{Volume of solution (L)}}$

(10). Van't Hoff factor

 $i = \frac{\text{Experimental colligative property (observed)}}{\text{Calculated (normal) colligative property}}$

$$\frac{P_A^B - P}{P_A^B} = \frac{(i \times n_B)}{(i \times n_B) + n_A}$$
$$\Delta T_b = i \times K_b \times m$$
$$\Delta T_f = i \times K_f \times m$$

 $\pi = iCRT$

(11). Association of Solute

 $\mathsf{nA} \to \mathsf{(A)}_\mathsf{n}$

$$i = \frac{(1 - \alpha) + \frac{\alpha}{n}}{1}$$
 {\$\alpha\$ = degree of association}

(12). Henry's Law

$$\rho = K_{H} . X \begin{cases} p = partial pressure of gas in vapour phase \\ K_{H} = Henry's law constant \\ X = Mole fraction of gas \end{cases}$$

8. ELECTROCHEMISTRY

(1). Ohm's law \Rightarrow V = RI

$$R = \rho \frac{\ell}{a}$$

V = Potential difference

R = Resistance

I = Current

 ρ = Specific resistance (resistivity)

 ℓ = length of conductor

a = cross-section area of conductor

(2). Conductance $G = \frac{1}{R}$

Specific conductance (conductivity) $\kappa = \frac{1}{\rho}$

(3). Cell constant $\sigma = \frac{\ell}{a}$

 $\kappa = G.\sigma$

(4). Molar conductance Λ_M (or ϕ_C) = $\frac{1000 \times \kappa}{C \text{ (or M)}}$ molarity}

{C = concentration of electrolyte in terms of

(5). Equivalent conductance Λ_{M} (or A_{C}) = $\frac{1000 \times \kappa}{C \text{ (or N)}}$

{C = concentration (normality)}

 $\Lambda_{\mathsf{M}} = \Lambda_{\mathsf{N}} \times (\mathsf{n-factor})$

$$\Lambda_0 = \lim_{C \to 0} \Lambda_C \qquad \{\Lambda_0 = \text{equivalent conductance at infinite dilution (or zero concentration)}\}$$

(6) For weak electrolyte, $\Lambda_C \propto \frac{1}{\sqrt{C}}$

For strong electrolyte, $\Lambda_{C} = \Lambda_{0} - B(C)^{1/2}$ {B = constant}

(7). At infinite dilution, for an electrolyte $A_x B_y$

$$A_x B_y \rightleftharpoons x A^{y_+} + y B^{x_-}$$

 $\Lambda^{o}_{A_{X}B_{y}} = x\lambda^{o}_{A} + y\lambda^{o}_{B} \qquad \qquad \{\lambda^{o}_{A}, \lambda^{o}_{B} = \text{equivalent conductance at infinite dilution of cation and anion}\}$

 $= x\lambda_{+}^{o} + \lambda_{-}^{o}$

$$\lambda_{C}^{o} = k\mu_{c}^{o}$$
 { μ = ionic mobility, K = 96500 coulomb}

 $\mu = \frac{\text{lonic velocity}}{\text{Potential gradient}}$

(8). For a weak electrolyte, $(CH_3COOH \rightleftharpoons CH_3COO^- + H^+)$

Degree of dissociation, $\alpha = \frac{\Lambda_M}{\Lambda_0}$, $K_{eq} = \frac{C(\Lambda_M / \Lambda_0)^2}{1 - (\Lambda_M / \Lambda_0)}$

(9). For solubility of salt
$$(AgCl \rightleftharpoons Ag^+ + Cl^-)$$

$$K_{sp} = \left(\frac{1000 \text{ K}}{\Lambda_0}\right)^2$$

(10). For a cell reaction in an electrochemical cell,

$$Zn + CuSO_4 \rightleftharpoons Cu + ZnSO_4$$

 $\begin{array}{l} \mbox{Cell representation} \Rightarrow \mbox{ } Zn \, | \, Zn^{2+} (aq.) \, || \, Cu^{2+} (aq.) \, | \, Cu \\ & \mbox{ } Anode(-) & \mbox{ } Cathode(+) \end{array}$

$$M \rightarrow M^{n_+}(aq.) + ne^-$$
; $E_{ox} = E_{M/M^-}$

$$M^{n+}(aq) + ne^{-} \rightarrow M$$
 ; $E_{red} = E_{M^{-}/M}$

emf of cell, $E_{cell}^{o} = E_{right}^{o} - E_{left}^{o}$

$$= E^{o}_{\substack{\text{cathode} \\ (R.P.)}} - E^{o}_{\substack{\text{anode} \\ (R.P)}} \qquad \{\text{R.P.} = \text{Reduction potential}\}$$

(12).
$$\Delta G = -nFE_{cell}$$

= - W
= $-\Delta G^{o} + 2.303 \text{ RT log Q}$
 $\Delta G^{o} = -nFE_{cell}^{o}$
 $E_{cell} = E_{cell}^{o} - \frac{2.303 \text{ RT}}{nF} \log Q$
 $\int \Delta G$ = Change in free energy
W = Useful work done
n = Number of electrons exchanged
F = Faraday constant (96500 coulomb)
Q = Reaction quotient

At room temperature (25°C)

$$\Rightarrow \qquad \text{Nernst's equation} \Rightarrow \text{E}_{\text{cell}} = \text{E}_{\text{cell}}^{\text{o}} - \frac{0.0591}{n} \log \text{Q}$$

(13). For electrode concentration cell, $(Pt, H_2(P_1) | H^+ | | H_2(P_2), Pt)$ anode cathode

 $E_{cell} = \frac{0.0591}{2} \log \frac{P_1}{P_2}$ (P = Pressure)

For electrolyte concentration cell

 $\begin{array}{c|c} (Cu \mid Cu^{2+}(C_1) \mid \mid Cu^{2+}(C_2) \mid Cu) \\ & \text{anode}(-) & \text{cathode}(+) \end{array}$

 $E_{cell} = \frac{0.0591}{2} \log \frac{C_2}{C_1}$

For concentration cells, $E_{cell}^{o} = 0$

(14). At equilibrium, $E_{cell} = 0$ (as $\Delta G = 0$)

(15). Temperature coefficient (T.C.) = $\left(\frac{\partial}{\partial T} E_{cell}\right)_{p}$

Change in entropy, $\Delta S = +nF \times (T.C.)$ { ΔH = heat of cell-reaction}

 $\mathsf{E}_{\mathsf{cell}} = \left(\frac{-\Delta \mathsf{H}}{\mathsf{nF}}\right) + \mathsf{T.}(\mathsf{T.C.})$

T.C.> 0 \Rightarrow Cell-reaction is endothermic and vice-versa.

(16). Faraday's 1st law of electrolysis

m = Zit

m = mass of substance deposited

Z = electrochemical equivalent

i = current

t = time

 $Z = \frac{Atomic mass}{n \times F}$

Faraday's 2nd law of electrolysis

 $\frac{m_1}{m_2} = \frac{E_1}{E_2}$ (E = equivalent weight)

(17). Oxidation potential for half-cell reaction : $M \rightarrow M^{+n} + ne^{-1}$

 $E_{ox} = E_{ox}^{o} - \frac{2.303}{nF} log [M^{n+}]$

Reduction potential for half-cell reaction : $M^{n_+} + ne^- \rightarrow M$

$$\mathsf{E}_{\mathsf{red}} = \mathsf{E}_{\mathsf{red}}^{\mathsf{o}} + \frac{2.303 \ \mathsf{RT}}{\mathsf{nF}} \ \mathsf{log}[\mathsf{M}^{\mathsf{n+}}]$$

9. CHEMICAL KINETICS AND NUCLEAR CHEMISTRY

(1). For a general chemical transformation

 $nA+mB \rightarrow pC+qD$

 $Rate = \frac{-1}{n}\frac{d[A]}{dt} = \frac{-1}{m}\frac{d[B]}{dt} = +\frac{1}{p}\frac{d[C]}{dt} = \frac{1}{q}\frac{d[D]}{dt}$

(2). For elementary chemical reaction

 $mA + nB \longrightarrow products$

Theoretical rate $= \frac{dx}{dt} = k[A]^{rm} \times [B]^n$

(3). For a general reaction ; $aA + bB \longrightarrow Pr oducts$

$$Rate = \frac{dx}{dt} = k[A]^m \times [B]^n$$

Order of reaction w.r.t. A = m overall order of reaction = (m + n)

Order of reaction w.r.t. B = n

(4). Unit of rate constant = $(mole)^{1-n} (litre)^{n-1} time^{-1}$

Where, n = order of reaction

(5) For a zero order reaction ; $A \longrightarrow B$

Rate =
$$\frac{-d[A]}{dt} = k[A]^{B} = k$$
 (constant)
$$K = \frac{[A_{0}] - [A]}{K}$$

(6). For a first order reaction ; $A \longrightarrow B$

Rate =
$$\frac{-d[A]}{dt} = k[A]$$

 $k = \frac{2.303}{t} \log_{10} \frac{[A]_0}{[A]_1} = \frac{2.303}{t} \log_{10} \left(\frac{a}{a-x}\right)$

(7). For a zero order reaction, $t_{1/2} = \frac{[A]_0}{2k}$

For a first order reaction, $t_{1/2} = \frac{0.693}{k}$

For an n^{th} order reaction, $\,t_{1/2}^{}\,\propto\,\frac{1}{[A]_0^{n-1}}\,\,$ (for $\,n\geq2)$

(8). For a parallel reaction

$$A \xrightarrow[K_2]{K_2} B$$

$$\frac{-d[A]}{dt} = (k_1 + k_2)[A]$$

(9). For a first order reaction : $A \longrightarrow B + C$, a reagent reacts with all A, B and C

$$k = \frac{2.303}{t} \log_{10} \left(\frac{V_{\infty} - V_0}{V_{\infty} - V_t} \right) \qquad \{V = vol. of reagent\}$$

(10). Temperature coefficient = $\frac{k_{T+10^{\circ}C}}{k_{T}}$

Arrhenius equation, $\mathbf{k} = A \mathbf{e}^{-E_a/RT}$

$$\log_{10} \frac{k_2}{k_1} = \frac{E_a}{(2.303 \text{ R})} \left(\frac{T_2 - T_1}{T_2 T_1} \right)$$

 $\log_{10} k = \log_{10} A - \frac{E_0}{2.303 RT}$

$$\begin{cases} A = Arrhenius's constant \\ E_a = Activation energy \end{cases}$$

$$\log_{10} k = \log_{10} A - \frac{E_0}{2.303 \text{ RT}}$$

(12). Binding energy, B.E. = $\Delta m \times 931.5$ MeV

 Δm = mass defect = calculated At. Mass – observed At. Mass

B.E. per nucleon
$$= \frac{B.E. \text{ (total)}}{\text{mass number}}$$

$$1 \text{ MeV} = 9.6 \times 10^{10} \text{ Joule mol}^{-1}$$

(13). Packing fraction. P.F. = $\frac{\text{Isotopic atomic mass-mass no.}}{\text{mass numer}} \times 10^6$

(14). In a radioactive decay, $N_t = N_0 e^{-\lambda t}$

Amount of radioactive substance after 'n' half-life periods

$$N = \left(\frac{1}{2}\right)^n N_0$$

(15). Activity, $A_t = A_0 e^{-\lambda t}$, $A = \lambda N$

10. SURFACE CHEMISTRY

(1). Freundlich Adsorption isotherm

$$\left(\frac{x}{m}\right) = Kp^{\left(\frac{1}{m}\right)}$$
; $n \ge 1$

(2). Langmuir Adsorption isotherm

$$\theta = \frac{K'P_A}{1 + KP_A}$$

Or,
$$\frac{x}{m} = \frac{aP}{1+bP}$$
 or $\frac{m}{x} = \frac{1}{aP} + \frac{b}{a}$

(3) $\frac{x}{m} = KC^{\left(\frac{1}{n}\right)}$; C = Concentration of solute in solution.

(4). Zeta potential, $Z = \frac{4\pi\eta\mu}{D}$

11. HYDROGEN

(1) At. Wt. of $H = \frac{\% {}_{1}^{1}H \times 1 + \% {}_{1}^{2}H \times 2 + \% {}_{1}^{3}H \times 3}{100}$

(2) Vapour density of a gas = $\frac{\text{molar mass of gas}}{\text{molar mass of H}_2}$

LHS and RHS both are unitless

- (3). Molecular wt. = $2 \times (V.D.)$
- (4). Vol. Strength of H_2O_2 = Molarity × 11.2

= Normality \times 5.6

12. S-BLOCK ELEMENTS

- (1) General Electronic Configuration ns¹⁻².
- (2) Atomic Radii increases down the group.
- (3) Hydration enthalpy decreases down the group.
- (4). Ionization enthalpy decreases down the group.
- (5). On reaction with oxygen give oxide, peroxide and superoxides.
- (6) On reaction with water produces hydroxide and hydrogen.
- (7). Some important compounds and their general names.

| Name | Chemical Formula | Prepared by |
|------------------|--|---|
| Caustic Soda | NaOH | Electrolysis in costner kellner cell |
| Washing Soda | Na ₂ CO ₃ , 10H ₂ O | Solvay's process |
| Baking Soda | NaHCO ₃ | Solvay's process |
| Glauber's Salt | Na ₂ SO ₄ , 10H ₂ O | $NaCl + H_2SO_4$ |
| Microcosmic salt | Na(NH ₄)HPO ₄ | NH ₄ Cl + Na ₂ HPO ₄ |

| Potash or Pearl Ash | K ₂ CO ₃ | Leblanc Process |
|---------------------|--|------------------------------------|
| Caustic potash | КОН | Electrolysis of KCl |
| Quick lime | CaO | Decomposition of CaCO ₃ |
| Slaked lime | Ca(OH) ₂ | Hydrolysis of CaO |
| Gypsum | CaSO ₄ , 2H ₂ O | $CaCl_2 + H_2SO_4$ |
| Plaster of Paris | CaSO ₄ , ½ H ₂ O | By heating gypsum |

13. P-BLOCK ELEMENTS

(1). In general metallic character, electropositive character, atomic radii, basic character, reducing character decreases on moving left to right in a period and increases down the group.

(2). Some important compound of p-block elements

| i. | Borax (Tincal) | Na ₂ B ₄ O ₇ , 10H ₂ O |
|-------|---------------------------|--|
| ii. | Colomonite | Ca ₂ B ₆ O ₁₁ , 5H ₂ O |
| iii. | Kemite | Na ₂ B ₄ O ₇ , 4H ₂ O |
| iv. | Sassolite or boric acid | H ₃ BO ₃ |
| ٧. | Diborane | B ₂ H ₆ |
| vi. | Borazole | $B_3N_3H_6$ |
| vii. | Alumina | Al ₂ O ₃ |
| viii. | Lithium aluminium hydride | LiAIH ₄ |
| ix. | Potash Alum | K ₂ SO ₄ , Al ₂ (SO ₄) ₃ , 24 H ₂ O |

14. COORDINATION COMPOUND

(1). Magnetic moment, $\mu = \sqrt{n(n+2)}$ B.M

(2)
$$\Delta_0(\text{CFSE}) = \left[\left(-4 \times n_{e^-} \atop (t_{2g}) \right) + \left(+6 \times n_{e^-} \atop (e_g) \right) \right] \text{Dq}$$

(3).
$$\Delta_{t}(CFSE) = \left[\left[+4 \times n_{e^{-}(t_{2g})} \right] + \left[-6 \times n_{e^{-}(e_{g})} \right] \right] Dq$$

 $(4). \ \Delta_{t} = \frac{4}{9}\Delta_{0}$

(5). For the reaction : $M + 4L \rightleftharpoons ML_4$, overall stability constant of complex (ML₄) is $\beta_4 = \frac{[ML_4]}{[M][L]^4}$

(6).
$$EAN = Z - O.N. + 2(C.N.)$$

15. ORGANIC CHEMISTRY

Relations for the estimation of elements in organic compounds.

% of C = $\frac{12}{44} \times \frac{\text{Mass of CO}_2 \text{ formed}}{\text{Mass of the compound}} \times 100$ % of H = $\frac{2}{18} \times \frac{\text{Mass of H}_2\text{O formed}}{\text{Mass of the compound}} \times 100$ % of N = $\frac{28}{22400} \times \frac{\text{Volume of N}_2 \text{ at NTP}}{\text{Mass of compound}} \times 100$ % of N = $\frac{1.4 \times \text{Normality of acid used} \times \text{Volume of acid used}}{\text{Mass of the compound}}$

% of X(Halogens) =
$$\frac{\text{At. mass of X}}{(108 + \text{At. mass of X})} \times \frac{\text{Mass of AgX formed}}{\text{Mass of the compound}} \times 100$$

% of S = $\frac{32}{233} \times \frac{\text{Mass of BaSO}_4 \text{ formed}}{\text{Mass of the compound}} \times 100$

% of P =
$$\frac{62}{222} \times \frac{\text{Mass of Mg}_2 P_2 O_2 \text{ formed}}{\text{Mass of the compound}} \times 100$$

(1). Inductive effect

(+I effect)
$$CH_3 < C_2H_5 < C_3H_7 < R_2CH < R_3C < -O-R$$

(2). Relative basic strength in aqueous medium.

| $R = CH_3$ | $2^{\circ} > 1^{\circ} > 3^{\circ} > NH_{3}$ |
|------------------|--|
| $R = C_2 H_5$ | $2^{\circ} > 3^{\circ} > 1^{\circ} > NH_3$ |
| Me_2CH^- | $1^{\circ} > NH_3 > 2^{\circ} > 3^{\circ}$ |
| M ₂ C | $NH_3 > 1^{\circ} > 2^{\circ} > 3^{\circ}$ |

(3). Stability of free radical

$$Me_{3}C > Me_{2}CH > MeCH_{2} > Me_{10}$$

(4) Heat of hydrogenation of alkenes

1-butene > cis-2-butene > trans-2-butene

(5). Leaving nature in Nucleophilic substitution reaction

$$ArSO_{3}^{-} > ROSO_{2}^{-} > CH_{3}COO^{-} > CN^{-} > O^{-}H > MeO^{-} > H^{-} > R^{-}$$

(6). Number of product formed during crossed aldol condensation

| S. | Carbonyl compound | Carbonyl compound (II) | Self | Cross | Total |
|-----|------------------------------|------------------------------------|--------------|--------------|---------|
| No. | (I) | | Condensation | Condensation | Product |
| | | | Product | Product | |
| 1. | One type of similar α | One type of similar $_{\alpha}$ H- | 2 | 2 | 4 |
| | H-atom | atoms | | | |

| | 0 | $CH_3 - CH_2 - CHO$ | | | |
|----|---|---|---|---|---|
| | | | | | |
| | CH ₃ – C – H | | | | |
| 2. | Two different types of dissimilar α H- atoms CH ₃ – COCH ₂ CH ₃ | One type of similar $_{\alpha}$ H- atoms CH ₃ – CH ₂ – CHO | 3 | 3 | 6 |
| 3 | Two different types of dissimilar α H- atoms CH ₃ CO - CH ₂ - CH ₃ | Two different types of dissimilar α H-atoms PhCH ₂ – CO – CH ₂ – CH ₃ | 4 | 4 | 8 |

16. ALCOHOLS, PHENOLS AND ETHERS

Structure of Alcohols :

sp³hybridised 142 pm 96 pm H C 108.9 H H H Methanol

(Alcohol)

Preparation of Alcohols

(i) From alkenes

(a) By acid catalysed hydration in accordance with Markownikoff's rule.



(b) By hydroboration-oxidation

$$CH_3 - CH = CH_2 + (H - BH_2)_2 \xrightarrow{B_2H_6, H_2O_2/OH^-} CH_3CH_2CH_2OH + B(OH)_3$$

(ii) From carbonyl compounds

(a) By reduction of aldehydes and ketones

$$R - CHO + H_2 \xrightarrow{Pd} RCH_2 - OH$$

$$RCOR' \xrightarrow{NaBH_4} R - CH - R'$$

$$|$$

$$OH$$

(b) By reduction of carboxylic acids and ester

$$\begin{array}{c} \text{RCOOH} & \xrightarrow{\text{(i) LiAlH}_4} \text{RCH}_2\text{OH} \\ & \xrightarrow{\text{(ii) H}_2\text{O}} \text{RCH}_2\text{OH} + \text{R'OH} \\ \end{array}$$

Reduction of aldehyde, ketones and esters with No alcohol is called Bouveault-blanc reduction.

v

Reaction of carbonyl compound with Grignard Reagent.

$$\begin{array}{cccc} HCHO + RMgX & \longrightarrow & RCH_{2}OMgX \xrightarrow{H_{2}O} & RCH_{2}OH + Mg & & & \\ & & & & \\ RCHO + R'MgX \xrightarrow{H_{2}O} & R \xrightarrow{-CH} & -OMgX \xrightarrow{H_{2}O} & -Mg(OH)X & R \xrightarrow{-CH} & -OH \\ & & & & \\ RCOR + R'MgX & \longrightarrow & R \xrightarrow{-C} & -OMgX \xrightarrow{-Mg(OH)X} & R \xrightarrow{-C} & -OH \\ & & & & & \\ R & & & & & \\ \end{array}$$

(iv) Hydrolysis of alkyl halides

$$\mathsf{R}-\mathsf{X}+\mathsf{KOH}_{(\mathsf{aq})} \rightarrow \mathsf{ROH}+\mathsf{KX}$$

Ease of hydrolysis of alkyl halides $RI > RBr > RCI > and 3^{\circ} > 2^{\circ} > 1^{\circ}$ alkyl halides.

(v) Hydrolysis of ethers

$$\mathbf{R} - \mathbf{O} - \mathbf{R} + \mathbf{H}_2 \mathbf{O} \xrightarrow{\mathbf{H}_2 \mathbf{SO}_4} \mathbf{2} \mathbf{ROH}$$

(vi) From primary amines by treatment with nitrous acid

$$RNH_2 + HONO \xrightarrow{(NaNO_2 + HCI)} ROH + N_2 + H_2O$$

Methylamine does not give methyl alcohol when treated with HNO₂. It gives CH₃OCH₃ and CH₃ONO.

(vii) By alcoholic fermentation

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Invertase}} C_6H_{12}O_6 + C_6H_{12}O_6$$
glucose fructose

$$\begin{array}{c} C_{6}H_{12}O_{6} & \xrightarrow{2\text{yindse}} 2C_{2}H_{5}OH + 2CO_{2(g)} \\ \text{glucose and fructose} & \text{ethyl alcohol} \end{array}$$

Preparation of Phenols

(i) From haloarenes



(ii) From benzene sulphonic acid



(iii) From diazonium salts



(iv) From cumene



Chemical properties of alcohols :

1. Reaction involving cleavage of O-H bond :

Alcohols react as nucleophiles :

(a) Reaction with metals

 $2R-O-H+2Na \rightarrow 2R-O-Na+H_2 \\ \text{Sodium alkoxide}$

(b) Esterification reaction

$$RO - H + R' - COOH \Leftrightarrow ROCOR' + H_2O$$

 $\underset{Alcohol}{RO-H} + (R'CO_2)O \Leftrightarrow ROCOR' + R'COOH$

 $\begin{array}{c} \mathsf{RO}-\mathsf{H}+\mathsf{R}'\mathsf{COCI} \xrightarrow{\mathsf{Pyridine}} \mathsf{R}-\mathsf{OCOR'+\mathsf{HCI}} \\ \mathsf{Alcohol} \end{array}$

(b) Reaction with phosphorus halides

$$ROH + PCI_5 \longrightarrow RCI + POCI_3 + HCI$$

- $3ROH + PBr_3 \xrightarrow{P/Br_2} 3RBr + H_3PO_3$
- $3ROH + PI_3 \xrightarrow{P/I_2} 3RI + H_3PO_3$
- (c) Reaction with thionyl chloride

$$ROH + SOCI_2 \longrightarrow RCI + SO_2 \uparrow + HCI \uparrow$$

(c) Dehydration reaction

Alcohol $\begin{array}{c} \underset{Or}{\overset{Or}{\overset{Or}{}}} \\ \text{Alcohol} \\ \end{array} \xrightarrow{\begin{array}{c} \text{Protic acids (conc. H_2SO_4 or H_3PO_4)} \\ \text{Catalysis (anhyd. ZnCl_2 or alumina)} \\ \end{array}} C = C + H_2O$

(d) Oxidation reaction



(ii) Secondary Alcohol
$$\xrightarrow{Cu, 573k}{CrO_3}$$
 Ketone

(iii) Tertiary Alcohol
$$\xrightarrow{Cu, 573k}{KMnO_4}$$
 Alkene

Phenols

Structure of Phenols :



Chemical properties of phenols :

(a) Reaction with metals



(b) Esterification reaction

$$\operatorname{Ar}_{\operatorname{Phenol}}^{\operatorname{H}^+} \operatorname{Ar}_{\operatorname{Phenol}}^{\operatorname{H}^+} \operatorname{Ar}_{\operatorname{POOR}}^{\operatorname{H}^+} \operatorname{Ar}_{\operatorname{POOR}}^{\operatorname{H}^+} \operatorname{H}_{\operatorname{2O}}^{\operatorname{H}^+}$$

 $\begin{array}{c} H^{+} \\ Ar - OH + (R'CO)_{2}O \Leftrightarrow Ar - OCOR' + R'COOH \\ Ar - OH + R'COCI \xrightarrow{Pyridine} ArOCOR' + HCI \end{array}$

(a) Halogenation



(d) Reimer-Tiemann reaction



(ii) Kolbe's reaction



iii) Reaction with zinc dust



(iv) Oxidation



(v) Fries rearrangement



Ethers

Structure of Ethers



Methoxymethane (Ether)

Preparation of Ethers

(i) By dehydration of alcohols

 $2CH_{3}CH_{2} - OH \xrightarrow{H_{2}SO_{4}(conc.)}{418K} CH_{3} - CH_{2} - \overset{"}{O} - CH_{2} - CH_{3} + H_{2}O$

Williamson's Synthesis Only primary alkyl halides when react with sodium alkoxide give ether while tertiary alkyl halides give alkene due to steric hindrance.

 $\mathsf{CH}_3\mathsf{CH}_2\mathsf{Br} + \mathsf{CH}_3\mathsf{CH}_2\mathsf{ONa} \longrightarrow \mathsf{CH}_3\mathsf{CH}_2\mathsf{OCH}_2\mathsf{CH}_3 + \mathsf{NaBr}$

Chemical Reactions of Ether

 $R - O - R' + HX \longrightarrow RX + R'OR$

The order of reactivity of hydrogen halides is as follows

HI > HBr > HCl

(ii) Halogenation

$$CH_{3}CH_{2}OCH_{2}CH_{3} \xrightarrow[Dark]{Cl_{2}} CH_{3}CH_{3}CHCIOCH_{2}CH_{3}$$

$$(\alpha-monochloro diethyl ether)$$

$$C_{2}H_{5}OC_{2}H_{5} + 10CI_{2} \xrightarrow{hv} C_{2}CI_{5}OC_{2}CI_{5} + 10HCI$$
(excess) (light) (perchlorodiethyl ether)

(iii) Reaction with PCI₅

 $R - O - R + PCI_5 \xrightarrow{\Delta} 2RCI + POCI_3$

(iv) Reaction with CO

 $ROR + CO \xrightarrow{BF_3/150^{\circ}C} RCOOR$

Electrophilic Substitution reactions



Other conversion reactions :
 (a) Phenol to salicylaldehyde



(b) Phenol to benzene diazonium chloride



Differentiate between organic compounds :

(a) Alcohols and phenols

Phenol on reaction with neutral FeCl₃ gives purple colour whereas alcohols do not give purple colour.

$$6C_6H_5OH + Fe^{3+} \longrightarrow [Fe(OC_6H_5)_6]^{3-} + 6H^+$$

Purple colour

(b) Primary, secondary and tertiary alcohols Lucas reagent test :

 $ROH + HCI \xrightarrow{\text{conc. HCI+ZnCI}_2/\text{lucas reagent}} RCI + H_2O$

If it is a primary alcohol, no turbidity appears at room temperature. Turbidity appears only on heating. If it is a secondary alcohol, turbidity appears in 5 minutes. If it is a tertiary alcohol, turbidity appears immediately.

(c) Methanol and ethanol

lodoform test : Ethanol when reacted with (I2 and NaOH) or NaOI gives yellow ppt of iodoform since it has the presence of CH₃-CH (OH)-group.

 $\text{C}_{2}\text{H}_{5}\text{OH} + 4\text{I}_{2} + 6\text{NaOH} \rightarrow \frac{\text{CHI}_{3}}{\text{Yellow ppt}} + 5\,\text{NaI} + 5\text{H}_{2}\text{O} + \text{HCOONa}$

 $CH_3OH + I_2 + NaOH \rightarrow No$ yellow ppt

17. ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

Preparation of Aldehydes and Ketones

(i) By oxidation of alcohols

Aldehydes and ketones are generally prepared by oxidation of primary and secondary alcohols, respectively.

$$RCH_2OH \xrightarrow{CrO_3} RCHO$$

$$\begin{array}{ccc} R - CH - R' & \xrightarrow{CrO_3} & R - C - R' \\ & & \parallel \\ & OH & O \end{array}$$

By dehydrogenation of alcohols

Primary and secondary alcohols give aldehydes and ketones, respectively.

$$R - CH_{2} - OH \xrightarrow{Cu}_{573 \text{ K}} RCHO$$

$$R - CH - R' \xrightarrow{Cu}_{573 \text{ K}} R - C - R'$$

$$| \qquad ||$$

$$OH \qquad O$$

(iii) By ozonolysis of alkenes



(iv) By hydration of alkynes

$$CH \equiv CH + H_2O \xrightarrow{HgSO_4} CH_3 - CHO$$

acetylene H_2SO_4 acetaldehyde

$$R - C \equiv CH + H_2O \xrightarrow[H_2SO_4]{H_2SO_4} R - CO - CH_3$$

ketone
Preparation of Aldehydes

(i) Rosenmund reduction



Formaldehyde cannot be prepared by this method as HCOCl is highly unstable.

(ii) From nitriles

 $RCN + SnCl_2 + HCI \longrightarrow RCH = NH \xrightarrow{H_3O^+} RCHO$

This reaction is called **Stephen reaction**.

Alternatively, nitriles are selectively reduced by diisobutylaluminium hydride, [DiBAL-H] to imines which on hydrolysis give aldehydes.

 $\mathsf{RCN} \xrightarrow[(ii) AIH(iBu)_2]{} \longrightarrow \mathsf{RCHO}$

Similarly, esters can also be reduced to aldehydes with DiBAL-H.

$$CH_{3}(CH_{2})_{3} - COOC_{2}H_{5} \xrightarrow{(i) \text{ DiBAL-H}} CH_{3}(CH_{2})_{3} - CHO$$

(iii) Etard reaction



toluene

Using chromium oxide (CrO₃) : Toluene or substituted toluene is converted to benzaldehyde in presence of chromic oxide in acetic anhydride.



(iv) Side chain halogenation is followed by hydrolysis of toluene



(v) Gattermann-Koch synthesis



Preparation of Ketones

(i) From acyl chlorides

$$2R-Mg-X+CdCl_{2} \longrightarrow R_{2}Cd+2Mg < X$$

$$Cl$$

$$2R'-C-Cl+R_{2}Cd \longrightarrow 2R'-C-R+CdCl_{2}$$

$$0$$

(ii) From nitriles



(iii) Friedel-Crafts acylation



(iv) Oppenauer oxidation

 $R_{2}CHOH+(CH_{3})_{2}C = O \xrightarrow{[(CH_{3})_{3}CO]_{3}AI} R_{2}C = O+(CH_{3})_{2}CHOH \xrightarrow{(a)_{2}CHOH} R_{2}C = O+(CH_{3})_{2}CHOH$

Chemical Reactions of Aldehydes and Ketones

(i) Addition of hydrogen cyanide



cyanohydrin

(ii) Addition of sodium hydrogen sulphite



(iii) Addition of Grignard reagent (RMgX) to form alcohol

 $>C \xrightarrow{B^{+}} O + \overset{8^{+}}{R} \leftrightarrow \overset{8^{+}}{Mg} - X \rightarrow \begin{bmatrix} >C - O & \overset{+}{Mg} - X \\ | & & \\ R & \\ Adduct & \end{bmatrix} \xrightarrow{H_2O} >C - OH + Mg(OH)X$

(iv) Addition of ammonia and its derivatives

$$>C = O + H_2 N - Z \implies \boxed{>C < OH_{NZH}} \xrightarrow{H_2 O} >C = N - Z + H_2 O$$

 $Z = Alkyl, aryl, OH, NH_2, C_6H_5NH, NHCONH_2, etc$

| Z | Reagent name | Carbonyl derivative | Product Name |
|-------------------|----------------------|---------------------------|-------------------|
| -R | Amine | -C = NR | Substituted imine |
| | | I | (Schiff's base) |
| | | | |
| -OH | Hydroxyl | -C = N - OH | Oxime |
| | amine | | |
| | | | |
| -NH ₂ | Hydrazine | $-C = N - NH_2$ | Hydrazone |
| | | I | |
| | | | |
| — NH — | Phenyl- bydrazine | $>$ C = N-NH \sim | Phenylhydrazone |
| | 7 4 - | | 2 4-dinitronhenyl |
| | dinitrophenyl | | hvdrazone |
| | hydrazine | $C = N - NH - NO_{2}$ | , |
| | | | |
| | Semi- | | Semi-carbazone |
| $- NH - C - NH_2$ | Carbazide | $>C = N-NH-\ddot{C}-NH_2$ | |

Reduction

(1). Clemmensen reduction

$$>$$
C = O $\xrightarrow{Zn-Hg}$ $>$ CH₂ + H₂O

(2). Wolff-Kishner reduction

$$>$$
C = O $\xrightarrow{H_2 N NH_2}$ $>$ C=N-NH₂ $\xrightarrow{KOH/ethyleneglycol}$ CH₂+N₂

(3). Oxidation

(i) Aldehydes are oxidized to acids in presence of mild oxidizing agents HNO_3 , $K_2Cr_2O_7$, $KMnO_4$

 $R - CHO \xrightarrow{[O]} R - COOH$

(ii) Ketones are oxidized under drastic conditions i.e. with powerful oxidizing agents like HNO_3 , $K_2Cr_2O_7 / H_2SO_4$, $KMnO_4 / H_2SO_4$ at higher temperature.

$$R - CH_2 - CO - CH_2 - R' \xrightarrow{[O]} R - COOH + R' - CH_2COOH + R - CH_2COOH + R' - COOH + R$$

(iii) Haloform reaction :

$$\begin{array}{c} O \\ \parallel \\ R - C - CH_3 \end{array} \xrightarrow{NaOX} R - C - ONa + CHX_3 (X = Cl, Br, I) \end{array}$$

(v) Aldol condensation



Cross aldol condensation

Base catalysed crossed aldol condensation between an aromatic aldehyde and an aliphatic aldehyde or ketone is called **Claisen-Schmidt condensation or Claisen reaction**.

Cannizzaro reaction



Test to distinguish aldehydes and ketones :

(1) Tollen's test : When an aldehyde is heated with Tollen's reagent it forms silver mirror.

Tollen's reagent is ammoniacal solution of AgNO₃

 $\mathsf{RCHO} + 2[\mathsf{Ag}(\mathsf{NH}_3)_2]^+ + 3\mathsf{OH}^- \longrightarrow \mathsf{RCOO}^- + 2\mathsf{Ag} + 2\mathsf{H}_2\mathsf{O} + 4\mathsf{NH}_3$

Ketones do not form silver mirror and hence do not give this test.

(2) Fehling's test : When an aldehyde is heated with Fehling's reagent it forms reddish brown precipitates of cuprous oxide.

Fehling's reagent : Fehling solution A (aqueous solution of CuSO₄) + Fehling solution B (alkaline solution of sodium potassium tartarate)

 $\mathrm{R-CHO}+2\mathrm{Cu}^{2+}+5\mathrm{OH}^{-}\rightarrow\mathrm{RCOO}^{-}+\underset{\mathrm{Re\,d-Brown\,\,ppt}}{\mathrm{Cu}_{2}\mathrm{O}}+3\mathrm{H}_{2}\mathrm{O}$

Ketones do not give this test.

Carboxylic Acids

Methods of Preparation of carboxylic Acids

From primary alcohols and aldehydes

(a) $RCH_2OH \xrightarrow{alkaline KMnO_4/H_3O^+} RCOOH$

(b) $RCH_2OH \xrightarrow{CrO_3-H_2SO_4} RCOOH$

From aldehydes

(a)
$$\text{RCHOH} + 2[\text{Ag}(\text{NH}_3)_2]^+ + 3\text{OH}^- \rightarrow \text{RCOO}^- + 2\text{Ag} + 2\text{H}_2\text{O} + 4\text{N}$$

(b) $R - CHO + 2Cu^{2+} + 5OH^- \rightarrow RCOO^- + Cu_2O + 3H_2O$

From alkyl benzenes



From acid derivatives

All acid derivatives like amides (RCONH₂), acid halides (RCOCI), esters (RCOOR'), acid anhydrides (RCO-O-COR) on hydrolysis give carboxylic acids. All acid derivatives break from RCO⁺.

 $RCOZ \xrightarrow{\text{Dil. HCl}} RCOOH$

 $Z = -NH_2$, -X(X = CI, Br, I), OR', RCOO - etc \cdot

Ease of hydrolysis : $RCOCI > (RCO)_2 O > RCOOR' > RCONH_2$

From nitriles and amides

$$\begin{array}{c} O \\ \parallel \\ R - CN \xrightarrow{H^+ \text{ or } OH^-/H_2O} & R - C - NH_2 \xrightarrow{H^+ \text{ or } OH^-/\Delta} RCOOH \end{array}$$

From alkenes

Suitably substituted alkenes are oxidized to carboxylic acids on oxidation with acidic potassium permanganate or acidic potassium dichromate.

(a) $R - CH = CH - R \xrightarrow{KMnO_4/H^+} 2R - COOH$

(b) $R - CH = CH - R_1 \xrightarrow{KMnO_4/H^+} R - COOH + R_1 - COOH$

From Grignard reagents

R-Mg-X + O=C=O
$$\xrightarrow{\text{Dry ether}}$$
 R - C \xrightarrow{O} $\xrightarrow{H_iO'}$ RCOOH

By heating germinal dicarboxylic acids

$$R-CN \begin{pmatrix} COOH \\ \frown \\ COOH \end{pmatrix} \xrightarrow{A} R-CH \begin{pmatrix} H \\ + CO_2 \\ COOH \end{pmatrix}$$

From alkynes

 $R-C \equiv C-R \xrightarrow{(i) O_3 (ii), H_2O_2 \text{ or}} 2RCOOH$ $KMnO_4/OH^-, \Delta$

Reactions of Carboxylic acids

Formation of anhydride

$$H_{3}C - C \begin{pmatrix} 0 \\ OH \end{pmatrix} + \begin{pmatrix} 0 \\ HO \end{pmatrix} C - CH_{3} & \frac{H^{+}, \Delta}{\text{or } P_{2}O_{5}, \Delta, -H_{2}O} \\ CH_{3} - C - O - C - CH_{3} & \begin{array}{c} H^{+}, \Delta \\ OH \end{pmatrix} \\ CH_{3} - C - O - C - CH_{3} & \begin{array}{c} H^{+}, \Delta \\ OH \end{pmatrix} \\ HO & O \end{pmatrix}$$

Esterification

 $RCOOH + R'OH \rightleftharpoons RCOOR' + H_2O$

Reactions with $\mathsf{PCI}_{\mathsf{5}}, \mathsf{PCI}_{\mathsf{3}}$ and $\mathsf{SOCI}_{\mathsf{2}}$

 $RCOOH + PCI_5 \longrightarrow RCOCI + POCI_3 + HCI$

 $3RCOOH + PCI_3 \longrightarrow 3RCOCI + H_3PO_3$

 $\mathsf{RCOOH} + \mathsf{SOCI}_2 \longrightarrow \mathsf{RCOCI} + \mathsf{SO}_2 + \mathsf{HCI}$

Reaction with ammonia (NH₃)

Carboxylic acids react with ammonia to give ammonium salt which on further heating at high temperature gives amides.

(a)
$$CH_3COOH + NH_3 \Leftrightarrow CH_3COONH_4 \xrightarrow{\Delta/-H_2O} CH_3CONH_2$$

Ammonium acetate Acetamide

(b)



Chemical reactions involving – COOH group

(a) Reduction

 $\begin{array}{c} \mathsf{RCOOH} \xrightarrow{(i) \ \mathsf{LiAIH}_4 \ / \ \mathsf{ether}} \\ & \mathsf{or} \ \mathsf{B}_2\mathsf{H}_6 \ (ii) \ \mathsf{H}_3\mathsf{O}^+ \end{array} \\ \end{array} \\ \begin{array}{c} \mathsf{R} - \mathsf{CH}_2 - \mathsf{OH} \end{array}$

(b) Decarboxylation

 $RCOONa \xrightarrow{\text{NaOH, CaO (Ratio 3:1)}} R - H + Na_2CO_3$

Substitution reactions in the hydrocarbon part

Hell-Volhard-Zelinsky reaction

$$\begin{array}{c} R-CH_2-COOH \xrightarrow{X_2/Re\ d\ Phosphorus/H_2O} R-CH-COOH \\ | \\ X \\ X=Cl, Br \\ \alpha-Halocarboxylic acid \end{array}$$

Arndt-Eistert reaction

$$\begin{array}{c} \text{RCOOH} \xrightarrow{\text{PCI}_5} \text{RCOCI} \xrightarrow{\text{CH}_2\text{N}_2} \xrightarrow{\text{RCOCHN}_2} \xrightarrow{\text{HOH}} \text{RCH}_2\text{COOH} \\ \text{diazo ketone} \end{array}$$

Reducing property

 $\mathsf{HCOOH} + \mathsf{HgCl}_2 \rightarrow \mathsf{Hg} + 2\mathsf{HCI} + \mathsf{CO}_2$

Electrophilic substitution reactions of aromatic acids



18. AMINES

Methods of Preparation of Amines

(i) By reduction of nitro compounds :

Nitro compounds can be catalytically reduced by passing hydrogen gas in presence of Raney Ni, finely divided Pt or Pd as catalyst at room temperature.

(a)
$$R - NO_2 + 3H_2 \xrightarrow{\text{Ni, Pt or pd}} R - NH_2 + 2H_2O_2$$

(b)
$$\operatorname{Ar} - \operatorname{NO}_2 + 3\operatorname{H}_2 \xrightarrow{\operatorname{Ni}, \operatorname{Pt} \text{ or } \operatorname{pd}} \operatorname{Ar} - \operatorname{NH}_2 + 2\operatorname{H}_2\operatorname{O}$$

Nitro compounds can also be reduced with active metals such as Fe, Sn, Zn etc. with conc. HCl.

(a)
$$R - NO_2 + 3H_2 \xrightarrow{Sn/HCl \text{ or } Fe/HCl} R - NH_2 + 2H_2O$$

(b) $Ar - NO_2 + 3H_2 \xrightarrow{Sn/HCl \text{ or } Fe/HCl} Ar - NH_2 + 2H_2O$

(ii) By Hoffmann's method (Ammonolysis of alkyl halides):

$$\begin{array}{ccc} \text{RNH}_{2} & \xrightarrow{\text{RX}} \text{R}_{2}\text{NH} & \xrightarrow{\text{RX}} \text{R}_{3}\text{N} & \xrightarrow{\text{RX}} \text{R}_{4} & \xrightarrow{\text{NX}} \\ \text{(1^{\circ})} & \text{(2^{\circ})} & \text{(3^{\circ})} & \xrightarrow{\text{Quaternary}} \\ \end{array}$$

• The free amine can be obtained from the ammonium salt by treatment with a strong base :

(a)
$$NH_3 + RX \rightarrow RNH_3^+X^- \xrightarrow{NaOH} RNH_2 + H_2O + Na^+X^-$$

(b) $RNH_2 + RX \rightarrow R_2NH_2^+X^- \xrightarrow{NaOH} R_2NH + H_2O + Na^+X^-$
(c) $R_2NH + RX \rightarrow R_3NH^+X^- \xrightarrow{NaOH} R_3N + H_2O + Na^+X$
(3° amine)

• Order of reactivity of halides is : RI > RBr > RCl

(iii) By reduction of nitriles :

Nitriles can be reduced to amines using H₂/Ni, LiAlH₄ or Na(Hg)/C₂H₅OH

$$\begin{array}{c} H_2/Ni \\ Or \\ Na(Hg)/C_2H_5OH \\ Or \\ LiAlH_4 \end{array} R - C \equiv N \xrightarrow{LiAlH_4} R - CH_2 - NH_2 \end{array}$$

(iv) By reduction of amides :

Amides are reduced to corresponding amines by LiAlH₄

$$R - C - NH_2 \xrightarrow{LuiH_4/H_2O} R - CH_2 - NH_2$$

(v) Gabriel's phthalimide reaction



potassium phthalate

(vi) Hofmann bromamide degradation reaction

 $R-CO-NH_2+Br_2+4NaOH \longrightarrow RNH_2+Na_2CO_3+2NaBr+2H_2O$

Reactions of Amines

(i) Alkylation

$$\mathbf{C}_{2}\mathbf{H}_{5}\mathbf{N}\mathbf{H}_{2} + \mathbf{C}_{2}\mathbf{H}_{5}\mathbf{B}\mathbf{r} \xrightarrow{-\mathbf{H}\mathbf{B}\mathbf{r}} (\mathbf{C}_{2}\mathbf{H}_{5})_{2}\mathbf{N}\mathbf{H} \xrightarrow{-\mathbf{C}_{2}\mathbf{H}_{5}\mathbf{B}\mathbf{r}} \rightarrow (\mathbf{C}_{2}\mathbf{H}_{5})_{3}\mathbf{N}$$

$$\downarrow \mathbf{C}_{2}\mathbf{H}_{5}\mathbf{B}\mathbf{r}$$

$$(\mathbf{C}_{2}\mathbf{H}_{5})_{4}\mathbf{N}\mathbf{B}\mathbf{r}$$



(ii) Acylation

$$C_{2}H_{5} - NH_{2} + CH_{3}COCI \xrightarrow{Base} C_{2}H_{5} - N - C - CH_{3} + HCH_{3}COCI$$

$$C_{2}H_{5} - NH_{2} + CH_{3} - C - O - C - CH_{3} \longrightarrow C_{2}H_{5} - N - C - CH_{3} + CH_{3}COOH$$

$$H_{0} = 0$$

$$H_{0} = 0$$

$$H_{0} = 0$$

(iii) Benzoylation

 $\mathsf{CH}_3\mathsf{NH}_2 + \mathsf{C}_6\mathsf{H}_5\mathsf{COCI} \xrightarrow{\operatorname{Pyridine}} \mathsf{CH}_3\mathsf{NHCOC}_6\mathsf{H}_5 + \mathsf{HCI}$

Benzoylation of aniline is known as Schotten Baumann reaction.

(iv) Carbylamine reaction [only by 1° amines]

 $\begin{array}{c} \mathsf{R}-\mathsf{NH}_2+\mathsf{CHCI}_3+\mathsf{3KOH} \xrightarrow{\mathsf{Heat}} & \mathsf{R}-\mathsf{N}\!\equiv\!\mathsf{C} \\ & \text{(a bad smalling compound)} \end{array} + \mathsf{3KCI}+\mathsf{3H}_2\mathsf{O} \end{array}$

Methyl isocyanate gas $(CH_3 - N = C = O)$ was responsible for Bhopal gas tragedy in December 1984.

(v) Reaction with nitrous acid

 $\mathsf{RNH}_2 + \mathsf{HNO}_2 \xrightarrow{\mathsf{NaNO}_2 + \mathsf{HCI}} [\mathsf{RN}_2^+\mathsf{CI}] \xrightarrow{\mathsf{H}_2\mathsf{O}} \mathsf{ROH} + \mathsf{N}_2 + \mathsf{HCI}$

Quantitative evolution of nitrogen is used in estimation of amino acids and proteins.

 $C_6H_6 - NH_2 \xrightarrow{NaNO_2 + 2HCI} C_6H_5N_2^+CI^- + NaCI + 2H_2O$

Reaction with aryl sulphonyl chloride [Hinsberg reagent]





Reaction with aldehydes

Schiff base is obtained.

 $C_{6}H_{5}NH_{2} + OHCC_{6}H_{5} \xrightarrow[]{ZnCl_{2}}{} C_{6}H_{5}N = CHC_{6}H_{5}$ benzaldehyde $\xrightarrow[]{A}_{-H_{2}O}$ benzylidene aniline (Schiff base)

Electrophilic substitution reactions



Nitration

(a) Under strongly acidic medium aniline gets protonated to form anilinium ion, which is deactivating group and is meta directing. Hence m-nitroaniline is also formed in 47 % along with ortho and para products.



Aromatic amines cannot be nitrated directly because HNO₃ being a strong oxidizing agent oxidizes it forming black mass.

(b) Nitration by protecting the -NH₂ group by acetylation reaction with acetic anhydride :



(c) Sulphonation On sulphonation, aniline gives sulphanilic acid, as the major product.



Oxidation

| Oxidising agent | Product |
|---|---------------------------------|
| Acidified KMnO ₄ | Aniline back (a dye) |
| (or $Na_2Cr_2O_7 + CuSO_4 + dill acid$) | |
| Chromic acid $(Na_2Cr_2O_7 + Conc H_2SO_4)$ | p-benzaquinone |
| Caro's acid (H ₂ SO ₅) | Nitrobenzene and nitrosobenzene |
| Conc. Nitric acid | decomposes |

Benzene Diazonium Chloride $(C_6H_5N_2^+; Cl^-)$

Preparation (Diazotisation reaction)

$$C_6H_5NH_2 + NaNO_2 + 2HCI \xrightarrow{273-278 \text{ K}} C_6H_5N = N - CI + NaCI + 2H_2O_6$$

Chemical reactions

$$\mathbf{C}_{6}\mathbf{H}_{5}\mathbf{N}_{2}^{+}\mathbf{C}\mathbf{l}^{-} \xrightarrow{\mathbf{C}\mathbf{u}^{+},\mathbf{H}_{3}\mathbf{PO}_{2}/\mathbf{H}_{2}\mathbf{O}} \mathbf{C}_{6}\mathbf{H}_{6} + \mathbf{N}_{2}^{+} + \mathbf{H}_{3}\mathbf{PO}_{3}^{+} + \mathbf{H}\mathbf{C}\mathbf{l}$$

$$\mathbf{C}_{6}\mathbf{H}_{5}\mathbf{N}_{2}^{+}\mathbf{C}\mathbf{l}^{-} \xrightarrow{\mathbf{C}\mathbf{H}_{3}\mathbf{C}\mathbf{H}_{2}\mathbf{O}\mathbf{H}} \mathbf{C}_{6}\mathbf{H}_{6}^{+} + \mathbf{N}_{2}^{+} + \mathbf{H}\mathbf{C}\mathbf{l} + \mathbf{C}\mathbf{H}_{3}\mathbf{C}\mathbf{H}\mathbf{O} \quad (\mathbf{D}ea\ min\ ation)$$

$$\xrightarrow{\mathbf{C}\mathbf{u}\mathbf{B}\mathbf{r}/\mathbf{H}\mathbf{B}\mathbf{r}} \mathbf{C}_{6}\mathbf{H}_{6}\mathbf{B}\mathbf{r} + \mathbf{N}_{2}$$

$$(\mathbf{b}\ rom\ ob\ en\ zen\ e)$$

(a) Reactions involving displacement of nitrogen :

$$\begin{array}{cccc} CuCl/HCl & ArCl + N_{s} \\ \hline CuBr/HBr & ArBr + N_{s} \\ \hline CuCN / KCN & ArBr + N_{s} \\ \hline CuCN / KCN & ArCN + N_{s} \\ \hline Cu/HCl & ArCl + N_{s} + CuCl \\ \hline Cu/HBr & ArBr + N_{s} + CuCl \\ \hline Cu/HBr & ArBr + N_{s} + CuCl \\ \hline Kl & ArI + KCl + N_{s} \\ \hline HBF_{4} & Ar - N_{s}BF_{4} \xrightarrow{\Delta} Ar - F + BF_{3} + N_{s} \\ \hline H_{s}PO_{s} + H_{s}O \\ \hline H_{s}O_{s} + H_{s}O \\ \hline H_{s}O_{s} + H_{s}O \\ \hline HBF_{4} & ArOH + N_{s} + H_{s}PO_{s} + HCl \\ \hline H_{s}O_{s}ArOH + N_{s} + CH_{s}CHO + HCl \\ \hline H_{s}BF_{4} & NO_{s} \\ \hline HBF_{4} & MaNO_{s} \\ \hline HBF_{4} & MaNO_{s} \\ \hline MaNO_{s} \\ \hline MaNO_{s} \\ \hline MBF_{4} & MaNO_{s} \\ \hline \end{array}$$

Azo coupling reactions



Alkyl Cyanides

Methods of Preparation

(i) From alkyl halides

$$RX + KCN_{(alc)} \xrightarrow{100^{\circ}C} RCN + RNC_{(major)}$$

(ii) From acid amides

 $\text{RCONH}_2 \xrightarrow{P_2O_5\Delta} \text{RC} \equiv \text{N}$

Reactions of Alkyl Cyanides

(i) Hydrolysis

$$\begin{array}{c} \text{RCN} \xrightarrow[\text{Alk } H_2O]{} \xrightarrow[\text{partiial hydrolysis}) \end{array} \xrightarrow[\text{amide}]{} \begin{array}{c} H_2O \\ H^+ \end{array} \xrightarrow[\text{carboxylic acid}]{} \begin{array}{c} \text{RCOOH} \\ \text{carboxylic acid} \end{array} + \text{NH}_3 \end{array}$$

(ii) Reduction

$$\mathsf{RCN} + 4[\mathsf{H}] \xrightarrow{\mathsf{Na} + \mathsf{C}_2\mathsf{H}_5\mathsf{OH}} \mathsf{RCH}_2\mathsf{NH}_2$$

$$RCN + 4[H] \xrightarrow{LiAIH_4} RCH_2NH_2$$

(Mendius reduction)

$$RCN \xrightarrow{SnCl_2/HCl} RCH = NH \cdot HCI \xrightarrow{H_2O} RCHO + NH_4CI$$

imine hydrochloride

(iii) Reaction with Grignard reagent

$$\begin{array}{ccc} R' & R' \\ | & | \\ RCN + R'MgX \xrightarrow{Ether} R - C = NMgX \xrightarrow{2H_2O} R - C = O \end{array}$$

Alkyl isocyanides

Methods of Preparation

(a) From alkyl halides

 $R - X + AgCN \xrightarrow{C_2H_5OH} RNC + RCN$

(b) Carbylamine reaction

 $RNH_2 + CHCI_3 + 3KOH_{(alc)} \xrightarrow{\Delta} RNC + 3KCI + 3H_2O$

(c) From N-alkyl formamide

 $R - NH - \underset{Pyridine}{CHO} \xrightarrow{POCI_3} R - N \equiv C + H_2O$

Reactions of Alkyl isocyanides

Hydrolysis

 $R - N \equiv C + 2H_2O \xrightarrow{H^+} RNH_2 + HCOOH$

(ii) Reduction

 $RN \equiv C + 4[H] \xrightarrow{\text{Na/C}_2\text{H}_5\text{OH}} \text{or Ni or Pt} \xrightarrow{\text{2° amine}} RNHCH_3$

(iii) Addition reaction

Due to the presence of unshared pair of electrons on C atom, alkyl isocyanides give addition reaction.

 $RNC + S \longrightarrow RNCS$

 $RNC + HgO \longrightarrow RNCO + Hg$

 $RNC + O_3 \longrightarrow RNCO$

(iv) Isomerisation At 250°C, it isomerizes to nitrile.

 $RNC \xrightarrow{\Delta} RCN$

Nitro Compounds

Methods of Preparation

(i) From alkyl halides

 $RX + AgNO_2 \xrightarrow{\Lambda} RNO_2 + AgX$

(ii) Nitration: Nitrating mixture is conc HNO₃ + conc H₂SO₄



Reactions of Nitro Compounds

Reduction

With Sn/HCl or catalytic hydrogenation, nitroalkanes are reduced to amines.

 $RNO_2 + 6[H] \xrightarrow{Sn/HCl} R - NH_2 + 2H_2O$

If neutral reducing agent like Zn dust + NH₄Cl is used, hydroxylamines are obtained as major product.

 $RNO_2 + 4[H] \xrightarrow{Zn+NH_4Cl} R - \underset{N-alkylhydroxylamine}{NHOH} H_2O$

In the presence of $(NH_4)_2S$ or Na_2S , selective reduction takes place.



Nitrobenzene gives different products with different reagents and in different mediums.

| Medium | Reagent | Product |
|---------|--|-------------------------------------|
| Acid | Sn/HCl | Aniline |
| Neutral | Zn/NH₄Cl | N-phenyl hydroxylamine |
| | Na ₃ AsO ₃ /NaOH | Azoxbenzene ($C_6H_5N = NC_6H_5$) |

| Alkaline | Zn/NaOH, CH₃OH | Azobenzene |
|------------------|------------------------------------|----------------|
| | Zn/NaOH, C₂H₅OH | hydrazobenzene |
| Metallic hydride | LiAlH ₄ | aniline |
| Electrolytic | dil H ₂ SO ₄ | p-aminophenol |

Action of HNO_2

1° nitroalkane gives nitrolic acid which gives red colour with NaOH.

 $\mathsf{RCH}_2\mathsf{NH}_2 \xrightarrow[-H_2O]{HNO_2} \mathsf{RC}(\mathsf{NO}_2) = \mathsf{NOH} \xrightarrow[\mathsf{NaOH}]{\mathsf{NaOH}} \mathsf{RC}(\mathsf{NO}_2) = \mathsf{NONa}$

2° nitrolkanes give pseudonitrol with HNO₂

$$R_{2}CH(NO_{2}) \xrightarrow{HNO_{2}} R_{2}C - NO \xrightarrow{NaOH} Blue$$

$$|$$

$$NO_{2}$$

$$Pseudonitrol$$

Nef carbonyl synthesis

$$R - CH_2NO_2 \xrightarrow{\text{NaOH}} R - CH = \overset{+}{N-} O^-Na^+ \xrightarrow{50\% H_2SO_4} R - CH = O$$

$$|$$

$$O^-$$

Electrophilic substitution On nitration



Nucleophilic substitution reaction -NO2 group activates the ring towards nucleophilic substitution.



19. HALOALKANES AND HALOARENES

General Methods of Preparation of Haloalkanes

From Alcohols

$$R-OH \xrightarrow{\text{HCl} + \text{Anhy. } ZnCl_2} R-Cl + H_2O \text{ (Groove's process)}$$

$$R-OH \xrightarrow{\text{Reflux}} 3R-X + H_2O$$

$$\frac{PX_3^{\text{Reflux}}}{3R-X} + H_3PO_3$$

$$\frac{PCl_5}{R-Cl} R-Cl + POCl + HCl$$

$$\frac{PYridine}{SOCl_2} R-Cl + SO_2^{\uparrow} + HCl^{\uparrow} \text{ (Darzen procedure)}$$

Free Radical Halogenation of Alkanes

$$CH_{3}CH_{2}CH_{2}CH_{3} \xrightarrow{Cl_{2}} CH_{3}CH_{2}CH_{2}CH_{2}CH_{2}CH + CH_{3}CH_{2}CHCH_{3}$$

Cl

Addition of hydrogen Halides on Alkenes



(i) Halogen Exchange method :

 $R-X+Nal \rightarrow R-I+NaX \qquad \mbox{(Finkelstein reaction)}$

 $R-Br + AgF \rightarrow R-F + AgBr$ (Swarts reaction)

Hunsdiecker Reaction

$$CH_3COOAg + Br_2 \longrightarrow CH_3Br + AgBr + CO_2$$

Preparation of haloarenes :
 (a) By electrophilic substitution reaction :



(b) Sandmeyer's reaction :



(c) Gattermann reaction :



X = Cl, Br

(d) From Diazonium Chloride :



(e) Balz-Schiemann reaction :



Nucleophilic Substitution Reactions

$$\overline{Nu} + -C \xrightarrow{\delta + \delta^{-}}{X} \longrightarrow -C \xrightarrow{\delta + Nu}{K} \xrightarrow{\delta^{-}}{Nu + X^{-}}$$

$$\frac{KOH (aq)}{KOH (aq)} C_{2}H_{5}OH + KBr$$

$$\frac{NH_{3}}{K} C_{2}H_{5}NH_{2}, (C_{2}H_{5})_{2}NH, (C_{2}H_{5})_{3}N$$

$$(C_{2}H_{5})_{4}N^{+}Br^{-}(Hofmann ammonolysis)$$

$$\frac{KCN}{C_{2}H_{5}}C_{2}H_{5}CN + KBr$$

$$\frac{AgCN}{C_{2}H_{5}NC} + AgBr$$

$$\frac{KNO_{2}}{C_{2}H_{5}-ONO} + KBr$$

$$\frac{ethyl nitrite}{AgNO_{2}} C_{2}H_{6}-ONO + KBr$$

$$\frac{ethyl nitrite}{Nitroethane}$$

$$(Williamson's synthesis)$$

$$\frac{R'ONa, \Delta}{C_{2}H_{5}-O-R'+NaBr}$$

$$\frac{Na - C = C - H, \Delta}{C_{2}H_{5}-O} - C = CH+NaBr$$

$$\frac{O}{R'COOAg, \Delta} C_{2}H_{5}-O - C - R' + AgBr$$

2. Elimination Reactions

Dehydrohalogenation is a β -elimination reaction in which halogen is from α -carbon atom and the hydrogen from the α -carbon according to Saytzeff rule, e.g.

Br

$$| CH_3 - CH_2 - CH - CH_3 \xrightarrow{Alc. KOH} CH_3 - CH = CH - CH_3 + CH_3CH_2CH = CH_2$$

$$| but-2-ene (major) butene-1 (minor)$$

Reduction

$$C_{2}H_{5} - Br + H_{2} \xrightarrow{\text{Ni, 575 K}} C_{2}H_{6} + HBr$$
$$C_{2}H_{5}I + HI \xrightarrow{\text{Red P, 420 K}} C_{2}H_{6} + I_{2}$$

Reaction with Metals

(i) Wurtz reaction

 $RX + 2Na + XR \xrightarrow{Dry ether} R - R(alkane) + 2NaX$

(ii) Wurtz-Fitting reaction

$$C_6H_5 + CI + 2Na + CI CH_3 \xrightarrow{\text{Dry ether}} C_6H_5 - CH_3 + 2NaCI$$

(iii) Reaction with Mg

 $C_2H_5Br + Mg \xrightarrow{Dry ether} C_2H_5 - Mg - Br$ Grignard's reagent)

Isomerisation

CI

$$(H_3CH_2CH_2 - CI \xrightarrow{573 \text{ K}} CH_3 - CH - CH_3$$

Chemical properties of haloarenes :

(a) Dow's Process



Electrophilic substitution Reactions

(b) With halogens



(c) With conc. sulphuric acid and nitric acid



(i) Other conversions :

 $R - X + KCN \rightarrow R - CN + KX$ $R - CN \xrightarrow{Na, C_{2}H_{5}OH \text{ or } LiAH_{4} \text{ or } Ni/H_{2}} \rightarrow R - CH_{2}NH_{2} \xrightarrow{HONO} RCH_{2}OH$ $R - CN \xrightarrow{H_{3}O^{+}} R - COOH \xrightarrow{NH_{3}} R - CONH_{2}$ $R - COOH \xrightarrow{LiAH_{4}} RCH_{2}OH$ $R - COOH \xrightarrow{PCl_{5} \text{ or } PCl_{3} \text{ or } SOCl_{2}} \rightarrow R - COCI$ $R - X + Mg \xrightarrow{Dry \text{ ether}} RMgX$ $RMgX + CO_{2} \rightarrow RCOOH$ $RMgX + HCHO \rightarrow Primary alcohol$ $RMgX + RCHO \rightarrow Sec \text{ ondary alcohol}$ $RMgx + R - CO - R \rightarrow Tertiary alcohol$



Alkanes

Preparation of Alkanes

(1) Wurtz reaction :

 $2CH_{3}CH_{2}Br + 2Na \xrightarrow[ether]{Dry} CH_{3}CH_{2}CH_{2}CH_{3} + 2NaBr$

Frankland reaction

 $RX + Zn + Rx \longrightarrow R - R + ZnX_2$

(2) From Grignard reagent (RMgX)

 $RMgX + HOH \rightarrow RH + Mg(OH)X$

 $RMgX + R'OH \rightarrow RH + Mg(OR')X$

 $RMgX + R'NH_2 \rightarrow RH + Mg(NHR')X$

(3) From unsaturated hydrocarbons :-

Sabatier-Senderens reduction

 $R - CH = CH_2 + H_2 \xrightarrow{Ni/\Delta} R - CH_2 - CH_3$

$$R - C \equiv CH + H_2 \xrightarrow{N_1/\Delta} R - CH_2 - CH_3$$

4. From carboxylic acids-

Decarboxylation -

 $\begin{array}{c} \mathsf{CH}_3\mathsf{COO}^-\mathsf{Na}^+ + \mathsf{NaOH} & \xrightarrow{\mathsf{CaO}} \mathsf{CH}_4 + \mathsf{Na}_2\mathsf{CO}_3 \\ \text{Sodium ethanoate} \end{array}$

Kolbe's electrolytic method -

 $2CH_{3}COO^{-}Na^{+} + 2H_{2}O \xrightarrow{Electrolysis} CH_{3} - CH_{3} + 2CO_{2} + H_{2} + 2NaOH$ Sodium acetate

Reactions

Combustion :-

 $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O, \qquad \Delta H = -217.0 \text{ K cal / mole}$

Oxidation :-

$$CH_{4} + O_{2} \xrightarrow{Cu} 2CH_{3}OH$$

$$CH_{4} + O_{2} \xrightarrow{Mo_{2}O_{3}} HCHO + H_{2}O$$
Methanal

Substitution :-

Halogenation :-

$$CH_{4} + CI_{2} \xrightarrow{UV} CH_{3}CI + HCI$$
$$CH_{3}CI \xrightarrow{UV} CH_{2}CI_{2} \xrightarrow{UV} CHCI_{3} \xrightarrow{UV} CCI_{4}$$

- (i) The reactivity of Halogens : ${\rm F_2} > {\rm CI_2} > {\rm Br_2} > {\rm I_2}$
- (ii) The rate of replacement of Hydrogens of alkanes is : $3^{\circ} > 2^{\circ} > 1^{\circ}$



Nitration

$$CH_{3}CH_{2}CH_{3} \xrightarrow{450^{\circ}C} CH_{3}CH_{2}CH_{2}NO_{2} + CH_{3}CHNO_{2}CH_{3} + CH_{3}CH_{2}NO_{2} + CH_{3}NO_{2}$$

$$25\% \qquad 40\% \qquad 10\% \qquad 25\%$$

Sulphonation : - replacement of hydrogen atom of alkane by – SO₃H group.



tert butyl sulphonic acid

Aromatization :-



(6) Thermal decomposition or Pyrolysis or cracking or Fragmentation : - when higher alkanes are heated at high temp (about 700 – 800 K) in the presence of alumina or silica catalysts, the alkanes break down to lower alkenes and alkanes.

 $CH_3 - CH_2 - CH_3 - CH_3 - CH - CH_2 + CH_3 - CH_3 + C_2H_4 + CH_4$

(7) Action of steam : - Catalyst : nickel, alumina Al₂O₃

$$CH_4 + H_2O(Steam) \xrightarrow{1000^{\circ}C} CO + 3H_2$$

Isomerization

$$CH_{3}(CH_{2})_{4}CH_{3} \xrightarrow{Anhy. AlCl_{3}/HCl} H_{2} \xrightarrow{Anhy. AlCl_{3}/HCl} H_{2}-CH_{3}+CH_{3}CH_{2}-CH_{3}+CH_{3}CH_{2}-CH_{2}-CH_{3}$$

Alkenes

Preparation :

1. From Alkynes : - Alkynes on partial reduction with partially deactivated palladised charcoal known as Lindlar's catalyst give alkynes.

$$CH \equiv CH + H_2 \xrightarrow{Pd/C} CH_2 = CH_2$$

Ethyne Ethene

2. From Haloalkanes :- dehydrohalogenation (E₂ or 1, 2-elimination or Beta-elimination)

$$\begin{array}{c} H \\ 1 \\ CH_2 \\ H_2 \\ I \\ Br \end{array} \xrightarrow{\text{CH}_2} CH_2 \xrightarrow{\text{Alc.KOH}} CH_2 = CH_2^+ \text{ KBr } + H_2O$$

3. From Dihaloalkanes :- Dehalogenation



4. From Alcohols :- Dehydration (E1 - elimination)

$$CH_{3}CH_{2}CH_{2}OH \xrightarrow{Conc. H_{2}SO_{4}} CH_{3}CH = CH_{2} + H_{2}O$$

$$CH_{3}CH_{2}CH_{2}CH_{2}OH \xrightarrow{Al_{2}O_{3}} CH_{3}CH_{2}CH = CH_{2}$$

Reactions of Alkenes

(1) Addition Reaction :- Alkene show electrophilic addition reaction.

1. Addition of Hydrogen :-

$$RCH = CH_2 \xrightarrow{H_2/N_i} RCH_2CH_3$$

2. Addition of Halogens :-

$$CH_2 = CH_2 + Br_2 \xrightarrow{CCl_4} BrCH_2 - CH_2Br$$

$$CH_{2} = CH_{2} + Br_{2} \xrightarrow[(Brown \ colour)]{H_{2}O} Br - CH_{2} - CH_{2} - OH + HBr$$
(Colourless)

3. Addition of hydrogen halides -

Addition reaction of HBr to symmetrical alkenes

$$CH_2 = CH_2 + H - Br \longrightarrow CH_3 - CH_2 - Br$$

Addition reaction of HBr to unsymmetrical alkenes takes place according to Markovnikov Rule

Markownikov rule :- negative part of the addendum (adding molecule) gets attached to that carbon atom which possesses lesser number of hydrogen atoms. E.g.



Peroxide effect or Kharasch (Anti Markownikoff's addition) :- In 1933 Kharasch and Mayo observed that when HBr is added to an unsymmetrical double bond in the presence of organic peroxide, the reaction take places opposite to the markovnikov rule.

 $CH_{3} - CH = CH_{2} \xrightarrow{HBr} CH_{3} - CH_{2} - CH_{2}Br$ Propyl bromide

4. Addition of water (Hydration):- Acid catalyzed addition of water



2. Oxidation :-

1. Combustion : $CO_2 + H_2O$

2. Hydrocarboration-oxidation:- Alkenes react with diborane to form trialkyl boranes which on oxidation with alkaline H_2O_2 give alcohols.

$$3CH_2 = CH_2 \xrightarrow{BH_3} CH_3CH_2 B \xrightarrow{H_2O_2/OH^-} 3CH_3CH_2OH$$

Triethylborane Ethyl alcohol

3. Oxymercuration-demercuration :-

$$H_2C = CH_2 \xrightarrow{Hg(OAC)_2} OH - CH_2 - CH_2 - Hg OAc \xrightarrow{NaBH_4} CH_3CH_2OH + Hg OH^-$$

4. Oxidation with potassium permanganate :-

$$2KMnO_4 + H_2O \longrightarrow 2KOH + 2MnO_2 + 3[O]$$



Bayer's Test

 $CH_{3} - CH = CH_{2} \xrightarrow{(i) \text{ Alk. KMnO}_{4}} CH_{3}COOH + CO_{2} + H_{2}O$

Oxidation with Ozone :- Ozonolysis-give carbonyls compounds



Alkynes

Preparation :-

From vicinal dihalides :- dehalogenation

 $CH_{3} - BrCH - CH_{2} - Br \xrightarrow{2KOH (alc)} CH_{3} - C \equiv CH + 2KBr + 2H_{2}O$

By the action of water on calcium carbide :-

 $CaC_2 + H_2O \rightarrow HC \equiv CH + Ca(OH)_2$

Reactions

(1) Addition Reaction : Alkyne show electrophilic addition reaction.

1. Addition of Hydrogen – Hydrogenation.

$$CH_{3}C \equiv CH + 2H_{2} \xrightarrow{Ni} CH_{3}CH_{2}CH_{3}$$
Propyne

Birch Reduction



2. Addition of Halogens :-

 $HC \equiv CH \xrightarrow{2Br_2} Br_2HC - CHBr_2$

3. Addition of hydrogen halides :-

 $HC \equiv CH + 2HBr \longrightarrow CH_3CH Br_2$

4. Addition of water (Hydration):- Acid catalyzed addition of water

$$HC \equiv CH + H_2O \xrightarrow{H_gSO_4} [CH_2 = CHOH] \rightleftharpoons CH_3CHO$$

5. Polymerisation -

(a) Linear polymerization : of ethyne gives polyacetylene or polyethyne which is a high molecular weight polyene containing repeating units of (CH = CH - CH = CH) and can be represented as – (CH = CH - CH = CH) n-

(b) Cyclic polymerization-results in the formation of aromatic compound.



Aromatic Hydrocarbon

Preparation of Benzene

(i) Decarboxylation of aromatic acids.

COONa + NaOH \xrightarrow{CaO} $\xrightarrow{()}$ + Na₂CO₃

(ii) Reduction of phenol: Phenol is reduced to benzene by passing its vapours over heated zinc dust




Benzene on treatment with excess of chlorine in the presence of anhydrous $AICl_3$ in dark yields hexachlorobenzene (C_6Cl_6)



Directive influence of a functional group in monosubstituted benzene :-

1. Ortho and para directing groups and activating

-OH, $-NH_2$, -NHR, $-NHCOCH_3$, $-OCH_3$, $-CH_3$, $-C_2H_5$ etc.

2. Meta directing group and deactivating :- _NO₂, _CN, _CHO, _COR, _COOH, _COOR, _SO₃H,

3. Ortho and para directing groups and deactivating – Halogens because of their strong – I effect, overall electron density on benzene ring decreases. However due to resonance the electron density on o- and p- position is greater than that at the m-position. Hence, they are also o- and p- directing groups.

21. POLYMERS

Important Addition Polymers

Polyolefins

1. Polythene

Polymer of ethylene or ethene.

(a) Low density polythene (LDP)

$$nCH_2 = CH_2 \xrightarrow[Ethene]{350-750k/1000 \text{ to } 2000 \text{ atm traces of } O_2}_{Polythene}} (CH_2 - CH_2)_n$$

(b) High density polythene (HDP)

$$nCH_{2} = CH_{2} \xrightarrow[]{333-343k/6-7 \text{ atm zieglar Natta catalyst}}_{\text{Ethene}} \rightarrow (CH_{2} - CH_{2})_{n}$$

(d) Polyacrylonitrile

- $\begin{array}{c} nCH_2 = CHCN & \xrightarrow{Polymerisation/Peroxide \ catalyst} & (CH_2 CN CN)_n \\ Acrylonitrile & Polyacrylonitrile \end{array}$
- 2. Polystyrene (Styrone)

$$n \begin{bmatrix} CH = CH_{2} \\ I \\ C_{6}H_{5} \end{bmatrix} \xrightarrow{(C_{2}H_{6}COO_{2})}_{Benzoyl \text{ peroxide}} \begin{pmatrix} -CH - CH_{2} - \\ I \\ C_{6}H_{5} \end{pmatrix}_{n}$$
styrene

3. Polyvinylchloride (PVC)



(vinyl chloride)

4. Polypropylene (PP)



5. Polytetrafluoroethene (Teflon)

$$\begin{array}{c} nCF_2 = CF_2 & \xrightarrow{\text{catalyst/High pressure}} (CF_2 - CF_2)_n \\ \hline \\ \text{Tetrafluorethene} & & \text{Teflon} \end{array}$$

6. Polyacrylonitrile

$$n(CH_{2} = CHCN) \xrightarrow{Polymerisation} (Peroxide catalyst) \xrightarrow{Polymerisation} -CN \\ I \\ -CH_{2} - CH_{3n} \\ Polyacrylonitrile \\ or \\ orlon$$

Condensation polymers

Polyamides

(a) Nylon 6, 6 : It is prepared by the condensation polymerization of hexamethylenediamine with adipic acid under high pressure and at high temperature.



(b) Nylon 6 : It is obtained by heating caprolactum with water at a high temperature



Polyesters

(a) Terylene or Dacron : It is manufactured by heating a mixture of ethylene glycol and terephtalic acid at 420 to 460 K in the presence of zinc acetate-antimony trioxide catalyst.



Ethylene glycol (Ethane-1, 2 - diol) Terephthalic acid (Benzene-1,4 - di

Terylene or dacron



Polymethylmethacrylate (PMMA)

The polymer is known by several commercial names such as lucite, acrylite, plexiglass and perspex.

Resins

1. Phenol-Formaldehyde Polymer

These polymers are obtained by the condensation reaction of phenol with formaldehyde in the presence of either acid or a base catalyst. The reaction involves the formation of methylene bridge at ortho, para or both ortho and para positions. A linear or cross linked material is obtained depending upon the condition of reaction.





(b) Novolac on heating with formaldehyde forms Bakelite

2. Urea-Formaldehyde Resin



4. Melamine – formaldehyde polymer : Melamine formaldehyde polymer is formed by the condensation polymerization of melamine and formaldehyde



4. Natural Rubber

Natural rubber is a coiled linear 1, 4-polymer of isoprene.

$$CH_3$$

$$|$$

$$CH_2 = C - CH = CH_2$$
isoprene

(a) Natural rubber : Natural rubber is a linear polymer of isoprene (2-methyl-1, 3-butadiene) and is also called as cis-1, 4-polyisoprene.



Vulcanisation of Rubber

The properties of natural rubber can be modified by introducing -S-S- polysulphide crosslinks in its structure.

The process of heating a mixture of raw rubber with sulphur and an appropriate addictive in a temperature range between 373 K to 415 K to improve upon physical properties like elasticity, strength etc.



Sulphur cross links in vulcanised rubber

Synthetic rubber

(A) Neoprene or polychloroprene



(B) Buna – N



(C) Buna – S

$$nCH_{2} = CH - CH = CH_{2} + nC_{6}H_{5}CH = CH_{2} \longrightarrow [CH_{2} - CH = CH - CH_{2} - CH_{2} - CH]_{n}$$

$$\underset{\text{Styreme}}{\text{Butadine-styreme copolymer}}$$

Biopolymers and Biodegradable Polymers

Aliphatic polyesters are the common examples of biodegradable Polymers.

(a) Poly- β -hydroxybutyrate-co- β -hydroxy valerate (PHBV):

It is obtained by the copolymerization of 3-hydroxybutanoic acid and 3-hydroxypentanoic acid



(b) Nylon 2-nylon 6 : It is an alternating polyamide copolymer of glycine $(H_2N - CH_2 - COOH)$ and amino caproic acid $(H_2N(CH_2)_5COOH)$

$$\begin{array}{ccc} & & O & & O \\ & & \parallel & \parallel \\ nH_2N-CH_2-COOH+nH_2N-(CH_2)_5-COOH \rightarrow (HN-CH_2-C-HN-(CH_2)_5-C)_n \\ & \text{Glycine} & \text{Amino expronic acid} \end{array}$$

Some polymers:

| S.N | Name of | Class of polymer | Name/s of monomer/s | Uses |
|-------|----------------------------|------------------------|--|---|
| 1. | Dynel | Copolymer | Vinyl chloride and acrylonitrile | Human hair wigs |
| 2. | Glyptal | Copolymer | Ethylene glycol and phthalic acid | In paints |
| 3. | Thiokol | Condensation | Ethylene chloride and sodium (Polysulphide rubber) | Rubber tetra sulphide |
| 4. | Superglue | Homopolymer | Methyl α -cyanoacrylate | Glue |
| 5. | Kevlar | Polyamide condensation | Terephthalic acid chloride and p-phenylene diamine | Bullet proof vests and helmets |
| 6. | Nomex | Polyamide condensation | m-phthalic acid and m- dinitrobenzene | Protective clothes for race car drives and fire fighters. |
| 7. | Lexan | Polycarbonate | Diethylcarbonate and bisphenol Ester condensation | Bullet proof windows and helmets |
| viii) | Polyurethane or Thermocole | Copolymer glycol | Toluene diisocyanate and ethylene | For padding and building insulation |
| ix) | Saran | Copolymer chloride | Vinyl chloride and vinylidene | Bumpers |