മികവ്

പഠന സഹായി

ഹയർ സെക്കണ്ടറി

രസതന്ത്രം

ജില്ലാ പഞ്ചായത്ത്, കാസർഗോഡ്

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മുഖമൊഴി

ഗുണനിലവാരമുള്ള വിദ്യാഭ്യാസം ഓരോ കുട്ടിയുടെയും അവകാശമാണ്. അത് ഉറപ്പു വരുത്തുക എന്നത് നമ്മുടെ കർത്തവ്യമാണ്. വിദ്യാർത്ഥികളുടെ പഠനനിലവാരം മികവുറ്റതാക്കുവാനുള്ള യത്നങ്ങൾ എല്ലാ സ്കൂളുകളിലും നടപ്പിലാക്കി വരുന്നത് ഏറെ സന്തോഷകരമാണ്. ഹയർ സെക്കണ്ടറി വിദ്യാർത്ഥികളുടെ പഠനനിലവാരം ഉയർത്തുവാൻ കാസറഗോഡ് ജില്ലാ പഞ്ചായത്തിന്റെ നേതൃത്വത്തിൽ നടപ്പിലാക്കിവരുന്ന മികവ് പദ്ധതി ജില്ലയിലെ ഹയർ സെക്കണ്ടറി വിജയശതമാനം ഗണ്യമായ രീതിയിൽ ഉയർത്തുവാനും ജില്ലയുടെ വിദ്യാഭ്യാസ പിന്നോക്കാവസ്ഥ ഒരു പരിധിവരെ പരിഹരിക്കുവാനും സഹായിച്ചിട്ടുണ്ട്. ഹയർ സെക്കണ്ടറി പരീക്ഷയ്ക്കുള്ള മുന്നൊരുക്ക പ്രവർത്തനങ്ങൾ എല്ലാ സ്കൂളുകളിലും നടന്നുവരുന്ന ഈ സന്ദർഭത്തിൽ കുട്ടികളിൽ ആശയങ്ങൾ കൂടുതൽ ദൃഢീകരിക്കാൻ ഉതകുന്ന, അദ്ധ്യാപകർക്ക് സഹായകമായ ഒരു കൈപുസ്തകം ***'മികവ് 2014'*** കാസറഗോഡ് ജില്ലാ പഞ്ചായത്ത് ഈ വർഷവും പുറത്തിറക്കുകയാണ്. ചോദ്യങ്ങൾ, ചർച്ചകൾ, ചെറു ഗ്രൂപ്പ് പ്രവർത്തനങ്ങൾ തുടങ്ങിയവയിലൂടെ ഇത് സാധിക്കുമെന്നു ഞങ്ങൾ വിശ്വസിക്കുന്നു. താഴ്ന്ന നിലവാരമുള്ള കുട്ടികൾക്കും ഉയർന്ന നിലവാരമുള്ള കുട്ടികൾക്കും ഒരു പോലെ ഗുണകരമാകുന്ന വ്യത്യസ്ത നിലവാരത്തിലുള്ള പഠന പ്രവർത്തനങ്ങൾ ഇതിൽ ഉൾപ്പെടുത്താൻ ഞങ്ങൾ ശ്രദ്ധിച്ചിട്ടുണ്ട്. ഈ വർഷം ജില്ലയിലെ മുഴുവൻ കുട്ടികളെയും C+ നു മുകളിലുള്ള ഗ്രേഡുകളിലേക്ക് ഉയർത്തുക എന്ന നമ്മുടെ ലക്ഷ്യം സാക്ഷാത്ക്കരിക്കാൻ ഇത് സഹായകമാകുമെന്ന് ഞങ്ങൾ പ്രത്യാശിക്കുന്നു. അതിനായി ജില്ലയിലെ മുഴുവൻ പ്രധാന അദ്ധ്യാപകരുടെയും, അധ്യാപകരുടെയും, കുട്ടികളുടെയും, രക്ഷിതാക്കളുടെയും നാട്ടുകാരുടെയും ആത്മാർത്ഥമായ സഹകരണവും പിന്തുണയും പ്രതീക്ഷിച്ചുകൊണ്ട്,

പ്രസിഡണ്ട്
ജില്ലാ പഞ്ചായത്ത്, കാസറഗോഡ്.

ഉള്ളടക്കം

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HIGHER SECONDARY

CHEMISTRY

Chapter - I

SOLID STATE

1) Typs of solid a) Amorphous & b) Crystalline

a) **Crystalline Solids**	b) **Amorphous Solids**
i) Particles are orderly packed - possess long range order of particles	i) Short range order
ii) Possess sharp melting point	ii) No sharp melting point
iii) Regular cleavage possible	iii) Irregular cleavage
iv) These are true solids eg: NaCl, Sugar	iv) Pseudo solids or super cooled liquids eg: Glass, Rubber, Plastics

2) Classification of crytalline Solids - based on the nature of interparticle forces.

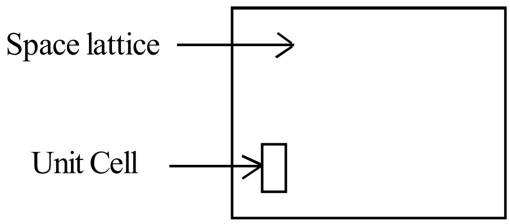
	Type	**Cosnstituent particles**	**Attractive force**	**Examples**
1)	Ionic	Ions(Cations & Anions)	Strong Electrostatic force	NaCl, KNO_3, MgO, LiF
2)	Molecular	Molecules	Van der Waal's force	I_2, Ice, CH_4
3)	Covalent or network solids	Atoms	Covalent bonds	Diamond Graphite, SiO_2
4)	Metallic Solids	Atoms	Metallic Bonding	All metals & some alloys

* Glass fixed to windows of old buildings are found to be slightly thicker at the bottom than at the top. - Amorphous solids have a tendency to flow.

* Some glass objects from ancient civilisations are found to become milky in appearance - on heating amorphous solids become crystalline at some temperature.

3) a) **Space lattice or crystal lattice :** Three dimensional arrangement of particles in space

b) **Unit Cell:** The smallest repeating unit of a crystal, when repeated in three dimensions results in entire crystal



4) Types of unit cells

	Type	**Position of Particles**	**Contribution**	**Number of Particles per unit cell**
1)	Primitive or simple cubic	8 corners	$\frac{1}{8}$	$\left(\frac{1}{8}\times 8\right)=1$
2)	BCC (Body Centred Cubic)	8 Corners + 1 body centre	$\frac{1}{8}$ 1	$\left(\frac{1}{8}\times 8\right)+1=2$
3)	FCC (Face Centred Cubic)	8 Corners + 6 face centres	$\frac{1}{8}$ $\frac{1}{2}$	$\left(\frac{1}{8}\times 8\right)+\left(\frac{1}{2}\times 6\right)=4$

Relation between a (edge length of unit cell) and r (Radius of a sphere)

SCC $a = 2r$ BCC $a = \frac{4r}{\sqrt{3}}$ FCC $a = 2\sqrt{2}\,r$	Packing efficiency SCC - 52.4% BCC - 65% FCC - 74%

5) Types of Close Packing in crystals

a) HCP (Hexagonal Close Packing)

A -First Layer

B- Second Layer

AB AB AB AB .... type arrangement of particles

b) CCP (Cubic Close Packing)

A -First Layer

B- Second Layer

C- Third Layer

ABC ABC ABC . . type arrangement

CCP - similar to FCC arrangement

The co-ordination number in the hop and CCP structures is 12.

6) Voids in crystals

The empty or unoccupied space in crystal lattice

Types a) Tetrahedral void, b) Octahedral void

Let the number of close packed spheres be N.

Then the number of Octahedral voids formed = N.

The number of Tetrahedral voids formed = 2N.

7) Calculation of Density of a crystal with edge length ‘a’ is ________

$$\rho = \frac{zM}{a^2.No.}$$

M - Atomic mass of the element

a^3 -Volume

No - Avogadro Number (6.022×10^{23})

z- 1, 2, 4 respectively for simple cube, BCC & FCC

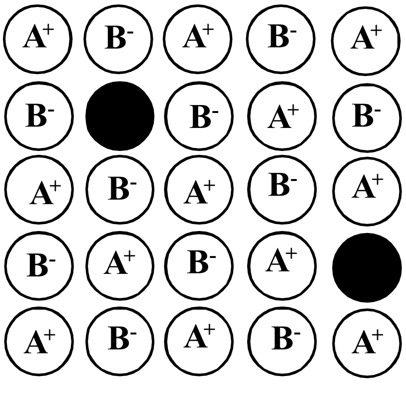
8) Crystal defects or imperfections

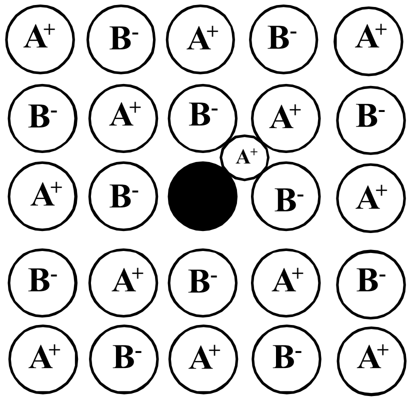
Any deviation from completely ordered arrangement in crystal is an imperfection.

Stoichiometric defects of ionic crystals

i) Schottky defect ii) Frenkel defect

Schottky defect		Frenkel defect	
a)	Equal number of anions and cations are missing from the crystal lattice	a)	Cation leaves its normal site and occupies a interstitial site
b)	Observed in ionic solids of high co-ordination number and ions of almost similar size.	b)	Observed in ionic compounds having low co - ordination number and crystals with anions are larger in size than cations.
c)	Density of the crystal is lowered due to this defect. Eg: NaCl, KCl, KBr etc	c)	It does not affect the density of the crystal Eg: AgCl, AgBr, AgI



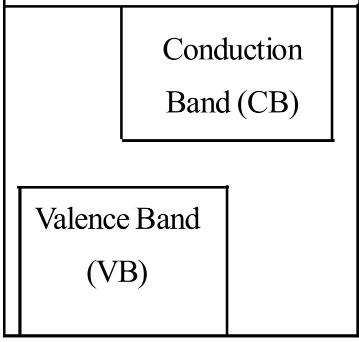
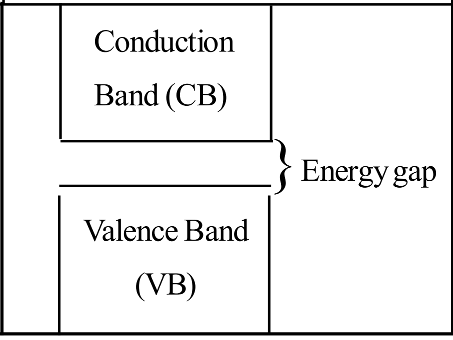
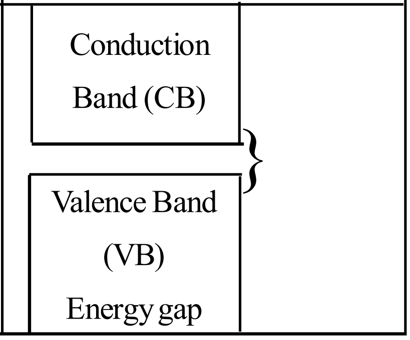


Note: AgBr shows both schotty and Frenkel defect

9) **Formation of F centres- Colour in crystals**

Here a negative ion is missing from its lattice leaving a hole which will be occupied by an excess electron to maintain electrical nuetrality. The holes occupied by electrons are called **F -Centres or Colour Centres**. These are responsible for colour in certain crystals. For eg: When NaCl is heated in an atmosphere of Sodium vapour, F- centres are formed which make the crystal yellow. Excess potassium in KCl makes it violet and excess Li in LiCl makes it pink.

10) Electrical conductivity of metals, insulators and semi conductors explanation based on Band Theory.

Metals	**Semi conductors**	**Insulators**
Valence band and Conduction band get overlapped, Conductivity maximum	**Energy gap** between valence band and conduction bans is small	Very large energy gap between valance band and conduction band, electrical conductivity minimum
		

Eg:- for Semi conductor - Silicon & Germanium.

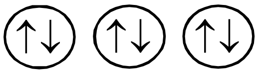
Electrical conductivity of semiconductors increases with rise in temperature. Substances like silicon and germanium show this type of behaviour and are called intrinsic semiconductors. Conductivity of semi conductors is increased by adding imparity (Dopling). Two types:

a) **n-type semi conductor** : When a group 14 element (silicon or germanium) is doped with a group 15 element (P or AS) one election becomes free to move and its conductance increaes.

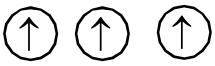
b) **p-type semi conductors :** When a group 14 element is doped with a group 13 element (B, Al or Ga) there is election deficiency which moves like a positive charge (hole) and its conductance increases.

11) Magnetic properties of solids

a) Diamagnetic substances
  i) Presence of paired electrons
  ii) Repelled by the meganetic field



b) Para magnetic
  i) Presence of unpaired electrons
  ii) Attracted by the magnetic field
  Eg:- Cu^{2+}, Fe^{3+}, O_2, Al, NO



c) Ferromagnetic
  i) Presence of very large number of unpaired electrons ↑ ↑ ↑ ↑ ↑ ↑
  ii) Strongly attracted by the field
  iii) Retain magnetism even when the field is removed
  Eg: Fe, Co, Ni, Alloys of Fe, Co, Ni

d) Ferrimagnetic
  Magnetic dipoles arranged in opposite directions unequally, there is a net magnetic moment
  Eg: Fe_3O_4, $MgFe_2O_4$ ↑ ↑ ↓ ↑ ↑ ↓ ↓ ↓ ↑

e) Anti ferromagnetic
  Magnetic dipoles are arranged in opposite directions equally, net magnetic moment= zero. Eg: MnO, MnO_2 etc ↑ ↓ ↑ ↓ ↑ ↓

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Chapter II

SOLUTIONS

- A solution is a homogeneous mixture of two or more substances. In a binary solution (Containing two components only), the component which is present is smaller amount is called the solute, and the other present in larger amount is called the solvent.

Methods of expressing the concentration of a solution.

W_B = Mass of solute
M_B = Molar mass of solute
n_B = Number of moles of solute (W_B/M_B)
W_A = Mass of Solvent
M_A = Molar mass of solvent
n_A = Number of moles of solvent (W_A/M_A)

1) **Molarity** (M) It is the number of moles of solute (n_B) present in one litre of the solution.

$$M = \frac{nB}{V(L)} = \frac{W_B}{M_B x V(L)} = \frac{W_B x100}{M_B x(V(mL)}$$

2) Molality (m): It is the number of moles of soluted (n_B) present in one kilogram of the solvent.

$$m = \frac{n_B}{Wa(Kg)} = \frac{W_B}{M_B W_A(Kg)} = \frac{W_B x1000}{M_B xWA(g)}$$

3) **Molefraction (χ):** Mole fraction of any component in a solution is the number of moles of that component divided by the total number of moles of all the components.

$$\text{Melefraction A} (\chi_A) = \frac{n_A}{n_A+n_B}$$

$$\text{Melefraction B} (\chi_B) = \frac{n_B}{n_A+n_B}$$

Molefraction and Molalty are independent of temperature.

Henry's law : The partial pressure of all the gas in vapour phase is proporional to the molefraction of the gas in the solution

$P=K_H.x$

K_H - Henry's constant.

Value of K_H increases with decrease of temperature.

- **Vapour pressure :** It is the pressure exerted by the vapour in equilibrium at a particular temperature. The vapour pressure of a liquid decreases if some non volatile solute is dissolved in it.
- **Raoult's law:** In a solution, the vapour pressure of a component at a given temperature is equal

to the molefraction of that component in the solution multiplied by the vapour pressure of that component in the pure state.

For a solution containing components A & B

$P_A = P^oA\chi_A$ & $P_B = P^o_B\chi_B$

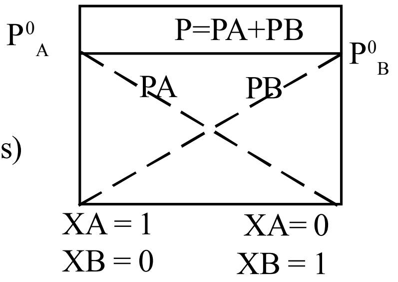
Ideal Solutions : Solutions which obey Raoults law at all temperatures and concentrations

A-B interaction = A-A interaction or B-B interaction

Eg: C_6H_5Cl & C_6H_5Br

ΔV mixing = 0 (The volume of solution could be equal to the sum of volumes of the two components)

ΔH mixing= 0 (No heat is absorbed or evolved when the components are mixed)



Non-Ideal Solution : Solutions which do not obey Raoult's law at all conditions of temperature and pressure.

a) Non-ideal solutions having positive deviation

A-B interation < A-A or B-B interactions

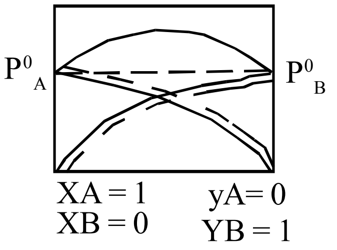
ΔV mixing>0 (volume of solution>volume of component A+volume of component B)

ΔH mixing>0 (heat is absorbed when the components are mixed, ie it is endothermie)

Eg : C_2H_5OH and Cyclohexane

$PA>P^0.xA$ (In such solutions vapour pressure of each

$PB>P^0B.xB$ component increases)



b) Non-ideal solution showing negatieb deviation

A-B interaction > A-A or B-B interaction

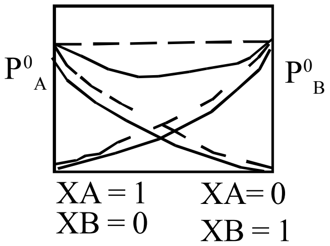
ΔV mixing<0 (volume of solution <volume of component A, volume of componen B)

ΔH mixing<0 (heat is evolved when the components are mixed ie it is exothermie)

Eg: Chloroform and acetons

$PA<P^0A.xB$ (In such solutions vapour pressure of

$PB<P^0B.xB$ each component decreases)



Colligative Properties

These are properties of a solution which depend only on the number of particles of the solute.

There are four types of colligative properties.

1) Relative lowering of vapour pressure

The vapour of a solution containing non volatile solute is always less than that of pure solvent

$$\frac{P^o_A\text{-}PA}{P_A} = X_B$$

2) Elevation of boiling point

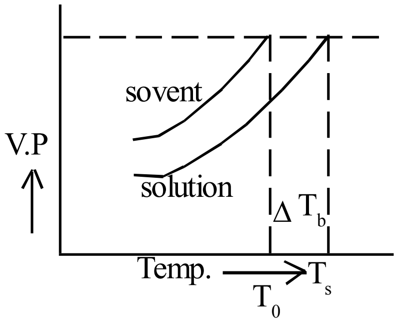
The boiling point of a solution containing non volatile solute is more than that of pure solvent

$$T_s > T_0 \quad \text{or} \quad T_s - T_0 = \Delta T_b$$

For dilute solutions $\Delta Tb\, \alpha m$ (molality of the solution)

$$\Delta T_b = k_b.m \ \text{ or } \ \Delta T_b = \frac{k_b \times W_B \times 1000}{M_B \times W_A}$$

1) Egg boils faster in salt solution. This is due to elevation of boiling point
2) The principle of pressure cooker.



3) Depression of freezing point

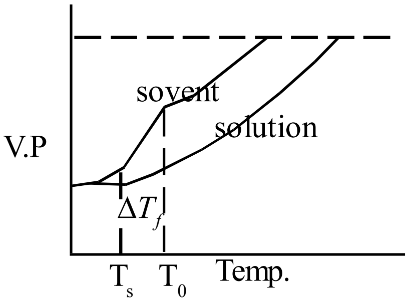
The freezing point of a solution containing non volatile solute is less than that of pure solvent

$T_0 > T_s$ or $T_0 - T_s = \Delta T_f$

For dilute solutions $\Delta T_f\, \alpha\, m$ (molarity of the solution)

$$\Rightarrow \ =\text{kf.m} \ \text{ or } \ \Delta T_f = \frac{K_f.W_B \times 1000}{M_B \times W_A}$$

1) Ethylene glycol is added to water in the car radioter to lower its freezing point.
2) During winter season salt is spreading on the road to lower the freezing point.



Osmosis

It is the passage of solvent molecules from the solvent to the solution or from a solution of lower concentration to higher concentration through semipermeable membrane.

4) Osmotic Pressure : It is the minimum pressure that must be applied to prevent osmosis.

$$\pi = \frac{n_B}{v} RT \quad \text{OR} \quad \pi = \frac{W_B RT}{M_B V}$$

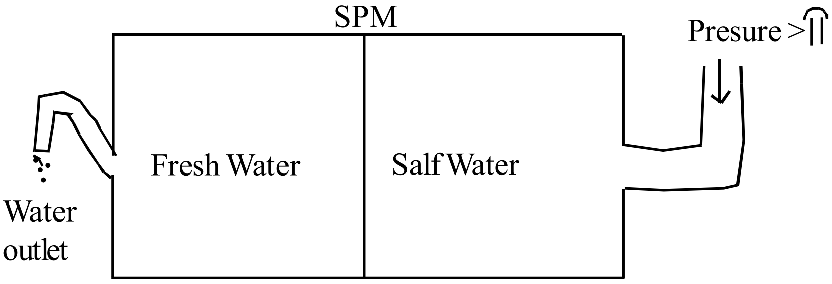
Isotonic solution : Solutions which have same osmotic pressure

Eg: 0.91% solution of pure NaCl is isotonic with human blood.

Hypotonic : Solution which have more osmotic pressure than the other.

Hypertonic : Solution which have less osmotic pressure than the other.

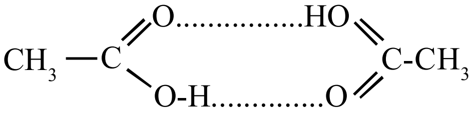
Reverse Osmosis and Purification of water



Abnormal molecules mass : These are wrong molecular mass obtained from colligative properties. Abnormal molecular mass is obtained when the substance in the solution undergoes association or dissociation.

- It is due to association or dissociation of solute particles.

Eg:- (1) Ethanoic in benzene undergoes dimerisation due to hydrogen boudering.



Here the number of particles (colligative property) is reduced. Thus the molar mass calculated on the basis of colligatie properties is lower then the expected value.

Eg:-(2) Nacl in water or ethanoic acid in water.

Nacl $\rightarrow Na^{+}+Cl^{-}$

Number of particles is increased due to dissociation. Thus the molar mass calculated on the basis of colligative properties in higher than the expected value.

Sale	Van't Hoff factor (i)
NaCl	2
KCl	2
K_2SO_4	3

Van't Hoff Factor(i)

The extent of association or dissociation is expressed in terms of Van't Hoff factor.

$$i = \frac{\text{Normal Molar mass}}{\text{Abnormal Molar mass}} = \frac{\text{Observed value of Colligative property}}{\text{Normal value of Colligative property}}$$

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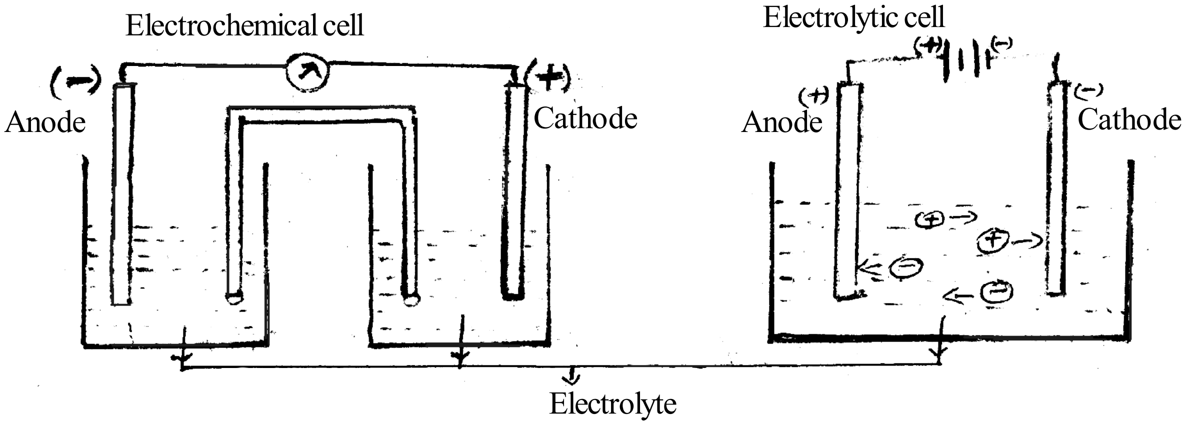
Chapter - III

ELECTROCHEMISTRY

I Differences between Electrochemical and Electrolytic Cell



Electrochemical Cell	Electrolytic Cell
1) Device used to convert Chemical energy into electrical energy	1) Device used to convert Electrical energy into Chemical energy
2) Electrical energy is produced	2) Electrical energy is consumed
3) Reaction is spontaneous	3) Reaction is non-spontaneous
4) Anode is -ve and Cathode is +ve	4) Anode is +ve and Cathode is -ve
5) Two electrodes are placed in different container	5) Two electrodes are placed in the same container.

II Cell representation and EMF

In Galvanic Cell (Electrochemical Cell)

Oxidation (Loosing of Electrons) takes place at anode

$Zn(S) \longrightarrow Zn^{2+}_{(aq)} + 2e- \ (Zn/Zn^{2+})$ .... (1)

Reduction (Gaining of Electrons) takes place at cathode

$Cu^{2+}_{(aq)} + 2e^{-} \longrightarrow Cu \ (Cu^{2+}/Cu)$ .... (2)

In the cell both oxidation and reduction takes place.

$(1)+(2) \Rightarrow Zn+Cu^{2+} \longrightarrow Zn^{2+} + Cu \ (Zn/Zn^{2+} \| Cu^{2+}/Cu)$

Oxidation Potential (E) Tendency of an electrode to loose electrons $E\ Z_{n}/Zn^{2+} = +0.76V$

Reduction Potential (E) : Tendency of an electrode to gain electrons $E_{Cu}{}^{2+}/Cu = +0.34V$

Higher the oxidation potential lower will be the reduction potential of an element. These two are numerically equal but opposite in sign.

Eg: $E\ Zn/Zn^{2+} = +0.76V$ & $E\ Zn^{2+}/Zn = -0.76V$

$E\ Cu^{2+}/Cu = +0.34V$ & $E\ Cu/Cu^{2+} = -0.34V$

Standard Electrode Potential : The electrode potential at standard conditions (ie at 298K, 1 bar Pressure and IM Concentration)

Cell Potential or EMF of a cell

EMF = Higher reduction potential - Lower reduction potential

= $E_{\text{Cathode}} = E_{\text{Anode}}$

For the cell

$Zn/Zn^{2+} || Cu^{2+}/Cu$

EMF = E^0 Cu^{2+}/Cu - E^0 Zn^{2+}/Zn

= 0.34 - -0.76 = 1.10V

Nernst Equation: A quantitative relationship between cell potential and concentration of the ions.

Consider an electrode reaction.

$$M^{N+}(aq)^{+ne-} \rightarrow Mcs$$

$$E_{M^{n+}/M} = E^0_{M^{n+}/M} - \frac{RT}{nF} \ell n \frac{1}{\left(M^{n+}\right)}$$

Eg:- Consider a cell reaction

$$Mg_{(s)} + 2Ag^+_{(aq)} \rightarrow Mg^{2+}_{(aq)} + 2Ag_{(s)}$$

$$E_{cell} = E^0 cell - \frac{RT}{nF} \ell n \frac{(Mg^{2+})}{(Ag^+)^2}$$

At Anode = $Mg_{(s)} \rightarrow Mg^{2+}{}_{(aq)} + 2e^-$

At Cathode = $2Ag^+_{(aq)}{}^{+2e-} \rightarrow 2Ag_{(s)}$

Cell representation

$$Mg_{(s)}\left|Mg^{2+}_{(aq)}\right\|Ag^+_{(aq)}\left|Ag_{(s)}\right.$$

SHE

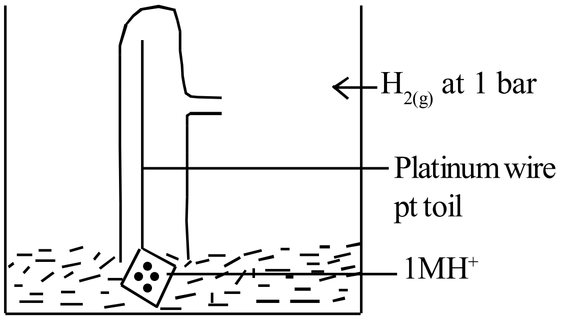
$Pt_{(s)}\left|H_{2(g)}\right|H^+_{(aq)}$

It is zero at all temperature.

It can act as anode or cathode. Cell reaction is,

$H^+_{(aq)} + 1e^- \rightarrow \frac{1}{2}H_2(g)$

For reaction aAxbB $\rightarrow$ CC+do



$$E_{cell} = E^0_{cell} \frac{-RT}{nF} \text{In} \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

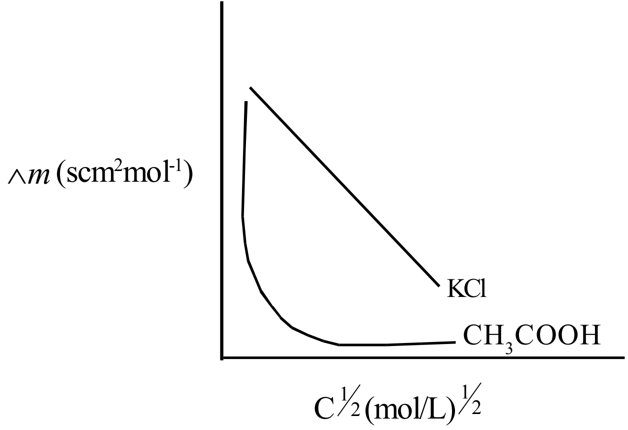
III Conductivity and Molar Conductivity

Conductivity (K) It is the conductance of a solution of unit volume (1m length and 1m^2 area of cross section, It is the reciprocal of resistivity)

Unit Ohm^{-1} m^{-1} or mhom^{-1} or Siemen m^{-1}(Sm^{-1})

Molar conductivity ($\wedge m$) : Conductance of the solution containing one mole of the electrolyte.

$$\wedge m = \frac{k}{c} = \frac{k(scm^{-1})}{1000ml^{-3} \times molarity(mol/k)}$$



Strong electrolytes : Which is almost completely ionised in aqueous solution. Eg: Hcl, Nacl, NaOH with dilution inter ionic forces decrease. As a result molar conductance increases slightly.

Weak electrolytes: Which is only slightly ionised in aqueous solution. Eg:- CH_3COOH, NH_4OH

On dilution the degree of dissociation of weak electrolyte increases and hence its molar conductance also increases sharply.

Kohlrausch's law

The molar conductance of an electrolyte at infinite dilution is the sum of ionic conductance of the cation and anion.

$$\wedge^0_m (NaCl) = \lambda^0_{Na^+} + \lambda^0_{Cl^-}$$

Application of Kohlrausch's law.

1) To calculate molar conductance of weak electrolytes.
2) To calculate the degree of dissociation of weak electrolytes.

λ^0_m for acetic acid can be calculated by knowing λ^0_m for CH_3COONa, Hcl and Nacl (obtained from the graph)

$$\lambda^0_m(CH_3COOH) = \lambda^0(CH_3COO^-) + \lambda^0_{(H^+)}$$

$$\lambda^0_m(CH_3COONa) = \lambda^0(CH_3COO^-) + \lambda^0_{(Na^+)} ....(1)$$

$$\lambda^0_m(Hcl) = \lambda^0(H^+) + \lambda^0_{(Cl^-)} ....(2)$$

$$\lambda^0_m(Nacl) = \lambda^0(Na^+) + \lambda^0_{(Cl^-)} ....(3)$$

Eqn ①+②-③

$$\lambda^0_m(CH_3COONa) + \lambda^0_m(Hcl) - \lambda^0_m(Nacl) = \lambda^0(CH_3COO^-) + \lambda^{0(H+)}$$

Faraday's law of Electrolysis

1) First law : The amount of any substance liberated or deposited at an electrode is directly proportional to the quantity of electricity passing through the electrolyte.

$W \times Q$ or $W = ZQ$

$W = ZIt$ ($\therefore$ Q=It)

2) Second law: The amount of different substances liberated by the same quantity of electricity passing through the electrolytes are proportional to their chemical equivalent,

Eg: While passing the same quantuty of electricity through $CuSO_4$ and $ZnSO_4$ then,

$$\frac{\text{Mass of Cu deposited}}{\text{Mass of Zn deposited}} = \frac{\text{Eq mass of A}}{\text{Eq mass of B}}$$

Product of electrolysis

1) Electrolysis of Molten NaCl

$NaCl_{(l)} \rightarrow Na^+ + Cl^-$

Anode : $Cl^- \rightarrow \frac{1}{2}Cl_2$ +e- (oxidation)

Cathode : $Na^+ + 1e^- \rightarrow Na$ (Reduction)

Sodium is deposited at the cathode and chlorine is liberated at the anode.

2) Electrolysis of Acqueous solution of NaCl

$NaCl_{(aq)} \rightarrow Na^+_{(aq)}\ Cl^-_{(aq)}$

Anode : $Cl^- \rightarrow \frac{1}{2}Cl_2 + e^-$ (oxidation)

Cathode : $H_2O(l)\ 2e^- \rightarrow \frac{1}{2}H_2 + OH^-$ (reduction)

Cl_2 gas is liberated at the anode whereas H_2 gas is liberated at the cathode.

Primary and Secondary Cells

I Primary Cells

Primary cells have definite life and become dead over time. They cannot be recharged

eg: Dry Cell, Mercury Cell

II Secondary Cell

Secondary Cells can be recharged by passing direct current through them

Eg : Lead storage Battery, Ni - Cd cell

Fuel Cell : Cells which convert Chemical energy obtained from combustian of fuel directly in to chemical energy are known as fuel cell

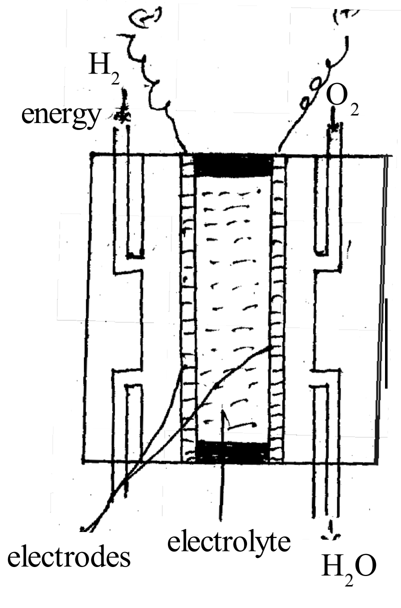
Eg $H_2 - O_2$ fuel cell

Working of a fuel cell

Anode : $2H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$

Cathode : $O_2 + 2H_2O + 4e^- \rightarrow 4HO^-$

Net cell reaction : $2H_2 + O_2 \rightarrow 2H_2O$ + energy



Advantages of fuel Cells

1) Pollution free working
2) High efficiency
3) Continuous source of energy

Corrosion : The process of slow conversion of metals into their undesirable compounds by reaction of moisture and other gases present in the atmosphere.

Eg:- Iron rusts, Silver gets tarnished

Copper develops green coating on its surface

Lead loses its lustre

Electro chemical theory of rusting

While rusting

at anode $Fe \rightarrow Fe^{2+} + 2e-$

at Cathode $2H^+ + 2e^- \rightarrow 2H$

$2H + \frac{1}{2}O_2 \rightarrow H_2O$

Net cell reaction

$Fe + 2H^+ + \frac{1}{2}O_2 \rightarrow Fe^{2+} + H_2O$

$2Fe^{2-} + \frac{1}{2}O_2 + 2H_2O \rightarrow Fe_2O_3 + 4H^+$

$Fe_2O_3 + \times H_2O \rightarrow Fe_2O_3 \times H_2O$

rust is chemically hydrated ferric oxide.

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Chapter - IV

CHEMICAL KINETICS

Chemical Kinetics deals with reaction rates and their mechanism

Average rate of a reaction is the rate for a time intervel

Instantaneous rate of reaction is the rate at any instant.

The unit of a rate of a reaction is mol $L^{-1}s^{-1}$ (for solution) or $atms^{-1}$ (for gases)

For the reaction $2HI \rightarrow H_2 + I_2$

Instantaneous rate $= -\frac{1}{2}\frac{d(HI)}{dt} = \frac{d(H_2)}{dt} = \frac{d(I_2)}{dt}$

[Since the concentration of reactants decreased with the time , a -ve sing is given in the equation]

Rate law or Rate Expression is an expression which related the rate of the reaction to the concentration of reactants. It is determined experimentally.

For the reaction $aA + bB \rightarrow cC + dD$ rate expression is given by rate = $K[A]^a [B]^b$

[A] is the molar concentration of A; ('a' is the order of the reaction with the respect to A]

[B] is the molar concentration of B; ('b' is the order of the reaction with the respect to B]

K is the rate consistant (a+b gives the overall order)

Order of a reaction : is the sum of the powers of concentration of reactants in the rate law expression

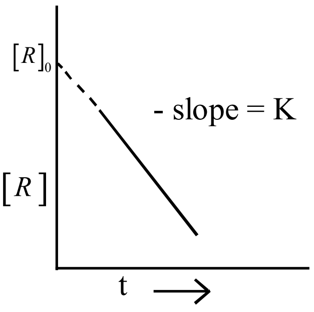
Molecularit of reaction : It is the number of reaction species taking part in an elementry reaction.

Difference between order and Molecularity

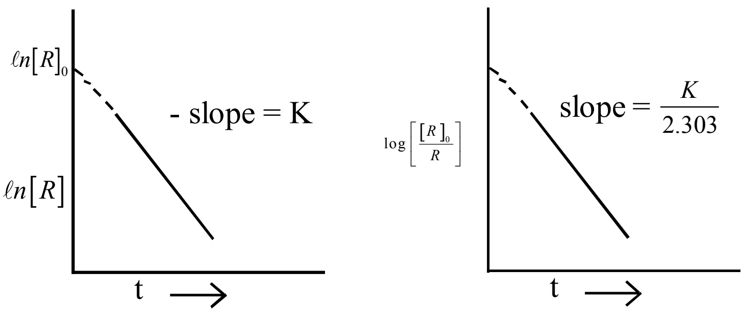
	Order		**Molecularity**
1)	Experimental Quantuty	1)	Theoretical quantity
2)	Applicable to both elementary and compelx reactions	2)	Applicable to elementary reactions only
3)	Can be zero, fractional or integer	3)	Only a whole number cannot be zero or fractional

If the overall order of a reaction is one, it is called I^{st} order reaction.

If the overall order of a reaction is zero, it is called Zero order reaction.



for zero order



first order reaction

Facts	Zero order reaction $R \rightarrow P$	First order reaction $R \rightarrow P$
1) Differential rate equation	$\frac{d(R)}{dt}=-K$	$\frac{d(R)}{dt}=-k(R)$
2) Integrated rate equation	$K=\frac{(Ro)-(R)}{t}$	$K=\frac{In(Ro)-In(R)}{t}$
3) Halflife period	$t\,{}^1\!/_2=\frac{(Ro)}{2k}$	$t\,{}^1\!/_2=\frac{In_2}{k}=\frac{0.693}{k}$
4) Unit of K	Con time-1 (Mol L^{-1}S^{-1})	time^{-1} (S^{-1})
5) Straight line plot	(R) vs time	In (R) vs time
6) Examples	Decomposition ofammonia gas on hot pt 2NH$_3$ pt N$_2$+3H$_2$ Rate = KCNH$_3$	Hydrogenation of ethene $CH_2=CH_2+CH_2\rightarrow CH_3-CH_3$ $Rate=K(C_2H_4)$
7) Expression of rate constant	$K=\frac{(R_1)-(R_2)}{t_2-t_1}$	$K=\frac{2.303}{t_2-t_1}\log\frac{(R_1)}{(R_2)}$
[CR constant rate of contribution]		

Pseudo Ist order reaction is the reaction involving two reactants but behaves as a first order reaction when one reactant is present in large excess.

eg : Ester hydrolysis; inversion of canesugar

(in presence of H$^+$) (in presence of H$^+$Acid)

Complex reaction is the reaction involving more than one step. In a complex reaction, the slowest step is the rate determining step.

Elementary reaction is the reaction involving one step only

Arrhenius equation gives temperarure dependence of rate constant

$K=A.e^{-Ea/RT}$

K= rate constant, A- Arrhenius factor, R- gas constant (8.314)

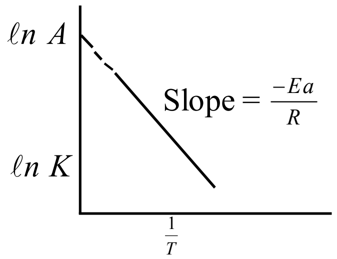
T - Temperature kelvin scale, Ea- Activation energy

Activation Energy is the extra energy needed for the conversion of reactant in to products.

Logarithamic form of Arrhenius equation is

$$\ln K = -\frac{Ea}{RT} + \ln A$$

If K$_1$ and K$_2$ are the rate constants at T$_1$ and T$_2$, then



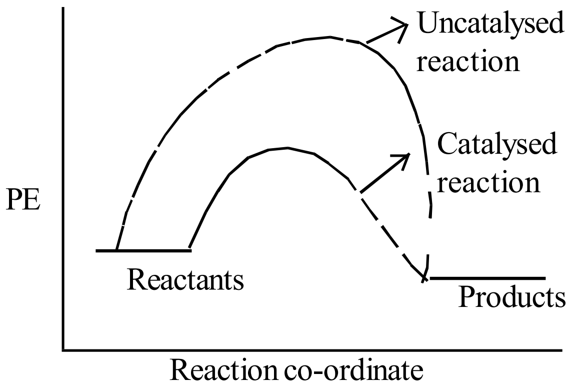
$$\log\frac{K_2}{K_1}=\frac{Ea}{2.303R}\left[\frac{1}{T_1}-\frac{1}{T_2}\right]$$

Effect of catalyst on reaction rate

A catalyst is a substance which alters the rate of reaction without being consumed in the reaction without being consumed in the reaction. A catalyst decreased the activation energy of the reaction.

$2\,KClO_3 \xrightarrow{MnO_2} 2\,KCl + 3O_2$

(MnO_2 is the catalyst)



Collision theory of Chemical reaction

Rate = $P.Z_{A\text{-}B}\,E^{-Ea/RT}$

In collission theory, the activation energy (Ea) and proper orientation (P) together determines the criteria for an effective collision and hence for the rate of the reaction.

Effective Collision is the collission between molecules with threshold energy and proper orientation, leading to the formation of products.

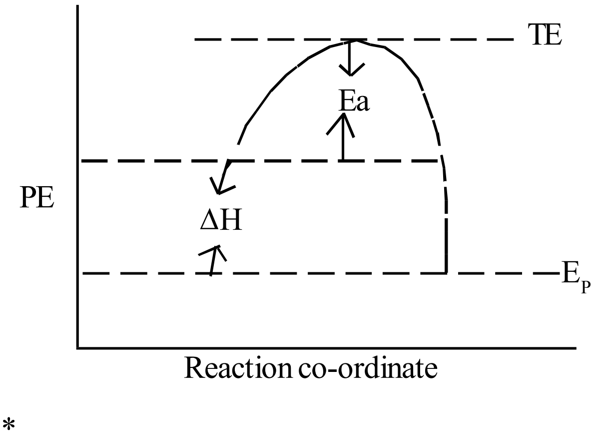
Collision frequency ($Z_{A\text{-}B}$) is the number of collisions per second per unit volume of reaction mixture.

Potential Energy curve for the reaction $H_2+I_2=2HI$

Enthalpy of reaction $E_P-E_R=H_P-H_R$

Activation energy $E_a=T_E-E_R$

Threshold energy $T_E=E_R+E_a$



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Chapter - V

SURFACE CHEMISTRY

Adsorption

The difference in concentration of a substance on the surface of another substance than in the bulk is called adsorption.

Eg:- Water vapours are absorbed by adhyclious calcium chloride but adsorbed by silica gel.

When a chalk stick is dipped in ink, the coloured particles are adsorbed by chalk while the solvent of ink absorbed by chalk stick.

Adsorbate

The substance gets adsorbed is called adsorbate

Adsobent

The substance on which adsorption takes place is called adsorbent.

Desorption

The removal of Adsorbate from the surface of adsorbent is called desorption.

Sorption

A process in which both adsorption and absorption takes place is called sorption.

Difference between Adsorption and Absorption

Adsorption	Absorption
1) It involves unequal distribution of the molecular species in bulk and at the surface	1) It involves uniform distribution of the molecular species throughout the bulk
2) It is rapid in the beginning and slows down near the equilibrium.	2) It occurs at uniform rate
3) It is a surface phenomenon.	3) It occurs throughout the body of the material

Types of Adsorption

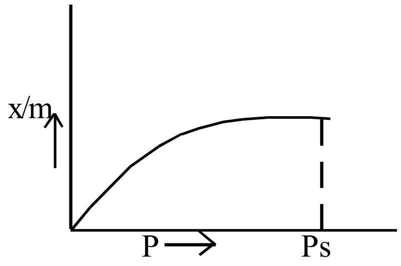
1) **Physical Adsorption** (Physisorption)It is a process in which weak van der Waal's forces exist in between adsorbate and adsorbent.
2) **Chemical Adsorption** (Chemisorption) It is a process in which strong Chemical bonds exist in between adsorbate and adsorbent.

Differecne between Physisorption and Chemisorption

	Physical Adsorption		Chemical Adsorption
1)	Exists weak van der Waal's force	1)	Exists strong chemical bonds
2)	It is reversible	2)	It is irreversible
3)	It forms multimolecular layer	3)	It forms unimolecular layer
4)	It is not specific	4)	It is specific in nature
5)	It decreases with temperature	5)	It first increases and then decreases with temperature
6)	The enthalpy of adsorption is low	6)	The enthalpy of adsorption is high
7)	Because no appreciable activation energy is required.	7)	High activation energy is required

The extent adsorption increases with the increases of surface area of the adsorbent. Thus, finely divided metals and porous substances having large surface area are good adsorbents.

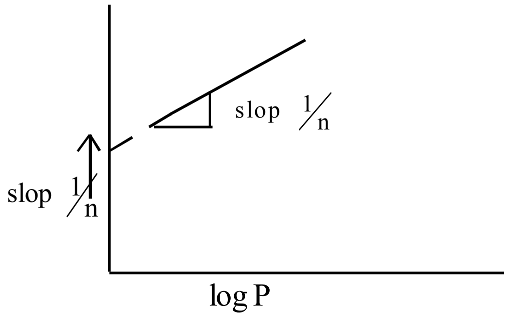
Adsorption isotherm : It is the plot of the extend of adsorption (x/m), versus pressure (p) at constant temperature.



Freundlich Adsorption isotherm

It is the plot of the log x/m versus log P

$$\frac{x}{m} = K.(P)^{1/n}$$



Applications of Adsorption

1. Production of high vaccium
2. Hetrogeneous catalysis
3. Control of humidity
4. Chromalographic analysis

Colloids

It is a heterogenous state of a system in which particle size lies in between 1-1000nm.

Dispersed Phase

This is the substance which has beeen dispersed.

Dispersion Medium

The medium in which the substance has been dispersed.

Classification of Colloids

1) Based on the affinity of dispersed phase for dispersion medium there are two types of colloids.

Lyophilic Colloids : Here the particles of the dispersed phase have a great affinity for the dispersion medium.

Lyophobic Colloids : Here the particles of the dispersed phase have little affinity for the dispersion medium.

Differences between Lyophilic and Lyophobic colloids

Lyophilic Colloids	Lyophobic Colloids
1) They are reversible sol	1) They are irreversible sols
2) These are self stabilized.	2) They are unstable and requires stabilisers
3) They are prepared by direct methods	3) They are prepared by indirect methods
4) They are obtained from organic materials	4) They are obtained from inorganic materials
5) The particles are hydrated	5) The particles are not hydrated

2) Based on the size of colloidal particles there are three types of colloids.

Multimolecular Colloids : They are formed by the aggregaration of large number of atoms or molecules having size less than 1 nm
eg: Gold Sol, Sulphur sol etc

Macro molecular colloids : They are molecules of large size
eg : Polymers

Associated Colloids : These are the solutions which behave as electrolytes at lower concentration and colloids at higher concentration.

Micelles : Associated colloids are formed by the aggregation of large number of ions; Such aggregated particles are called Micelles.

Critical Micelle Concentration (CMC) : The concentration above which micelles are formed is called CMC.

Kraft Temperature : The temperature above which micelles are formed.

Cleansing action of soaps : It is due to the fact that soap molecular term micelle aroung the dirt particle.

Bredig's Arc Method : Eg: For the preparation of colloidal sols of metals such as gold, silver, platinum etc.

Preparation of Colloids

1) **Bredig's Arc Method**
This method involves passing electricity through electrodes made of metals whose solutions are to be prepared. A direct current is passed when an electric arc is formed and metal passed in to solution in the colloidal form.

2) **Peptization :** It is the process of conversion of a freshly prepared precipitate into a colloidal solution by shaking with a suitable electrolyte.

Purification of Colloids

1) **Dialysis :** It is the process of seperating the colloid from impurities by diffusion.
2) **Electrodialysis :** It is the process of dialysis by applying electricty.
papers made from ordinary filter papes by reduced pore size.
3) **Ultratiltration:** It is the process of filtration through specimal

Properties of Colloids

1) **Brownian Movement -** The zig zag movement of colloidal particles in dispersion medium.
2) **Tyndall Effect :** Scattering of light by colloidal particles
3) **Electrophoresis :** The movement of colloidal particles towards one of the electrodes on passage of electricity through colloidal solution.
4) **Electro Osmosis :** The movement of dispersion medium towards oppositely charged electrodes on passage of electricity,
5) **Coagulation :** The precipitation of a colloid by the addition of some suitable electrolyte.

Hardy - Schulze rule

It states that greater the valency of the oppositely charged ion being added, faster is the coagulation. For -vely charged sol (As_2S_3) the order is $Al^{3+} > Ba^{2+} > Na^+$
for +vely charged sol ($Fe(OH)_3$) the order is $PO_4^{3-} > SO_4^{2-} > Cl^-$

Emulsion : Colloids in which both the dispersed phase and dispersion medium are liquids.

Types of Emulsion	Dispersed Phase	Dispersion Medium	Example
Water in oil type	Water	Oil	Butter, Cold Cream
Oil in water type	Oil	Water	Milk, Varnishing Cream

Eg:- of Colloids

1. Blue colour of sky
2. Blood : Alum and terric chloride solution are used to stop bleeding.
3. Formation of delta
4. Artificial rain

Applications of Colloids

1. Tanning
2. Electrical precipitation of smoke
3. Rubber industry
4. Purification of drinking water.

Catalysis : A catalyst is a substance which increases the rate of a reaction without undergoing any chemical change.

Homogeneous Catalysis : When the catalyst is present in the same phase as the reactants, it is called a homogeneous catalyst and the process is called homogenous catalysis

$$2SO_{2(g)} + O_{2(g)} \xrightarrow{NO(S)} 2SO_{3(g)}$$

$$CH_3COOC_2H_{5(\ell)} + H_2O_{(\ell)} \xrightarrow{H_2SO_4(\ell)} CH_3COOH + C_2H_5OH$$

Heterogeneous catalysis : When the catalyst present in the different phase than that of the reactants, it is called a heterogeneous catalyst and the process is called heterogenous catalyst is

$$2SO_{2(g)} + O_{2(g)} \xrightarrow{V_2O_5(S)} 2SO_3(g)$$

$$N_2(g) + 3H_2(g) \xrightarrow{Fe(s)} 2NH_3(g)$$

Adsorption theory of hetrogeneous catalysis : It involves five steps

1. Diffusion of reactants to the surface of the catalyst.
2. Adsorption of reactant moleculer on the surface of the catalyst.
3. Chemical reaction on the surface of the catalyst theory formation of an intermediate..
4. Decription of products from the catalyst's surface making the surface available again for more reaction to occur.
5. Diffusion of reaction products away from the catalyst's surface.

Shape selective Catalysis : A catalytic process that depends on the pore structure of the catalyst and the size of the reactant and product molecules.
eg: Zeolites

Bio Catalysts : These are Catalyst produced by living cells which catalyse the biochemical reaction in living organism
eg:- enzymes.

Mechanism of Enzyme catallysis : Key lock mechanism.

$$\underset{\text{Enzyme}}{E} + \underset{\text{Substrate}}{S} \rightarrow \underset{\substack{\text{Activated}\\ \text{complex}}}{[E-S]} \rightarrow \underset{\text{Enzyme product}}{E+P}$$

<u>**Enzyme**</u>	<u>**Reaction Catalised**</u>
Inverstace	Sucrose → Glucose + Fructose
Maltase	Maltose → Glucose + Glucose
Zymase	Glucose → Ethanol

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Chapter - VI

METALLURGY

General Principles and Process of Isolation of Elements)

1) Principal ores of some important Metals

Metal	Ore
1) Aluminium (Al)	a) Bauxite ($Al_2O_3.H_2O$) b) Kaolinite (A form of Clay)
2) Iron (Fe)	a) Haematite, (Fe_2O_3) b) Magnetite, (Fe_3O_4)
3) Copper (Cu)	a) Malachite [$CuCO_3.Cu(OH)_2$] b) Copper Pyrites ($CuFeS_2$)
4) Zinc (Zn)	a) Calamine ($ZnCO_3$) b) Zinc Blende (ZnS)

2) Metallurgical Process

a) Crushing and grinding of the ore
b) Concentration or benefication of the ore
c) Extraction of metals from the ore
d) Refining or purification of the ore

3) Concentration methods

a) Hydraulic washing or Levigation - For the concentration of Gold & Cassiterite (SnO_2)

b) Megnetic Seperation - For separating tungsten ore from cassiterite
Eg: for the concentration of iron ores.

c) Froth Floatation method : For the concentration of sulphide ores of Zn, Cu & Pb
This method is based on the preferential wetting properties of the ore and gangue particles with frothing agent (oil) and water.

Finely powdered ore is agitated with water containing a little frothing agent (pine oil) by passing air. The froth carries the lighter ore particles at the surface of H_2O and the heavier gangue particles are left behind at the bottom.

d) Leaching - Chemical method, ore is treated with a suitable reagent which dissolves the ore but not the impurities. The undissolved impurities are removed by filtration. The ore is recovered from the solution by a suitable chemical method.

Eg: Bauxite (Ore of Aluminium $Al_2O_3.H_2O$) is concentrated by leaching, the reagent used is NaOH.

$Al_2O_3.H_2O \rightarrow 2Na_3AlO_3$ (Sodium Aluminate) + $3\ H_2O$

$Na_3AlO_3 + 3\ H_2O \rightarrow Al(OH)_3 + 3\ NaOH$

$2Al(OH)_3 \xrightarrow{\Delta} Al_2O_3 + 3H_2O$

2) Silver ores and gold present in rocks are leached with sodium cyanide or KCN solution; The metal is then recovered from the solution by adding zinc to it. This method is called hydrometallurgy.

Extraction of crude metal from concentrated ore

a) Conversion of concentrated ore to oxide

i) Calcination - Ore is strongly heated below its melting point in the absence of air

$Al_2O_32H_2O \xrightarrow{\Delta} Al_2O_3 + 2H_2O$

$ZnCO_3 \xrightarrow{\Delta} ZnO + CO_2$

ii) Roasting - Ore is strongly heated in the presence of excess of air in a reverberatory furnace

$ZnS + 3O_2 \rightarrow ZnO + 2SO_2$

$2PbS + 3O_2 \rightarrow 2PbO + 2SO_2$

Reduction of metal oxides

a) Chemical reduction using carbon - smelting

$ZnO + C \rightarrow Zn + CO$

$Fe_2O_3 + 3C \rightarrow 2Fe + 3CO$

b) To remove infusible impurities (gangue) from calcined or roasted ore, flux is added which combines with gangue particles to form fusible mass called slag.

The added flux may be either acidic or basic which depends on the nature of gangue particles.

Eg: $SiO_2 + CaO \rightarrow CaSiO_3$

Acidic gangue Basic flux (Slag) Calcium Silicate

Refining or Purification of metals

i) Distillation : Low boiling metals like Zn, Cd and Hg are purified by this method. Pure metal distills over leaving behind non volatile impurities.

ii) Liquation : A low melting metal (Eg: Tin, Lead, Bismuth) can be made to flow on a slopping surface and thus seperated from higher melting impurities.

iii) Electrolytic refining

For the Purification of Cu, Sn, Zn, Ni, Ag & Au

Anode - Impure metal

Cathode - Pure metal

Electrolyte : Solution of a suitable salt of the metal.

On passing electric current, pure metal is deposited on the cathode. The solid impurities fall to bottom of the cell and ore recovered as anode mud. The soluble impurities go in to the solution.

iv) Zone refining

Extra pure Ge, Si, Ga etc. used as semiconductors are refined by this method. It is based on the fact that impurities are more soluble in the melt than in the pure metal. So that when an impure metal in the molten state is cooled crystals of pure metal are solidified first and the impurities will remain in the molten part.

v) Vapour phase refining

a) Mond's process for the refining of Nickel

$$\underset{\text{(impure)}}{Ni + 4CO} \xrightarrow{60\text{-}80^{0}C} \underset{\text{(volatile carbonyl)}}{Ni(CO)_4} \xrightarrow{180^{0}\text{-}200^{0}C} \underset{\text{(pure)}}{Ni + 4CO}$$

b) Van Arkel Process

This method is based on the thermal decomposition of a metal compound and is used for the purification of Zr, Ti, Th.

$$\underset{\text{(Impure)}}{Zr} + 2I_2 \xrightarrow{870^{0}K} \underset{\text{(vapour)}}{ZrI_4} \xrightarrow[\text{W- filament}]{2075K} Zr + \underset{\text{(pure)}}{2I_2}$$

vi) Chromatographic Method

This method is useful for the purification of elements, which are available in minute quantities and the impurities are not very different in chemical properties from the element to be purified.

It is based on the principle that different components of a mixture are differently adsorbed on an adsorbent (Eg: Alumina,Al_2O_3)

Thermodyanamic principles of metallurgy

Ellingham diagram

It is the graphical representation of Gibb's free energy. Such a diagram helps to predict the spontaneity of thermal reduction of an oxide ore. Gibb's free energy is plotted against temperature in the diagram and it provides a sound basis for considering the choice of reducing agent in the reduction of oxides.

Extractiom of some important metals

I Iron (Fe) Ores Haemetite, Fe_2O_3,
Magnetite, Fe_3O_4

It is carried out in a blast furnance, and the roasted ore is mixed with limestone (flux) and coke.

Reduction of Fe_2O_3, Fe_3O_4 takes place at relatively lower temperature by CO.

Pig Iron : 4% Carbon. Iron obtained from Blast furnace

Cast Iron : 3% Carbon content

Wreaght Iron : Purest form of commercial iron.

Steel

Steel is an alloy of Fe containing 0.2 to 2% carbon. If it contains some other elements like Cr, Ni, Co, Mn etc along with Fe, Steel obtained is called Alloy steel.

Eg: Stainless Steel - Fe (73%) , Cr (18%).
Ni (8%)$_A$ & C(1%)Nickel steel Fe(96%)$_P$ & Ni (4%)

II Copper (Cu) Ore-copper Pyrites ($CuFeS_2$)

Alloys

i)	Bronze	Cu, Sn
ii)	Brass	Cu, Zn
iii)	German Silver	Cu, Zn, Ni

III Aluminium (Al)

It is usually isolated from bauxite ($Al_2O_3.2H_2O$) by electrolysis.

Purified alumina is mixed with cryolite which lowers the melting point of the mix and increases conductivity.

$$Steel - Cathode - Al^{3+} + 3e^{-} \rightarrow Al$$

$$Graphite - Anode - 20^{2-} \rightarrow O_2 + 4e^{-}$$

The oxygen liberated at the anode reacts with the carbon of anode producing CO and CO_2.

Concentration Methods	
1. Hydraulic washing	Cassiterite (Sno_2)
2. Magnetic separation	Classiterite, Iron
3. Froth Hoatation	Sulphide Ores
4. Leaching	Ore of Al, Au & Ag
Conversation of concentrated Ore to Oxide:	
1. Calcination	Oxides and carbonates term of ores
2. Roasting	Sulphide form of ore]
Refining of Metals	
1. Distillation	Zn, Cd &Hg (Low boiling metals)
2. Liquation	Tin, Lead, Bismath (Low melting metals)
3. Electrolytic refinery	Cu, Au &b Ag
4. Zone refining	Semi conductors - Silicon, Germanium, Coallium etc.
5. Vapour phase refining	
(a) Mend's process	Nickel
(b) Van Arkel process	Zirconium, Titanium, Thorium

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Chapter - VII

P - BLOCK ELEMENTS

(Group 13 to 18)

Group No.	Elements	Outer Electronic Configuration
15	Ni, O, As, Sb, Bi	ns^2, np^3
16	O, S, Se, Te, Po	ns^2, np^4
17	F, Cl, Br, I, At	(Hologens) ns^2, np^5
18	Ni, O, As, Sb, Bi	ns^2, np^6

Properties of Hydrides of P - Block Elements

Group	Hydrides	Stability & Basic Character	Reactivity & Acidity
15	NH_3, PH_3, AsH_3, SbH_3, BiH_3	Decreases from NH_3 to BiH_3	Increases from NH_3 to BiH_3
16	H_2O, H_2S, H_2Se, H_2Te, H_2Po	Decreases from H_2O to H_2Po	Increases from H_2O to H_2Po_3
17	HF, HCl, HBr, HI	Decreases from HF to HI	Increases from HF to HI

Important Hydrides, their properties and uses

Compound	Preparation	Uses
Ammonia NH_3	$N_2 + 3H_2 \underset{Iron\ Oxide}{\overset{750K}{\rightleftharpoons}} 2NH_3$ Iron Oxide Haber Proces	i) Preparation of Nitrogenous fertilizers ii) Liquid ammonia as refrigerant
Phosphine PH_3	$Ca_3P_2 + 6H_2O \rightarrow PH_3 + 3(NaOH)_2$	i) In Holme's signal ii) In smoke screen
Hydrochloric acid HCl	$NaCl + M_2SO_4 \rightarrow Na_2SO_4 + HCl$	i) In the manufacture of glucose, NH_3 ii) As a laboratory reagent

Sulphuric Acid (H_2SO_4)

Manufacture of Sulphuric Acid by Contact Process

$$S + O_2 \rightarrow SO_2$$

$$2SO_2 + O_2 \overset{v_2O_5}{\rightleftharpoons} 2SO_3$$

$$2SO_3 + H_2SO_4 \rightarrow H_2S_2O_7 \text{ (Oleum)}$$

$$H_2S_2O_7 + H_2O \rightarrow H_2SO_4$$

Properties of H_2SO_4

a) Acidic Properties i) $H_2SO_4 \rightarrow H^+ + HSO_4^-$

ii) $HSO_4^- \rightarrow H^+ + SO_4^{2-}$

b) Dehydrating Propertiy (This reaction is called Charring)

$$C_6H_{12}O_6 \xrightarrow{H_2SO_4} 6C + 6H_2O$$

c) Oxidising property

i) $Cu + 2H_2SO_4 \rightarrow CuSO_4 + 2H_2O + SO_2$
ii) $C + 2H_2SO_4 \rightarrow CO_2 + 2H_2O + 2SO_2$
iii) $HBr + H_2SO_4 \rightarrow Br_2 + 2H_2O + SO_2$

Uses

a) For the manufacture of Fertilisers, TNT, Nitroglycerone
b) In petrolieum industry
c) In lead storage battery

Nitric Acid (HNO_3)

Manufacture of Nitric acid by <u>Ostwald Process</u>

$$4NH_3 + 5O_2 \xrightleftharpoons[9\,bar]{Pt\ Rh\ 500K} 4NO + 6H_2O$$

$$2NO + O_2 \rightarrow 2NO_2$$
$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$$

Properties

Acidic Properties

$$2HNO_3 \rightarrow H^+ + NO_3^-$$

Action on metals a) <u>with Copper</u>

i) $Cu + 4HNO_{3(Conc)} \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$
ii) $3Cu + 8HNO_{3(Dilute)} \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$

With Zn

$$4Zn + 10HNO_{3(Conc)} \rightarrow 4Zn(NO_3)_2 + N_2O + 5H_2O$$
$$Zn + 4HNO_{3(Dilute)} \rightarrow Zn(NO_3)_2 + NO_2 + 2H_2O$$

Action on Non metals

$$C + 4HNO_{3(Conc)} \rightarrow CO_2 + 4NO_2 + 2H_2O$$
$$P_4 + 20HNO_{3(Conc)} \rightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$$

Sulphur	Rhombic Sulphur (α)	Yellow coloured most stable form consits of S_8 molecules
	Monoclinic Sulphur (β)	Dull yellow coloured needle shaped crystals, consists of S_8 molecules
	Plastic Sulphur(λ)	Amorphous form with zig zag chains of Sulphur Atoms

Oxo Acids of Phosphorus

Name Formula	**Basicity**	**Characteristic**	**Bonds**
Hypophosphorous Acid	H_3PO_2	Monobasic	Two PH, One P OH
Orthophosphorous Acid	H_3PO_3	Dibasic	One PH, Two P OH
Pyrophosphorous Acid	$H_4P_2O_5$	Dibasic	Two PH, Two P OH
Hypophosphoric Acid	$H_4P_2O_6$	Tetra basic	Four P OH
Orthophosphoric Acid	H_4PO_4	Tri basic	Three P OH
Pyrophosphoric Acid	$H_4P_2O_7$	Tetra basic	Four P OH
Metaphosphoric Acid	$(HPO_3)_n$	Tri basic	Three P OH

Note : $H_3PO_{2,}$ H_3PO_3 $H_4P_2O_5$ are reducing acids as they have P-H bond

Oxo acids of Sulphur

H_2SO_3 - Sulphurous Acid

$H_2S_2O_3$ - Thio Sulphuric Acid

$H_2S_2O_7$- Perodi sulphuric Acid

H_2SO_4 - Sulphuric Acid

$H_2S_2O_5$- Peroxo Mono Sulphuric Acid

$H_2S_2O_6$- Dithonic Acid

Oxo Acids of Chlorine

HOCl Hypochlorous acid, $HClO_2$ Chlorous Acid (HOClO), $HClO_3$ Chloric Acid, $HClO_4$ Perchloric Acid $HOClO_3$

Acids strength increases with order of $HOCl < HOClO < HOClO_2 < HOClO_3$

Oxides : Binary compound of oxygen with other element

Simple Oxides

Oxide of an elements with one oxidation state only.

a) Acidic Oxide

They combine with water to give acids

eg: CO_2, SO_2, P_4O_{10}, SO_3 etc.

b) Basic Oxide

They combine with water to give acids

eg: Na_2O, MgO , CaO

c) **Amphoteric Oxide**

They show both acidic and basic properties

eg: Al_2O_3, ZnO , SiO_2

d) **Neutral oxide**

They are neither acidic nor basic properties

eg: CO, N_2O, NO etc

Bleaching Powder $Ca(OCl)_2$ $CaCl_2.Ca(OH)_2.2H_2O$

It is prepared by passing Chlorine gas on dry slacked lime. It is used as bleaching agent

Phosgene : $COCl_2$ (Carbonyl Chloride)

It is a poisonous gas used in warface

Tear Gas CCl_3NO_2

It is a poisonous gas ued in warface

Mustard Gas

$(Cl\text{-}CH_2\text{- }CH_2)_2 S$

It is a poisonous gas ued in warface

Aquaregia

Conc. HCl and Con. HNO_3 in 3:1 ratio. It dissolves gold and platinum.

Inter halogen Compound

Halogens react with each other to form inter halogen compounds. They are covalent compounds.

They are more reactive than halogens.

Type	Examples	Geometry	Hybridisation
AX	ClF, BrF, IF, BrCl, ICl, IBr	Linear	
AX_3	ClF_3, BrF_3, IF_3, ICl_3	T Shapes	sp^3d
AX_5	ClF_5, BrF_5, IF_5	Square Pyramidal	sp^3d^2
AX_7	IF_7	Pentaganal Pyramidal	sp^3d^3

Allotropic forms of P, O, and S

Element	Allotropic forms	Propertoties
Phosphorus	White Phosphorus	P_4 molecules highly reactive, glowing in dark
	Red Phosphorus	Linear chains of P_4 units, less reactive.
	Black Phosphorus	Layer structure of P atoms non reactive
Oxygen	Dioxygen	(O_2) Colourless gas, Odour less Gass Non Poisonous O=O
	Ozone (O_3)	Pale blue gas with pungent smell. It is Poisonous

Mixed Oxides

Oxide of an element with more then one oxidation states. They are mixture of two oxides

Eg:- Pb_3O_3 : $(Pb_2^{(+3)}O_3+Pb^{(+2)}O)$

Fe_3O_4 : $(Fe_2^{(+3)}O_3+Fe^{(+2)}O)$

Brown ring test for Nitrates

Nitrates on reaction with $FeSO_4$ and Conc. H_2SO_4 and gives a brown ring between the aqueous and acidic layer

Phosphorus Halides

Preparation & Properties	Phosphorous Trichloride PCl_3	Phosphorous Pentachloride PCl_5
1) Preparation	$P_4+6Cl_2 \rightarrow 46Cl_3$	$PCl_3+Cl_2 \xrightarrow{CCl_4} PCl_5$
2) Reaction with moisture	$PCl_3+3H_2O \rightarrow H_3PO_3+ 3HCl$	$PCl_5+4H_2O \rightarrow H_3PO_4+ 5HCl$
3) Structure	Pyramidal	Trigonal bipyramidal
4) Hybridisation	sp^3	sp^3d

Compound of Xenon

Fluorides a) XeF_2 : Linear Shape sp^3d : (3 lone pairs)
b) XeF_4 : Square Shape sp^3d^2 : (2 lone pairs)
c) XeF_6 : Distorted Octahedral : sp^3d^3 (one lone pairs)

Oxide XeO_3 Pyramidal : sp^3(one lone pair)

Oxi Fluorides $XeOF_2$ T Shaped sp^3d (2 lone pairs)

Oxi Fluorides $XeOF_4$ Square Pyramidal sp^3d^2 (one lone pair)

[Xe- Fe single bond, X=O double bond]

Use of Noble gases or Inert gases

- Being light and non inflammable, He is used in weather baloons and airships
- He is used as cryogenic agent
- Ne is used in discharge tubes
- Ar is used for filling electric bulbs
- Kr - He mixture in flash bulbs
- Rn is used in the treatment of cancer

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Chapter - VIII

THE ‘d’ AND ‘f’ BLOCK ELEMENTS

The general outer electronic configuration of d block elements is (n-1)$d^{1-10}ns^{1-2}$. This block consists of four series. 3d, 4d, 5d and 6d series. They are known as transitional elemets.

Zn, Cd and Hg are not regarded as transitional elemetns as they have completely filled d sub shell (n-1)d^{10}

d - block elements with partially filled d orbitals have following properties.

a) Variety of oxidation states (except Sc)

b) Formation of cloured compound.

When white light falls on a transition metal compound, some of its energy corresponding to a certain is absberbed for d-d transition. The remaining colour of while light are transmitted and the compound appears coloured.

c) Formation of complexes.

d) Exhibit catalytic and paramagnetic properties.

- Mn shows highest oxidation state of +7
- E^0_{m2+m} of copper is posetive as the sum of Ist ionisation enthalpy and IInd ionisation enthalpy is much higher than hydration enthalpy.
- Cu(I) compound are unstable in acqueous solution and under go disproportionation reaction. ($2Cu^+ \rightarrow Cu^{2+} + Cu$)
- Cu^{2+} (aq) is more stable than Cu^+ (aq) due to higher negative hydration enthalpy of Cu^{2+} (aq) than Cu^+(aq)
- Magnetic moment of, $\mu = \sqrt{n(n+1)}$

  ‘n’ is the number of unpaired electrons μ is expressed in BM units
- $K_2Cr_2O_7$: Potassium Dichromate

Preparation

- Chromate ore ($FeCr_2O_4$) $\xrightarrow{Na_2CO_3 + O_2}$ Sodium Chromate (Na_2CrO_4)

  $\xrightarrow{H+}$ Sodium Dichromate $Na_2Cr_2O_7$ $\xrightarrow{KCl}$ $K_2Cr_2O_7$
- Chromates (CrO_4^{2-}) on acidification give dichromates ($Cr_2O_4^{2-}$)
- Dichromates on adding alkali give chromates.

Uses of $K_2Cr_2O_7$

a) Used as a oxidising agent

Eg: - $Sc^{3}+ \; - \; colourless \; (d^{0})$

b) As a primary standard in volumetric analysis

c) In Leather industry

Potassium Permanganate $KMnO_4$

Preparation : Pyroluste $MnO_2 \xrightarrow{KOH + O_2}$ Manganate coin

$\left(MnO_4^{2-}\right)\dfrac{Electrolytic}{Oxidation}$ Potassium permanganate $KMnO_4 + e^-$

- $KMnO_4$ is used as a oxidising agent.

  Eg: - $Zn^{2}+ \; - \; colourless \; (d^{10})$
- Acidified $KMnO_4$ oxidises iodide (I^-) to iodine (I_2) and itself reduced to Mn^{2+} ions
- Neutral $KMnO_4$ oxidieses iodide (I^-) to Iodate IO_{3}^{-} and itself reduced to MnO_2
- $2KMnO_4 \xrightarrow[513K]{heating} K_2MnO_4 + MnO_2 + O_2$

  (Permanganate) (Manganate)
- HCl is not used in permanaganometric titrations as HCl is oxidised to Cl_2

F- block elements or Inner transitional elemets

F-block consists of lanthanoids ($4f^{1-14}5d^{0-1}6s^{2}$) and actinoids ($5f^{1-14}$, $6d^{0-1}\,7s^{2}$)

Lanthanoid Contraction is the over all decrease in atomic or ionic radii from lanthanum to lutetium, due to poor sheilding of nuclear attractions by 4f electrons.

Consequences :

1) Indentical Radii of Zr and Hf
2) Similar Physical and Chemical properties of lanthanoids
3) Difficulty in seperation of lanthanides

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Chapter - IX

CO-ORDINATION COMPOUNDS

1. Co-ordination Compound $[\underbrace{CO}_{\text{Central metal atom}}(\overbrace{NH_3}^{\text{Ligands}})_6]\underbrace{Cl_3}_{\text{Ionisable}}$

A compound in which central metal atom or ion is linked to a number of ions or neutral molecules by co-ordinate bond.

Eg : $Ni(CO_4)$, $\underbrace{K_4}_{\text{Ionisation sphere}}\ [\underbrace{Fe(CN_6)}_{\text{Co-ordination sphere}}]$

2) Werner's theory of complexes

i) In co-ordination compounds metals show two types of valencies

a) Primary valency b) Secondary valency

ii) Primary valency (Ionisable, satisfied by negative ions)

iii) Secondary valency (Co-ordination number, fixed for a metal) non-ionisable, satisfied by neutral molecules or negative ions.

iv) Secondary valency can give direction regarding the spatial arrangements of molecules and the geometry of the co ordination compound.

3) Difference between double salts and complex salts

Double salts : They dissociate completely in to component ions, when dissolved in water

Eg; Mohr Salt

$$FeSO_4.(NH_4)_2SO_4.6H_2O \rightarrow Fe^{2+} + 2NH_4^{+} + 2SO_4^{2-} + H_2O$$

Complex Salts : They do not dissociate completely.

Eg: $K_4.[Fe(CN)_6] \xrightarrow{H_2O} 4K^{+} + [Fe(CN)_6]^{4-}$ Complex ion

Ligands : The neutral molecules or ions that are attached directly to the central atom or ion in a complex.

Eg: H_2O, NH_3, CN, Cl, F, CO

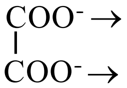
Types of ligands

I **i) Monodentate Ligands :** It contains only one donor atom or co - ordination site

Eg : NH_3, H_2O, $CN^- \rightarrow Cl^-$

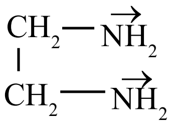
ii) **Bidentate Ligands** - Having two donor sites.

Eg : Oxalate $(C_2O_4)^{2-}$



$$\begin{matrix} COO^- \rightarrow \\ | \\ COO^- \rightarrow \end{matrix}$$

Ethylene Diamine (en)

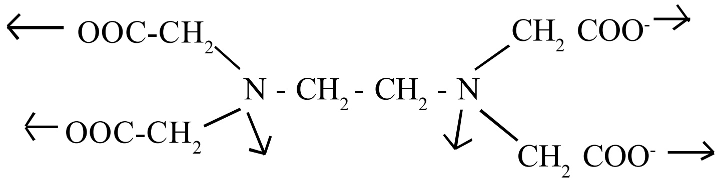


$$\begin{matrix} CH_2 - \vec{N}H_2 \\ | \\ CH_2 - \vec{N}H_2 \end{matrix}$$

iii) Polydentate Ligands

Have more than two donor sites. These may be tridentate, tetradentate, Pentadentate or hexadentate etc.

eg : EDTA (Ethylene Diammine Tetra Acetate)



II

i) Neutral ligands

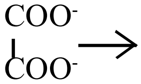
Eg:- NH_3, CO, H_2O, (en) etc.

Charge zero

ii) Charged ligands

a) Negatively Charged

CN^-, Cl^-, F^- etc } Charge = -1



$$\begin{matrix} COO^- \\ | \\ COO^- \end{matrix} \rightarrow \text{Charge} = -2$$

b) Positively charged NO^+ - Charge = +1

III **Ambidentate linagands**

Ligands having two donor atoms but ligate through one atom to the central metal atom or ion

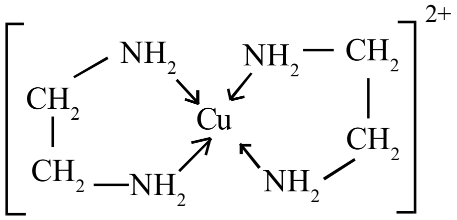
Eg:- a) CN^- & NC^- b) NO_2^- & ONO^-

(C-donor) (N-donor) N-donor) (O-donor)

IV **Chelate Ligands**

Bidentate or Polydentate ligands which are attached by two or more donor atoms to the same central metal ion and forming a ring structure.

Eg:- $[Cu\ (en)_2]^{2+}$



Chelates are generally more stable than ordinary complexes formed from monodentate ligands

4) Co-ordination Number

Total number of monodentate ligands which are directly attached to the cenrtral metal atom or ion.

Complex	Central metal atom	Co-ordination number
$[Ag(NH_3)_2]Cl$	Ag	2
$[Cu(NH_3)_4]SO_4$	Cu	4
$[Co(NH_3)_3Cl_3]$	Co	6
$K_4\ [Fe\ (CN)_6]$	Fe	6

5) Naming of Complexes

a) $[Co(NH_3)_6\ Cl_3$ - Hexammine Cobalt (III) Chloride

second (2) First(1) Third(3)

b) $[Ag(NH_3)_2]Cl$ - Diammine silver (I) chloride

c) $[Ni(CO)_4]$ - Tetra carbonylnickel (0)

d) $[CoBr(NH_3)_5]SO_4$ - Pentaamminebromo cobalt (III) Sulphate

e) $K_4[Fe(CN)_6]$ - Potassium hexacyanoferrate (II)

First(1) Third(3) second (2)

f) $[CoF_6]^{3-}$ - Hexafluorocobaltate (III) ion.

g) $[Ag(CN_2)^-]$ - Dicyanoargentate (I) ion.

h) $[Co(NH_3)_4Cl_2]^+$ - Tetraamminedichloro cobalt (III) ion.

i) $[Cr(en)_3]^{3+}$ - Tris (ethane - 1,2 diammine) Chromium (III) ion.

Isomerism in co-ordination compounds

2 Types

a) Structural Isomerism

b) Stereo Isomerism

A Structural Isomerism

a) Ionisation isomerism

Here is an interchange of groups between the co ordination sphere of the metal ion and ions outside the sphere

$[Co(NH_3)_5Br]SO_4$ & $[Co(NH_3)_5 SO_4] Br$.

b) Linkage isomerism

It arises in a co - oridination compound containing ambidentate ligands like CN, $-NO_2$ etc.

Eg:- $[Co(NH_3)_3 (-ONO)] Cl_2$ → O-donor in -ONO
(red coloured)
and
$[Co(NH_3)_3 NO_2] Cl_2$ → N-donor in - NO_2
(yellow coloured)

c) Hydrate isomerim

Hydrate isomers differ by whether or not a water molecule is directly bonded to the metal ion or merely present as free solvent molecule in the crystal lattice.

Eg:- $[Cr(H_2O)_6 Cl_3$, $[Cr(H_2O)_5Cl]Cl_2. H_2O$ & $[Cr(H_2O)_4Cl_2] Cl.H_2O$
(violet) (green) (green)

d) Co ordination Isomerism

This isomerism is caused by the interchange of ligands between the two complex ions

Eg:- $[Co(NH_3)_6] [Cr(CN)_6]$
$[Cr(NH_3)_6] [CO(CN)_6]$

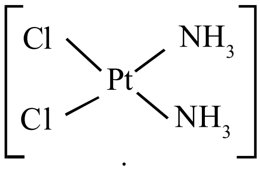
B Stereo isomersm

Steoreo isomers possess same molecules formula but different spatial arrangements

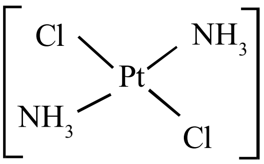
Two types

a) Geometrical or cis trans isomerism

This type of isomerism arises due to different Possible geometrci arrangements of ligands two geometrical isomers of [$PtCl_2(NH_3)_2$] are



cis



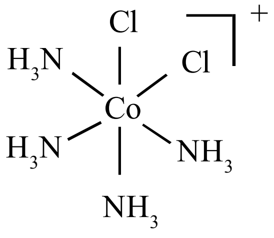
cis

Cis [$PtCl_2(NH_3)_2$]

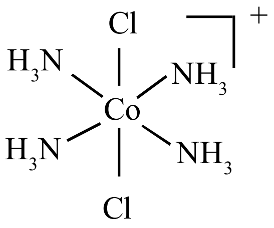
Similar ligands are arranged adjacent to each other around the central metal.

Trans [$PtCl_2(NH_3)_2$] Similar ligands arranged opposite to each other around the central metal atom.

Similarly octabedral complexes like [$Co(NH_3)_4Cl_2$]$^+$ & [$CoCl_2(en_2$] exist as cis trans isomers



cis isomer [$Co(NH_3)_4Cl_2$]



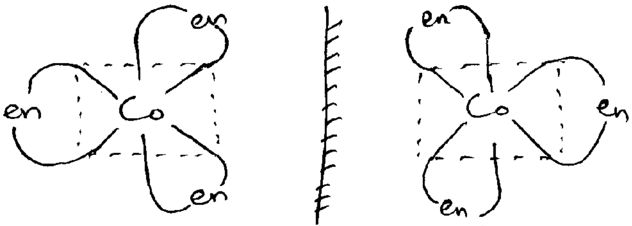
trans [$Co(NH_3)_4Cl_2$]

Another type of geometrical isomers are facial (fac) and meridinel (mer) isomers

b) Optical Isomerism

Optical isomers are mirror images that can't be superimposed on one another called enantiomers. Molecules with non-superimposable mirror images are called chiral molecules. The two forms are dextro(d) and laevo(l) depending upon the direction they rotate the plane of polarised light in a polarimeter. (d- rotates to the right, l - to the left) Optical isomerism is common in octahedral; complexes with bidentate ligands

Optical isomers of [$Co(en)_3$]$^{3+}$



dextro mirror laevo

In a complex ion of the type $[PtCl_2(en)_2]^{2+}$ only the cis isomer exhibits optical activity.

Bonding in Complexes

i) Valence Bond theory

ii) Crystal field theory

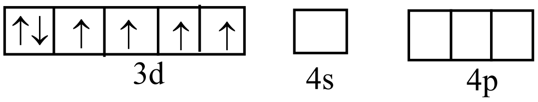
i) Valence bond theory

According to this theory, the metal atom or ion under the influence of ligands use its (n-1)d or ns, np or ns, np, nd orbitals for hybridisation to yield a set of equivalent orbitals of definite geometry. These hybrid orbitals are allowed to overlap with ligand orbitals.

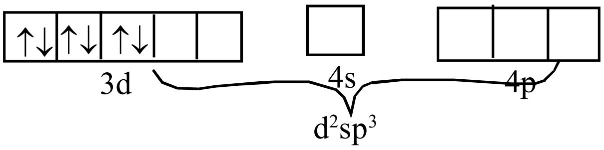
Co - ordination Number	**Type of Hybridisation**	**Geometry**
4	sp^3	Tetrahedral
4	dsp^2	Square Planar
5	sp^3d	Trigonal bipyramidal
6	sp^3d^2	Octahedral
6	d^2sp^3	Octahedral

Eg $[Co(NH_3)_6]^{3+}$ - Co^{3+}-

3d - orbitals electrons get paired / Co^{3+} -



d^2sp^3 hybrid orbitals of Co^{3+} -

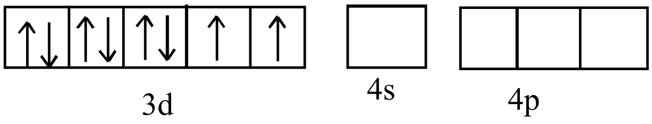


The complex is diamagnetic and low spin one with octahedral geometry.

But $[CoF_6]^{3-}$ is paramagnetic and sp^3d^2 hybridised as $\bar{F}$ is a weak ligand.It is a high complex.

3) $[NiCl_4]^{2-}$ is paramagnetic and sp^3 hybridised

Ni^{2+} -



Since Cl^- is a weak ligand, no pairing of electrons occurs. It is an outer orbital complex.

4) $[Ni(CN)_4]^{2-}$ is diamagnetic and dsp^2 hybridised. But $[Ni(CO)_4]$ is sp^3 hybridised & diamagnetic [Here Ni is in zero oxidation state]

Magnetic properties of complexes

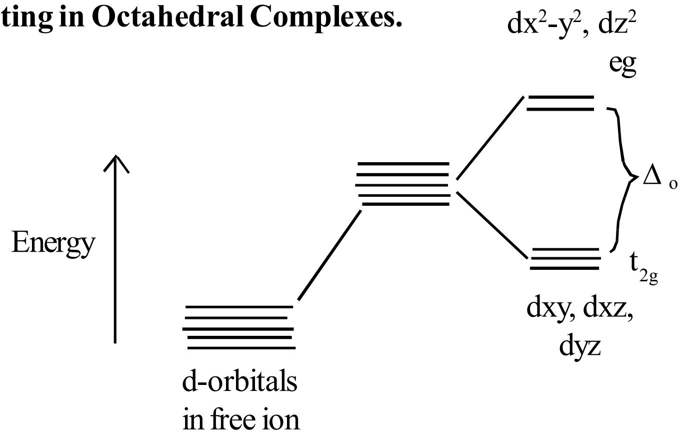
Spin only Magnetic moment, $\mu_{spin} = \sqrt{n(n+2)}BM$

n=no. of unpaired electrons.

Crystal field theory

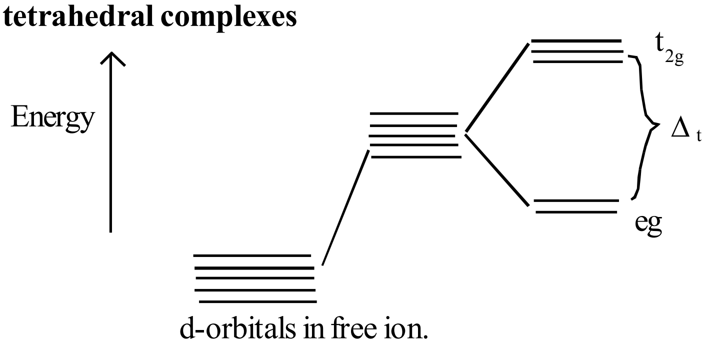
Ligands to be point charges and there is electrostatic force of attraction between ligands and metal atom or ion. When ligands approach the central metal ion then the five degenerate orbitals split which depends upon the nature of ligand field strength.

Crystal Field splitting in Octahedral Complexes.



Δ_o - Crystal field stabilization energy

Crystal field splitting in tetrahedral complexes



Spectrochemical series

It is a series in which lignds are arranged in the increasing order of field strength.

$I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < H_2O^- < NH_3 < en < CN^- < CO^-$

Important & Applications of co-ordinations compounds

i) Detection and estimation of metals

ii) Estimation of hardness of H_2O using EDTA

iii) For the purification of metals

iv) Importance in biological systems

- Chlorophyll - Mg containing Complex
- Haemoglobin - Fe containing pigment
- Vitamion B_{12} - Cyanocobalamine (Cobalt containing vitamin)

v) Industrial catalyst (Wilkinson's catalyst, $[RhCl(PPh_3)_3]$- in the hydrogenation of alkanes

vi) In the medical field

cis - Platin - Anti Cancer reagent

EDTA In the treatment of Lead Poisoning

***

Chapter - X

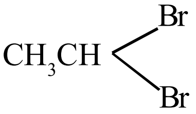
HALOGENS AND HALOARENES

- **Halo Alkanes** - Compounds obtained from alkanes by the replacement of on or more hydrogen by corresponding number of halogen atoms (F, Cl, Br, I) are termed as Haloalkanes.
- **Halo Benzene**

  When hydrogen atoms of Benzene nucleus is substituted by a halogen, it is known as halobenzene adn has a general formula

  $-C_6H_5X$
- When hydrogen aton of the side chain attached to benzene is substituted by a halogen, then it is known as Aralkyl Halides

  Eg: Benzyl Halide $C_6H_5CH_2Cl$
- **General formula and nomenclature of alkyl/aryl halides**
  - Monohalogen derivatives - $C_nH_{2n+1}X$(alkyl halides)
  - Dihalogen derivatives $C_nH_{2n+1}X_2$
  - Chemical dihalides are formed when both halogens are on the same atom



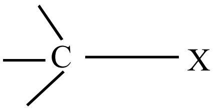
$CH_3CH<^{Br}_{Br}$ (Ethylidene Bromide)

  - Vicinal dihalides are formed when both halogens are attached to adjacent carbon atom

    Eg: ClH_2C-CH_2CL (Ethylene Dichloride)

Nature of -X bond

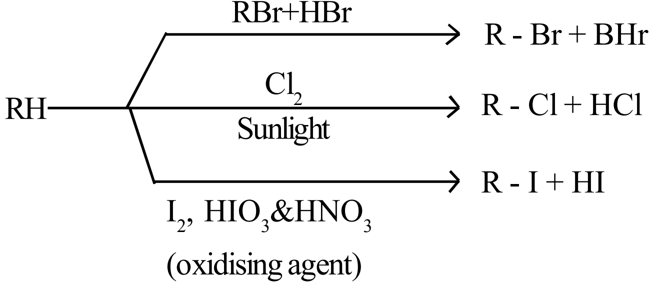
- Since halogen atom are more electronegative than carbon, the C-X bond of an alkyl halide is polarised; the carbon atom bears a partial positive charge whereas the halogen atom bears a partial negative charge.



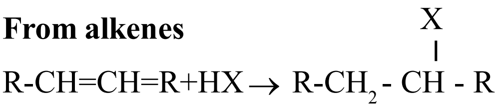
- Since the size of halogen atom increases a we go down the group in the peridic table Fluoride atom is the smallest and iodice aton, the largest consequently the carbon halogen bond length increases from C-F to C-I

General methods of preparation of alkyl halides

i) From alkanes

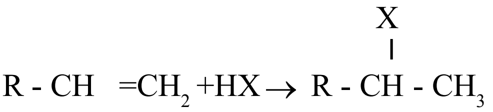


ii) From alkenes



$$R\text{-}CH{=}CH{=}R + HX \rightarrow R\text{-}CH_2\text{-}\underset{}{\overset{X}{\overset{|}{C}}}H\text{-}R$$

Symmetrical Alkene



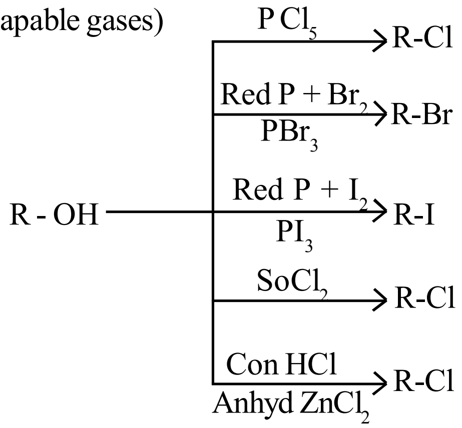
$$R\text{-}CH = CH_2 + HX \rightarrow R\text{-}\overset{X}{\overset{|}{C}}H\text{-}CH_3$$

(Unsymmetrical alkene)

- In the addition of halogen acids to unsymmetrical alkenes, generally Markownikoff's rule is followed by the addition occurs through an electrophilic attack. However, in case of reaction with HBr in presence of peroxide,anti Markoffnikoff's rule is followed known as peroxide effect or Kharasch effect.
- The order of reactivity of halogen acids with alkene is HI>HBr>HCl>HI

iii) From Alcohols

$R - OH \xrightarrow{SoCl_2} RCl + SO_4 + HCl$ (Pure alleyl halide is obtained because the other two products are exapable gases)



iv) Swarts reaction

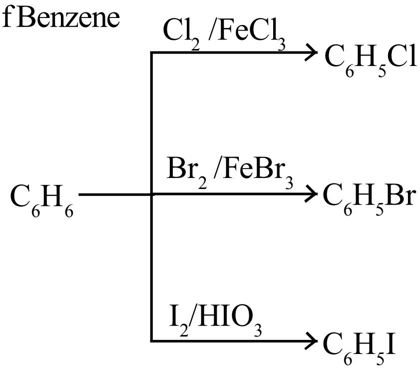
$$CH_3Br + AgF \rightarrow AgBr$$

v) Finkelstein reaction [Halide exchange]

$$C_2H_5Br \quad NaI \xrightarrow[Heat]{Acetone} C_2H_5I \qquad + NaBr$$

General methods of preparation of aryl halides

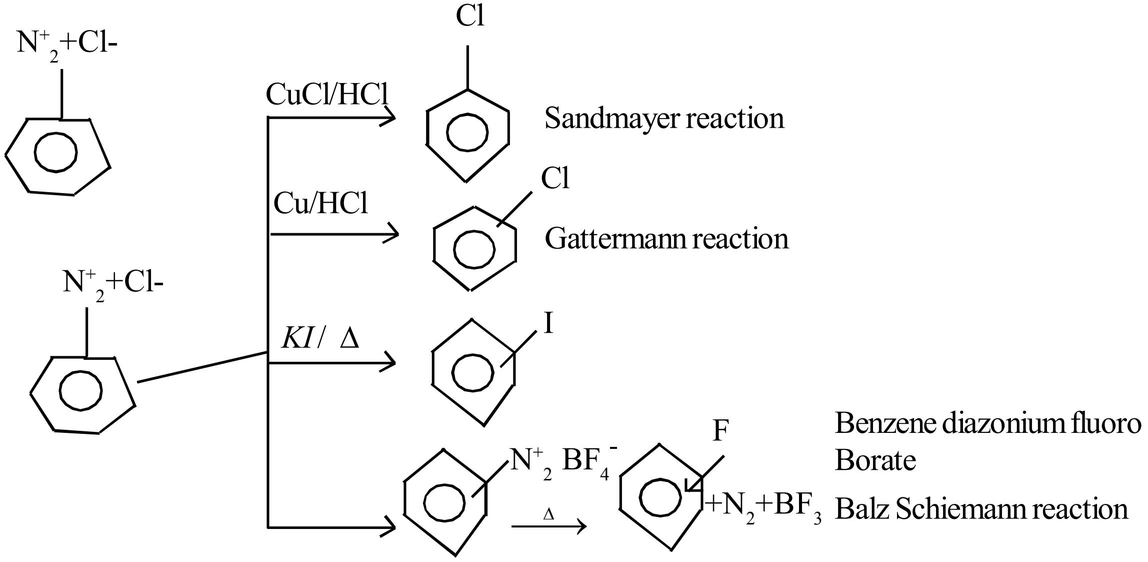
i) By direct halogenation of Benzene



- It is an electrophilic substitution reaction
- Low temperature and the presence of a halogen carries favours nucleus substitution. The function of the halogen carries is to generate the electrophile for the attack.

$$Cl_2 + FeCl_3 \rightarrow \overset{\text{Electrophole}}{Cl^+} + FeCl^-_4$$

ii) From Benzene diazonium salt



iii) By Raschig Process

$$2C_6H_6+2HCl+O_2 \xrightarrow[500k]{CuCl2} 2C_6H_5Cl+2H_2O$$

iv) By Hundsdiecker reaction

$$C_6H_5OOAg+Br_2 \xrightarrow[CCl_4\ +350K]{\text{Distillation}} C_6H_5Br+AgBr+WCO_2$$

Physical Properties of alkyl halides

- Lower member [CH_3Cl,CH_3Br and C_2H_5Cl] are gases and the others are sweet smelling liquids.
- Alkyl halides are polar in nature but are insoluble in water due to their inability to form H bond with water
- They are solube in alcohol, ether Benzene etc
- Halo alkanes have higher molecular weight than coresponding alkanes because of which they have considerably higher boiling points.
- Gradation in densities and boiling point of alkyl halides increases with the increase in the size of the alkyl group.
- Alkyl halides usually darken on standing for sometime due to the decomposition by ligtht and liberation of iodine.

$$2RI \xrightarrow{h\upsilon} R\text{-}R + I_2$$

Chemical Reaction of alkyl halides

S_N1 Reaction

- Substitution nulcleophilic uni molecular reaction are abbreviated as S_N1. Considet a general reaction.

  $R\text{-}LG + NO^- \rightarrow R\text{-}NO + LG^-$

  $Rate = K[R\text{-}LG]$
- Reaction follows first order kinetics
- The rate of reaction is independent of the concentration of nucleophile.
- The S_N^1 mechanism is a two step process, first one thing being the slow and the rate determining step.

Order of Reactivity

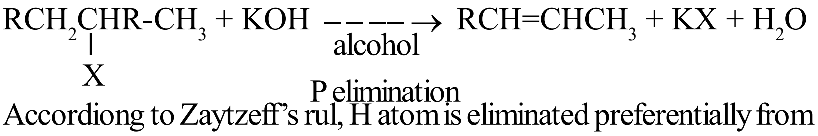
Benzyl > Ally1>3^O>2^O>1^O>CH_3 - X

S_N2 Reaction

- S_N1 mechanism is a single step process with no intermediate. Bond making and breaking take place simultaneously with the reaction centre.
- **Order of reactivity**

  CH_3-X>1^O>2^O>3^O> Allyl > Benzyl

Dehydrohalogenation



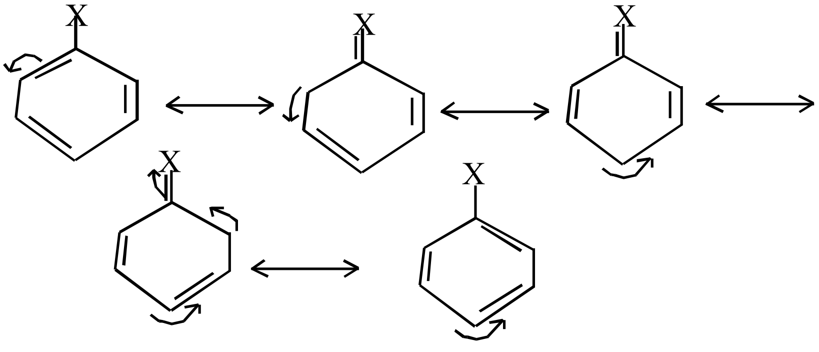
$$RCH_2\underset{\underset{X}{|}}{C}HR\text{-}CH_3 + KOH \xrightarrow[\text{alcohol}]{} RCH{=}CHCH_3 + KX + H_2O$$

P elimination

- Accordiong to Zaytzeff's rul, H atom is eliminated preferentially from the adjacent C atom which is joined to the least H atom.
- The reactivity of halo alkanes towards elimination reaction is 3°>2°>1°

  Halobenzene is less reactive than halo alkanes.
- Delocalisation of electron by resonance

  The C-X bond is halo benzene has a partial double bond character. Due to involvement of halogen electrons in resonance with Benzene ring



- **Polarity of C-X bond**

  The C-X bond in aryl halogens is less polar compared to that in alkyl halides

Necleophile Substitution reaction of Chlorobenzene

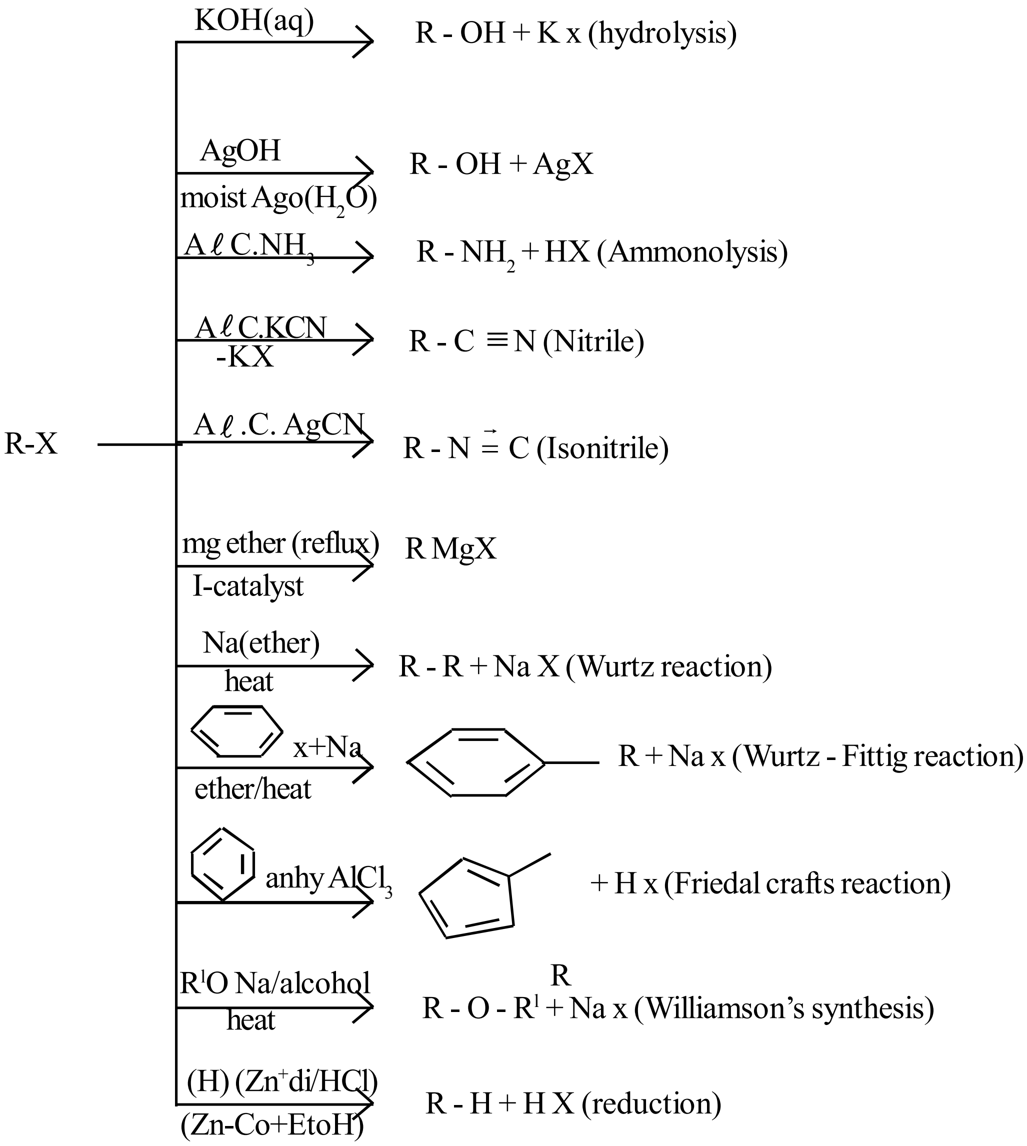
Reaction with NaOH: **Dows Process**

$$C_6H_5Cl+2NaOH \xrightarrow[320atm]{360^{\circ}C} C_6H_5ONa \xrightarrow[C_6H_5OH]{dil\ HCl}$$

The reaction proceeds through benzene intermediate.

For different halogen, the order is I>Br>Cl

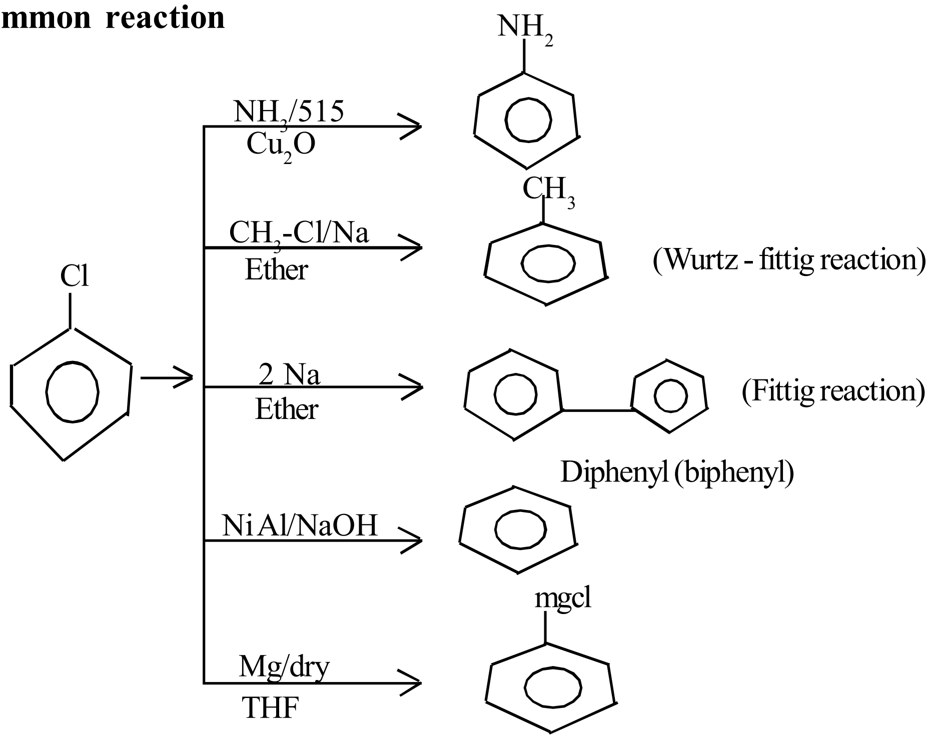
Common Reaction



Chemical properties Aryl Halides

- The aryl halides are relatively less reactive towards necleophile substitution reaction as compared to alkyl halides, This low reactivity can attributed to the following factors.
- Due to resonance, the electron density increases more at ortho and para position than at meta positions. Further the halogen atom, because of its - I effect has some tendency to with draw electrons from the benzene ring. As a result the ring get some what deactivated as compared to benzene and hence, the electrophilic substituition reaction in halo arenes occurs slowly and requires more drastic conditions as compared to those in benzene.

Common reaction



Electrophile Substitution reaction

- Halo arenes undergo the usual electrophile reaction of the benzene ring such as halogenation Nitration, Sulphonation and Fiedel Crafts reaction.
- Halogen atom besides being slightly de activating is O, P directing, there fore further substitution occurs at ortho and para position with respect to halogen atom.
- It is used in carbylamine test for primary amines.
- It is used in organic solvent
- It is used in the preparationof important compounds like Chloropicrin
- Upon action of air and light, it forms a poisonous gas phosgene

$$2CHCl_3+O_2 \xrightarrow{\text{light}} \underset{\text{Phosgene}}{2COCl_2} + 2\,HCl$$

- So it is kept in a dark coloured bottle

Poly halogen compounds

1) Di-Chloromethane [CH_2Cl_2]

- It is used as a solvent, paint remove, propellant in aerosols and as a process solvent in the manufacture of drugs.
- It is used as a metal cleaning and finishing solvent.
- Methylene Chloride harms the human central nervous system. Exposure to lower level of methylene chloride in air can lead to slightly impaired hearing and vision.
- High level of methylene chloride in air cause dizziness, nausea, tingling and numbness in the fingers and toes.
- Direct contact with cornea can burn it

2) Chloroform($CHCl_3$)

- Previously, it was used as an anaesthetic but has been replaced now due to its ill effects. Since in this reaction. first elimination of HCl occurs and then addition of NH_3 takes place it is called elimination- addition reaction.
- If both the o position with respect to Cl atom is blocked, then benzyne intermediate is not obtained

3) Iodoform [CHI_3]

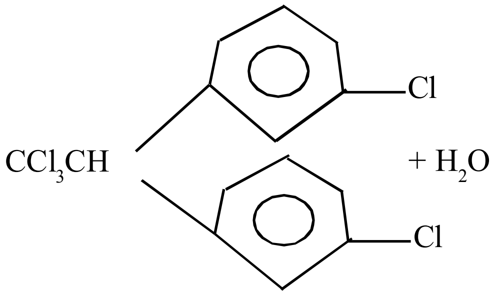
- Order of reactivity of trihaligen derivatives is iodoform > bromoform>chloroform
- Iodoform gives yellow precipitate of AgI with silver
- On heating with a primary amine and alkali foul smell of isocyanide is produced.

4) Freons

- Poly chloro fluro alkanes are known as freons. They are colourless, odourless, non toxic, non inflammable liquids with very less chemical reactivity and high stability.
- Chlorofluoro carbons (CFC's) known as freons commercially used for refrigeration purpose are highly volatile and stable in nature.
- They react with ozone and deplete it and clears the path for the uv rays to get in to earth.

5) DDT (PP^{I} dichlorodiphynyl trichloro ethane)

- It is a powerful insecticide and is effective against mosquito that spreads malaria
- Prepared by heating chlorobenzene and chlorine in presence of conc H_2SO_4



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Chapter - XI

ALCOHOLS, PHENOLS AND ETHERS

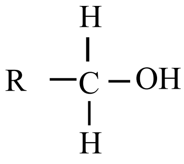
- The compound obtaineds by replacing one hydrogen atom from aliphatic hydrocarbons by -OH group are called alcohols where as those obtained by replacing hydrogen of aromatic hydrocarbons are known as phenols.
- Compounds conataining an oxygen atom bonded to two (same / different) alkyl/aryl groups are knwon as ethers)

General Formula

- Alcohol : [R-OH]
- Phenol : [Ar-OH]
- Ethers : [R-O-R/R-OR’] n>1

Alcohols and Phenols

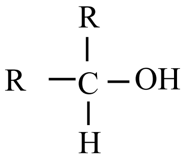
- Monohydric alcohols can be classified as primary, secondary and tertiary depending upon whether the OH group is attached to 1°, 2° or 3° C- atom.



$$R-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-OH$$

Primary Alcohol

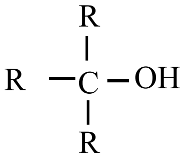
1^0



$$R-\overset{\overset{R}{|}}{\underset{\underset{H}{|}}{C}}-OH$$

Secondary Alcohol

2^0

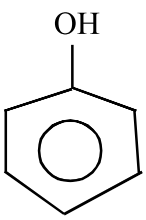


$$R-\overset{\overset{R}{|}}{\underset{\underset{R}{|}}{C}}-OH$$

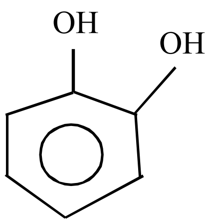
Tertiary Alcohol

3^0

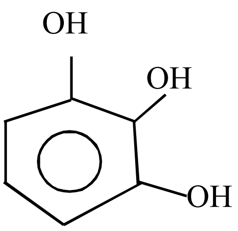
- Phenols may be classified as mono, di or trihydric according to the no of -OH group attached to Benzene group.



(Monohydric)



(Dihydric)



(Trihydric)

Ethers may be classified as

- Alphatic ethers

  CH_3-O-CH_3 Dimethylether

  CH_3-O-CH_2CH_3 Ethylmethyl ether

- Aromatic ethers

  Eg: C_6H_5O-CH_3 Methyl Phenyl Ethers

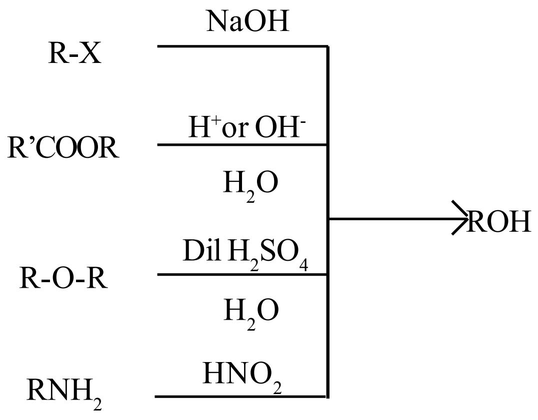
  C_6H_5O-C_6H_5 Diphenylether

Structure of functional group

- In alcohol, the oxygen of the -OH group is attached to carbon by a sigma bond formed by the overlape of the sp^3 hybrid orbitals of carbon with a sp^3 hybrid orbital of oxygen.
- The bond angle in alcohols is slightly less than the tetrahedral angle [109°28']

  It is due to the repulsion between the unshared electron pair oxygen.
- In phenols OH group is attached to sp^2 hybridised carbon of an aromatic ring.

General Methods of Preparation of Alcohols

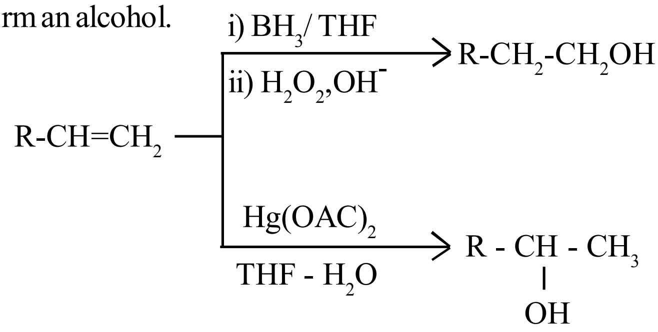


- Hydration of alkenes

  Step I $H_2O + H^+ \rightarrow H_3O^+$

  Step II nuclephilic attack of water on carbocation

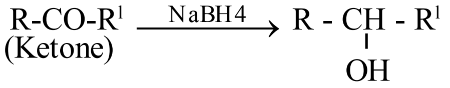
  Step III De protonation to form an alcohol.



- From Carbonyl compounds

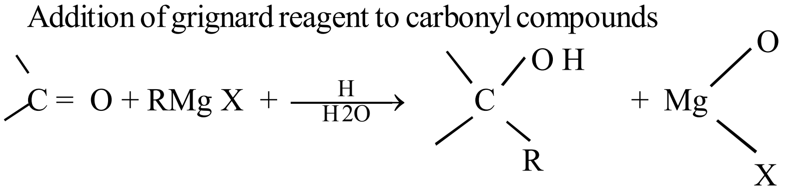
$$\underset{\text{(Aldehyde)}}{RCHO+2H} \xrightarrow{LiAlH_4} RCH_2OH \text{ } (1^0 \text{ alcohole})$$

$$RCHO+ H_2 \xrightarrow{Pd} RCH_2OH$$

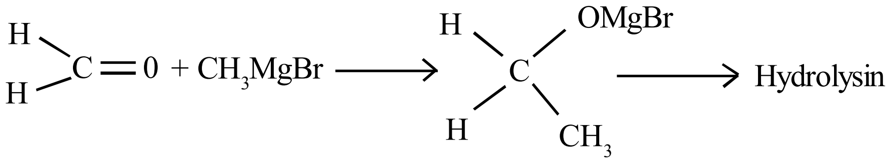


$$\underset{\text{(Ketone)}}{R\text{-}CO\text{-}R^1} \xrightarrow{NaBH4} R - \underset{\underset{OH}{|}}{CH} - R^1$$

- Addition of grignard reagent to carbonyl compounds



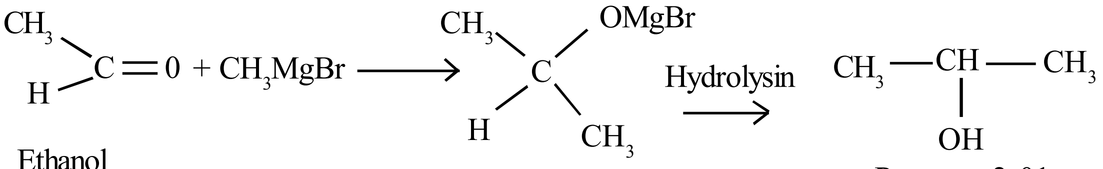
Eg:-(1)



Methanol

CH_3-CH_2-OH+MgBr(OH)
Ethanol

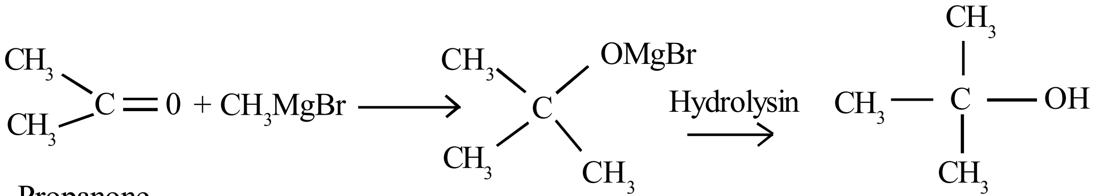
(2)



Ethanol

Propan - 2-01

(3)



Propanone

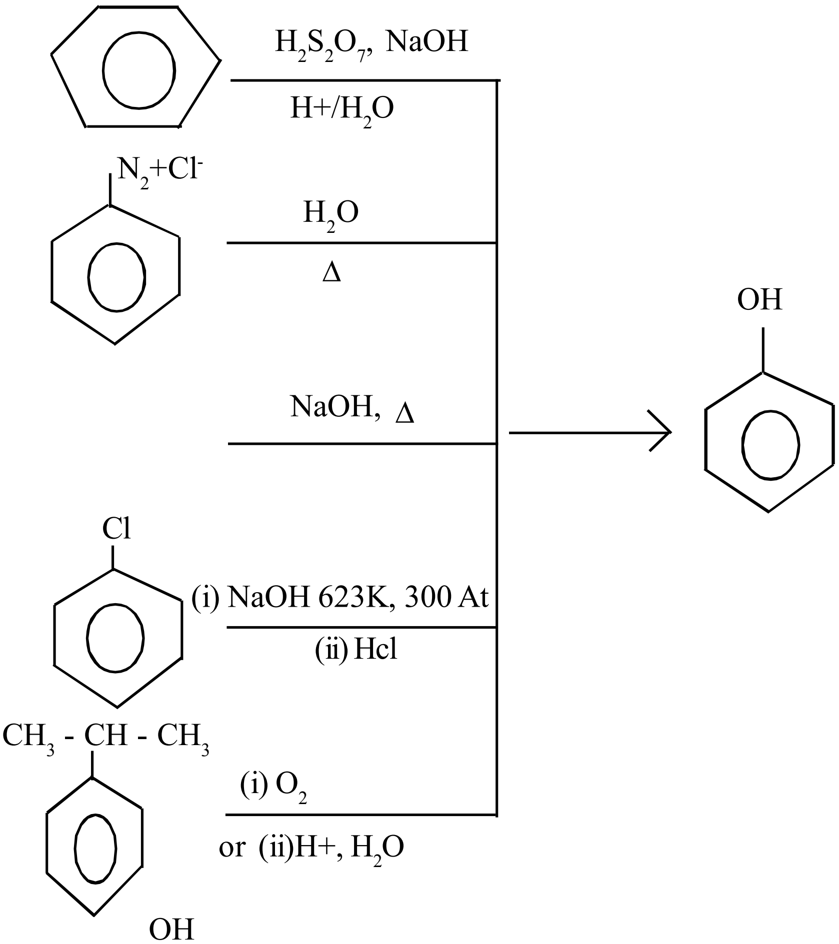
2-Methyl Propan - 2-01

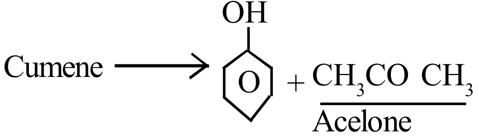
1^o Alcohol is obtained from HCHO

2^o Alcohol is obtained from RCHO

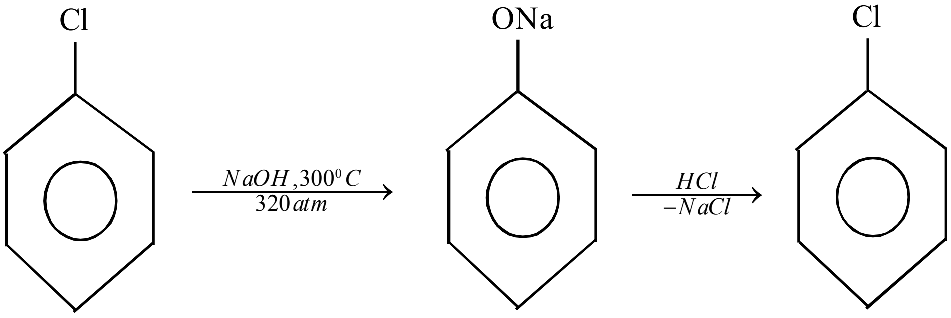
3^o Alcohol is obtained from RCOR, R may or may not be equal to R’

Preparation of phenol





- Hydrolysis of Aryl halides [Dows process]



Physical Properties of Alcohols

- Physical State : Alcohols are colourless, volatile liquids having characteristic colour and bruning taste.
- Smell and taste of alcohols become less pronounced with increase in molecular weight.

- Boiling point - Due to the presence of -OH group alcohols undergo intermolecular hydrogen bonding and exist as associated molecule. Hence the boiling point of alcohols are much higher thanthe corresponding hydrocarbons of comparable molecular weight,
- Amongst isomeric alcohols boiling point follow the order $1^{o}>2^{o}>3^{o}$ which can be explained by the decrease in surface are a with branching.
- Solubilty -Lower alcohols are soluble in water due to hydrogen bonding. But the solubility decreases with increase of molecular mass since hydrocarbon part increase which interrupts the hydrogen bond formation.
- Among the isomeric alcohols solubility increases with branching since surface area of hydrocarbon part decreases with increase of branching.

Physical Properties of Phenols

- Physical State : Phenols are colourless liquids or low melting solids. But they turn reddish brown due to auto oxidation on exposure to air and light.
- Boiling point :Phenols have much higher boiling points than the corresponding hydrocarbons due to intermolecular hydrogen bonding.
- Solubility - Phenols form H Bonds with water molecules and hence are soluble in water. But their solubility is lower than that of alcohols because of large hydrocarbon part.

Chemical Properties of Alcohol

Acidic Nature

i) Reaction with metals : Alcohols react with active metals (Sodium, K, Al) to yield corresponding Alkoxides / Phenoxides and hydrogen

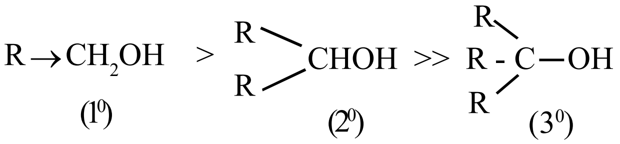
$$2R\text{-}O\text{-}H + 2\,Na \rightarrow 2R\text{-}O\text{-}Na + H_2$$

Sodium Alroxide

- Alcohols are Bronsted acids, ic they can donate a proton to a stronger base

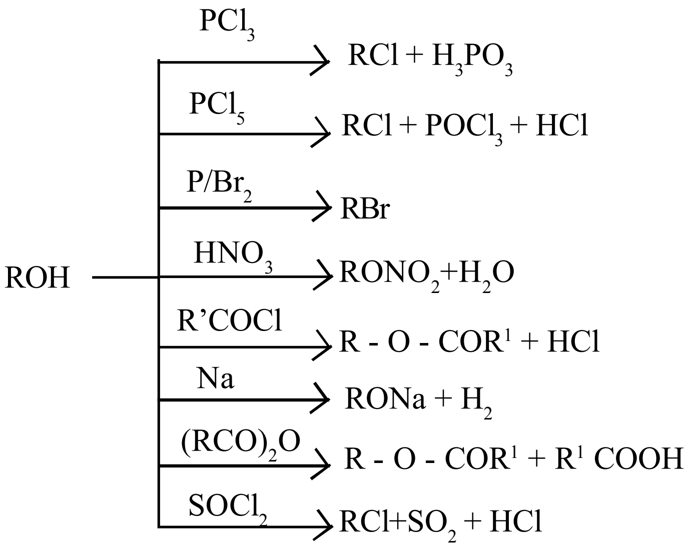
iii) Acidic character of alcohols is due to the polar nature of O-H bond. An electron density on oxygen tendency to decreases. The Polarity of O-H bonds. This decreases the acid strength

- Acids strength of alcohols decreases as per the order



$$\underset{(1^{0})}{R\rightarrow CH_2OH} > \underset{(2^{0})}{R_2CHOH} >> \underset{(3^{0})}{R_3C\text{—}OH}$$

- Alcohols are weaker acids than water
- Water is a better proton donor (ie stronger acid)
- Alcohols act as Bronsted bases due to the presence of unshared electron pairs
- Common reactions of alcohols



- **Dehydration**

$$CH_3CH_2OH \xrightarrow[120^\circ C]{Con\ H_2SO_4} CH_2{=}\ CH_2{+}H_2O$$

- **Esterification**

$$CH_3COOH{+}CH_3CH_2OH \xrightarrow{H_2SO_4} CH_3COOCH_2CH_3$$

Reactively of alcoholes

CH_3OH>Primary>Secondary>Tertiary

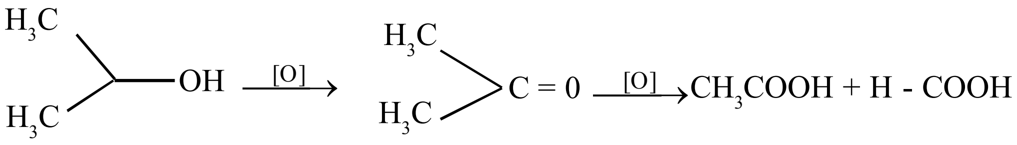
Reactively of acides

$HCOOH>CH_3COOH>CH_3CH_2COOH$

- **Oxidation**

$$CH_3CH_2OH \xrightarrow{[O]} CH_3CHO \xrightarrow{[O]} CH_3COOH$$

1^0 Alcohol



2^0 Alcohol

- **Iodoform test**

$$CH_3CH_2OH \xrightarrow{I^2/\ NaOH} CHI_3\ + HCOONa{+}NaI{+}H_2O$$

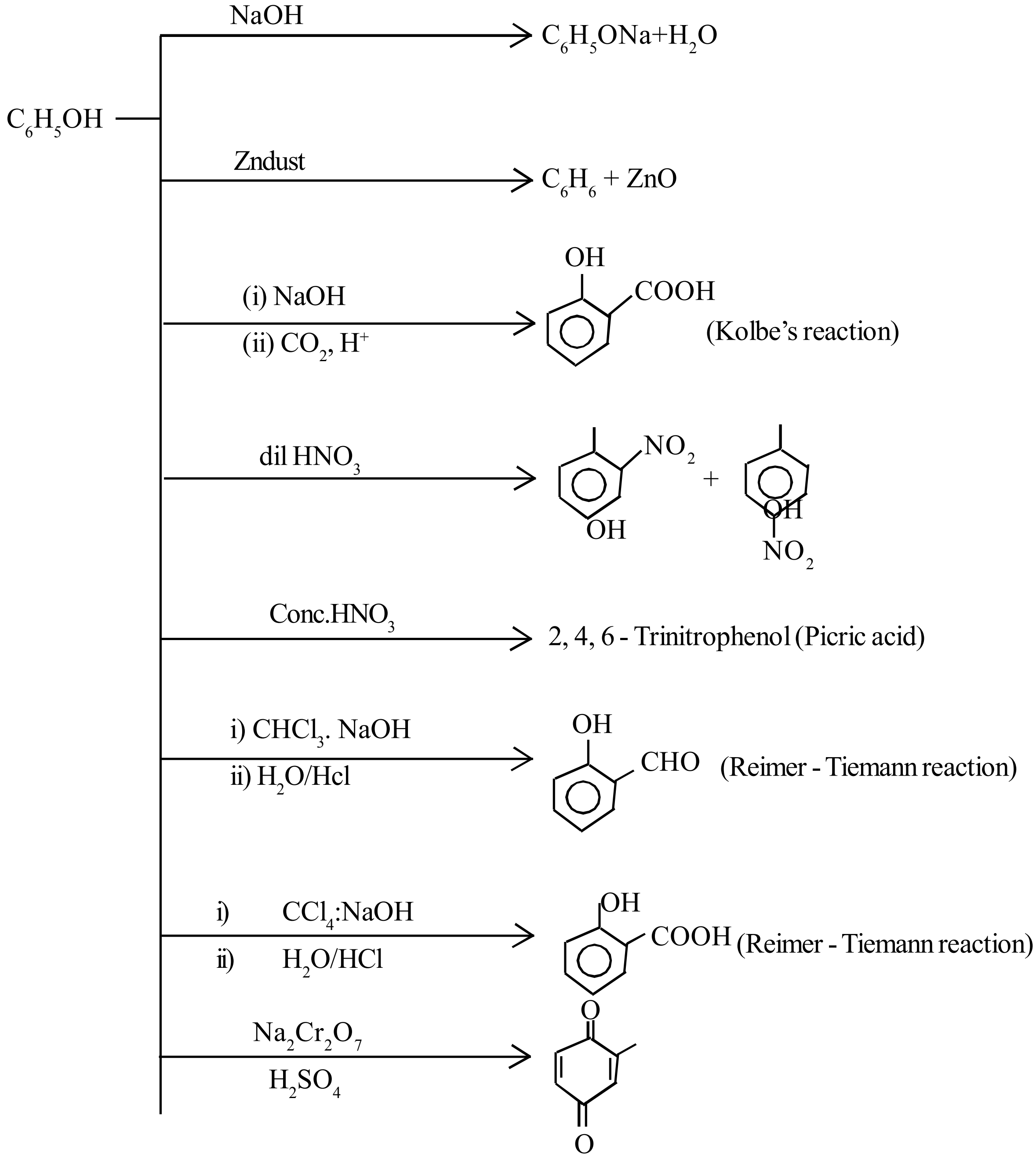
- **Lucas test :** When alcohols are treated with Lucas reagent (con Hcl&2ncl$_2$) turbidity (Alkyl chlorids) is produced. In case of 3^0 alcohols, turbidity is produced immediately. 1^0 alcohols do not produce turbidity at room temperature.

Chemical Properties of Phenol

Audic Nature

Phenol is acidic in nature due ti greater resonence stabilization of phenoxides ion than phenol itself.

- It turns blue litmas to red and reacts with alkali metal to form salt.
- Reaction of Phenols



Benzoquinone

Some Commercially important alcohols

- Wood Spirit
- Methanol is also known as wood spirit sence it was originally obtained by destrictive distillation of wood.

$CO+2H_2 \xrightarrow[200-300atm500]{ZnO-Cr_2O_3} CH_3OH$

- It is highly poisonous. That is why it is used for denaturing ethyl alcohol ie, to make it unfit for drinking purpose.

  Denatured spirit is also called methylated spirit.
- It is used as an Antificez for automobiles radeator and a substitute for petrol.

Rectified Spirit

- 95% ethanol solution is known a reactified spirit and it is prepared by fementation of carbohydrate,

  $C_{12}H_{22}O_{11} + H_2O \longrightarrow \underset{\text{(glucose)}}{C_6H_{12}O_6} + \underset{\text{(fructose)}}{C_6H_{12}O_6}$

  $C_6H_{12}O_6 \longrightarrow 2C_2H_5OH + 2CO_2$
- It is mainly used for manufacturing alcoholic beverages ie, Whisky, brandy, beer, rum etc.
- It is also used as antifieeze in automobile radiators and as a substitute for petrol.
- It is also used as an important solvent for plaints, varneshes, dyes, cosmetics, perfumes etc.
- Absolute alcohol

  100% alcohol is known as absolute alcohole and it is prepared from rectified spirit.

Ethers - alkoxy alkanes

Classification

Ethers are classified into the following two categories.

- Allphatic ethers: Here two alkyl groups are linked to oxygen atom.

  Eg: CH_3-O-CH_3 - Methoxymethane

  H_3C-CH_2-O-CH_2-CH_3 - Ethoxy ethane
- Aromatic ethers - Here either one or two a aryl groups are linked to oxygen atom.

  Eg: C_6H_5-O-CH_3 (anisole)

  C_6H_5-O-CH_2CH_3

General Methods of Preparation

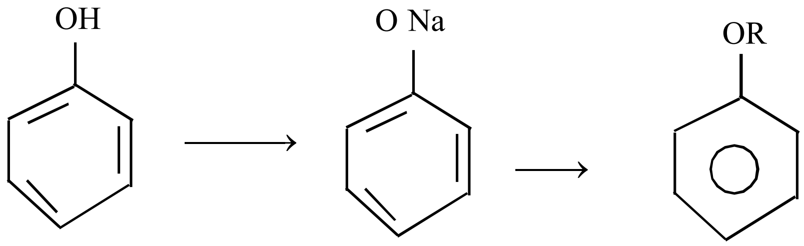
- William son's synthesis

  CH_3-CH_2-Br+CH_3-O Na^+ $\rightarrow CH_3CH_2$-O-CH_3
- For better yields the alkyl halide should be 1^0 and Alkoxide should be 2^0 or 3^0

- **Dehydiation of alcohols**

  $CH_3CH_2OH+CH_3CH_2OH \longrightarrow CH_2\ CH_2\ OCH_2\ CH_3$
- **Action of diasomethane on alcohols**

  $R\text{-}CH_2OH + CH_2\ N_2 \longrightarrow RCH_2 - OCH_3 + N_2$
- We can get aromatic ether from phenol as



Structure of ether

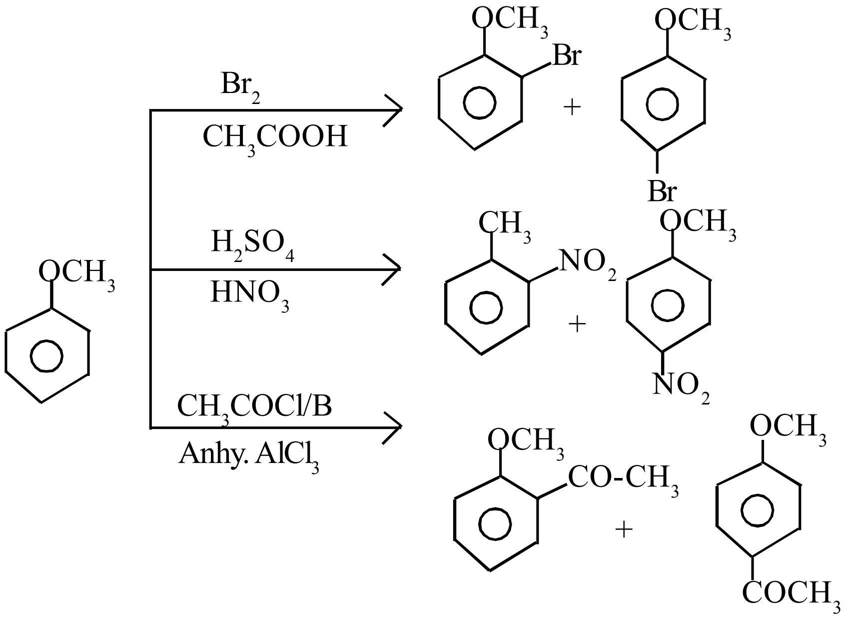
- In ether 'O' atom is in sp^3 hybridised state ie, it has four sp^3 hybrid orbitals. Two of these sp^3 hybrid orbitals contain lone pair of electrons and rest of the two sp^3 hybrid orbetals contain unpaired electron which overlap with sp^3 hybrid orbetal of carbon of two alkyl groups having unpaired electrons and form a bond.
- ....C-O-C... bond angle in ether is about 110^0 which is slightly greater than that of H_2O molecular (having 104.5^0)
- In ether the bond angle is slightly greater than the tetra hedral angle due to the repulsive interaction between the two bulky (-R) groups. The C-O bond length (141p.m.) is almost the same as in alcohols. This ether has a bent structure and are polar in nature.

Physical Properties of ether

- Dimethyl/ether, ethyl/methyl/ether are gases
- All other ethers are colourless liquids with good odour.
- Low polarity and water solubility.
- Boiling point increase gradually with increase in molecular mass.

Chemical Properties of ethers

- **Reaction of aromatic ethers**



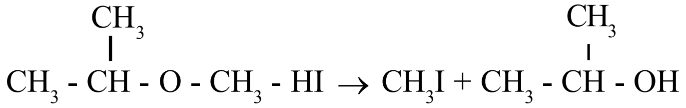
- **Cleavage of unsymmetrical ether**

During the cleavage of unsymmetrical ether. Smaller alkyl group produce alkyl halides.

Eg:- CH_3 - O - CH_3 CH_3 + HBr → CH_3 Br + CH_3CH_2OH

ethy / methy / ether methyl promide ethanol

- If ether consists of one methyl group and one 1^0 or 2^0 alkyl group, then S_N2 mechanism takes place. In such a case methyl halide is obtained with alcohol of bulky alkyl group.



$$CH_3 - \overset{\overset{\large CH_3}{|}}{CH} - O - CH_3 - HI \rightarrow CH_3I + CH_3 - \overset{\overset{\large CH_3}{|}}{CH} - OH$$

Mehylso-propyl ether methyl iodide Iso propyl alcohol

If ether consists of one methyl group and one 3^0 alkyl group, then reaction is completed by S_N1 mechanism.

* * *

Chapter XII

ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

Aldehydes and Ketones

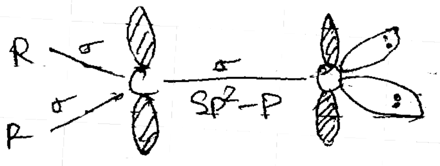
- Aldehydes and Ketones contains carbonyl > C=0 groups
- These are funcional isomers having general molecular formula $C_nH_{2n}O$

Nomenclature

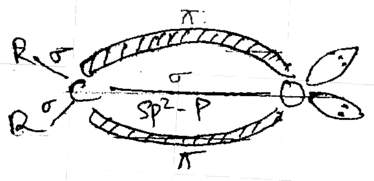
- In IUPAC system, aliphatic aldehydes are named as alkanals. In the aromatic aldehydes the parent member is called Benzaldehyde.
- In IUPAC aliphatic and Aromatic retones are names as alkanones.

Structure

- Carbonyl carbon of both aldehydes and ketones is Sp^2 hybridised.
- One of the three sp^2 hybridised orbital gets involved in a bond formation with half filled p - orbital of oxygen aton whereas rest fo the two are consumed in bond formation with hydorgen and carbon depending upon the structure of aldehydes or ketone.



aldehydes



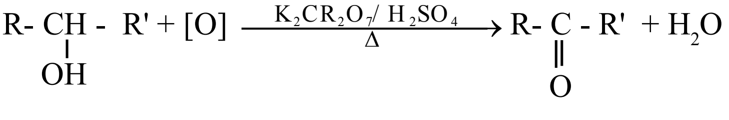
ketones

General methods of preparation

- **By oxidation of alcohols:**

$$RCH_2\text{-}OH + [O] \xrightarrow[\Delta]{K_2CR_2O_7/\ H_2SO_4} RCHO + H_2O \text{ aldehyde}$$

1°alcohol

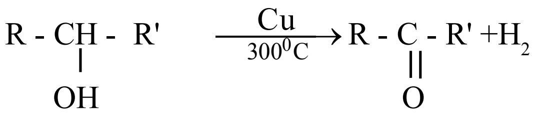


$$R\text{-}\underset{\substack{|\\ OH}}{CH}\text{-}R' + [O] \xrightarrow[\Delta]{K_2CR_2O_7/\ H_2SO_4} R\text{-}\underset{\substack{\|\\ O}}{C}\text{-}R' + H_2O$$

- **By dehydration of alcoholds**

$$R\text{-}CH_2\text{-}OH \xrightarrow[300^0C]{Cu} R\text{-}CHO + H_2$$

1°alcohol aldehyde



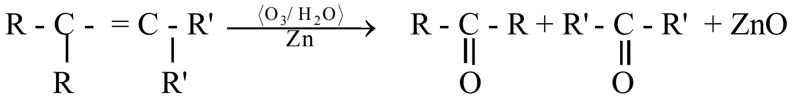
$$R-\underset{\underset{OH}{|}}{CH}-R' \xrightarrow[300^0C]{Cu} R-\underset{\underset{O}{||}}{C}-R' + H_2$$

2°alcohol ketones

- **By oxidation of alkenes**

$R-CH=CH-R \xrightarrow[Zn]{\langle O_3/H_2O\rangle} 2(R\text{-}(CHO) + Zn\,O$

alkene aldehyde



$$R-\underset{\underset{R}{|}}{C}-=\underset{\underset{R'}{|}}{C}-R' \xrightarrow[Zn]{\langle O_3/H_2O\rangle} R-\underset{\underset{O}{||}}{C}-R + R'-\underset{\underset{O}{||}}{C}-R' + ZnO$$

alkenes

- **By reduction of acid chloride [Rosemund reaction]**

$R-COCl + H_2 \xrightarrow[140^0C]{Pd-BaSO_4} R-CHO + HCl$

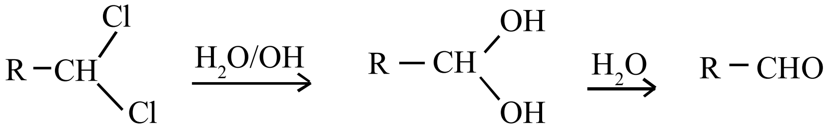
Formaldehyde can not be prepared by this method.

$2R-COCl + CdR_2' \rightarrow 2RCOR' + CdCl_2$

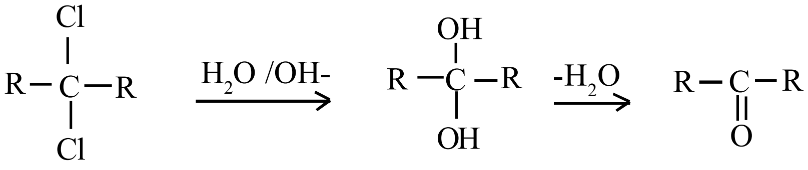
$RCOCl + R'CdCl \rightarrow RCOR' + CdCl_2$

acid chloride ketones

- **By hydrolysis of gem dihalides**



gem dichloride unstable aldehyde



$$R-\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{C}}-R \xrightarrow{H_2O\ /OH-} R-\underset{\underset{OH}{|}}{\overset{\overset{OH}{|}}{C}}-R \xrightarrow{-H_2O} R-\underset{\underset{O}{||}}{C}-R$$

unstable Ketone

- **By heatiing calcium salt of fatty acid**

$(R\text{-}COO)_2Ca + (H\text{-}COO)_2Ca \xrightarrow{\Delta} 2(R\text{-}CHO) + 2CaCO_3$

Calcium salt Calcium formate aldehyde

$(R\text{-}COO)_2Ca \xrightarrow{\Delta} + R-CO-R + CaCO_3$

Calcium salt Ketone

- **By stephen's reduction reaction**

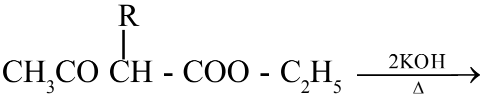
$R - CN + 2H \xrightarrow[\Delta]{SnCl_2 - HCl} R - CH = NH$

Alkyl Cyanide Aldimine

$\xrightarrow[\Delta]{H_2O} R\text{-}CHO + NH_3$

aldehyde

- **By hydrolysis of aceto acetic ester**



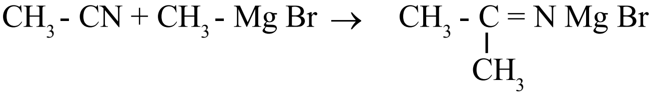
$CH_3CO\overset{\overset{R}{|}}{C}H - COO - C_2H_5 \xrightarrow[\Delta]{2KOH}$

Alkyl acetoaciti acid

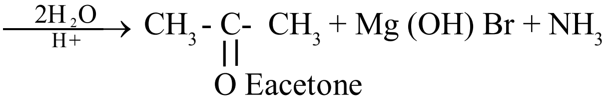
$CH_3COCH_2R + K2CO_3 + C_2H_5OH$

Ketone

- **From Grignard reagent**



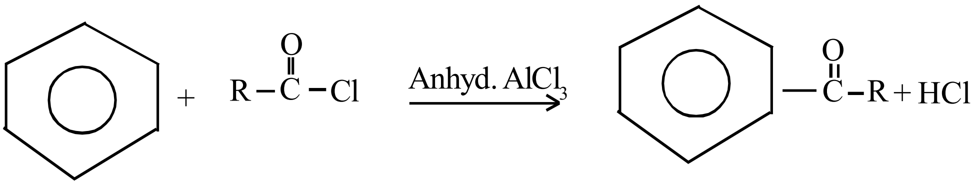
$CH_3 - CN + CH_3 - Mg\ Br \rightarrow CH_3 - \underset{\underset{CH_3}{|}}{C} = N\ Mg\ Br$



$\xrightarrow[H+]{2H_2O} CH_3 - \underset{\underset{O}{||}}{C} - CH_3 + Mg\ (OH)\ Br + NH_3$

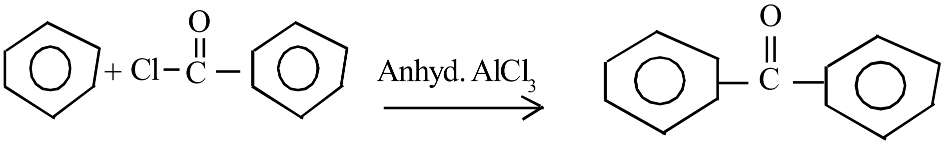
Eacetone

- **Field Carfts Acylation**



Benzene

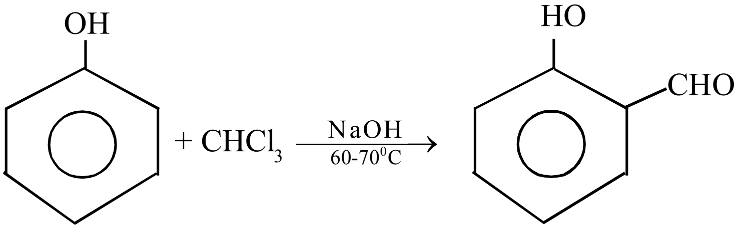
Aromatic Ketone



Benzyl chloride

Benzophenone

- **Reemer Tiemen Reaction**



Salicyladehyde

Physical Properties

Only formaldehyde is a gas, where as higher members are liquids or solids.

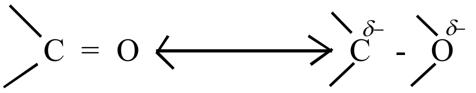
- Boiling point of aldehydes and ketones are less than that of corresponding alohols because of the lack of H-bonding in them. But more than corresponding alkanes because of the presence of dipole - dipole interaction between them

Solubility

- Lower member of aldehydes and ketones are soluble in water due to the H - Bonding between polar carbonyl group and water.
- Solubility decreases with increase in molecular weight.
- Aromatic aldehydes and ketones are much less soluble than corresponding aliphatic aldehydes and ketones due to large benzene ring.

Chemical Property

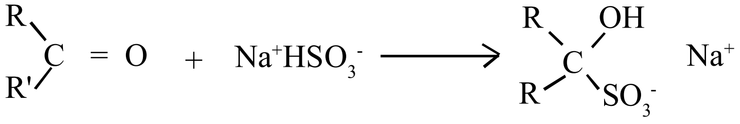
- Carbonyl compunbd have C = O group which as polar due to presence of more electronegative oxygen atom. The result in polarisation of electron as



- The rate determining step is attack of necleophile over carbonyl carbon atom.
- The only difference between >C=O group reaction and >C=C<group reaction is that the former one undergo nuclephile addition and latter one undergoes electrophilic addition reaction.
- The nucleophile addition depend on the positive charge.

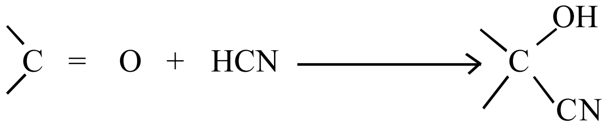
Nucleophile Addition reaction

Addition of NaHSO$_3$



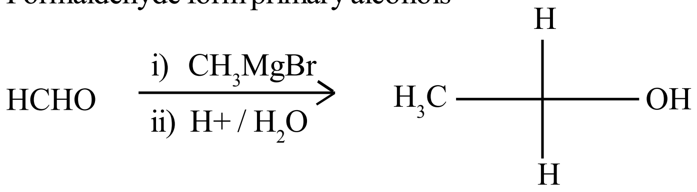
- Ketones containing bulky alkyl group such as diethyl ketone, methyl felt butyl ketone etc do not react with $NaHSO_3$
- Only benzaldehyde forms sodium bisulphite

Addition of HCN

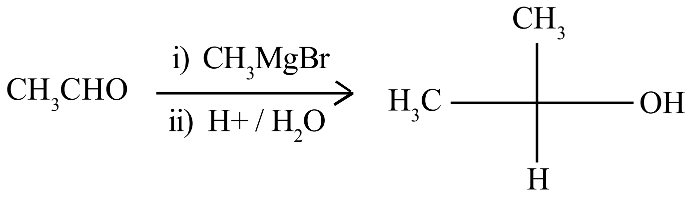


Cyanohydrin

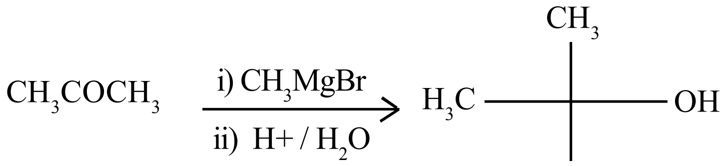
- Addition of Gridnard reagent
- Formaldehyde form primary alcohols



$$HCHO \xrightarrow[\text{ii) } H+/H_2O]{\text{i) } CH_3MgBr} H_3C-\overset{H}{\underset{H}{C}}-OH$$



$$CH_3CHO \xrightarrow[\text{ii) } H+/H_2O]{\text{i) } CH_3MgBr} H_3C-\overset{CH_3}{\underset{H}{C}}-OH$$

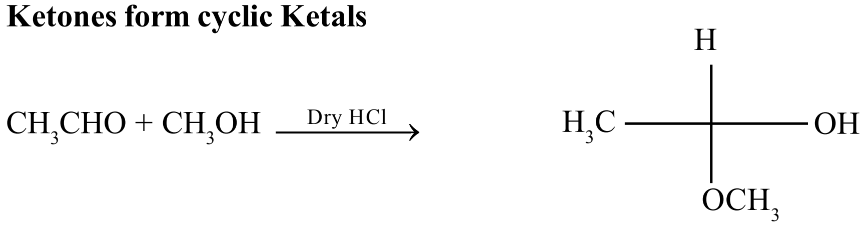


$$CH_3COCH_3 \xrightarrow[\text{ii) } H+/H_2O]{\text{i) } CH_3MgBr} H_3C-\overset{CH_3}{\underset{CH_3}{C}}-OH$$

Addition of Alcohols

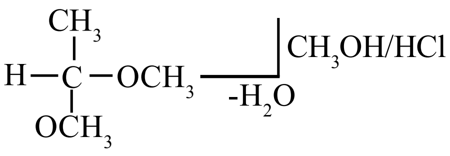
Aldehydes react with alcohols in presence of dry HCl to form dialkoxy alkanes called acetals

- **Ketones form cyclic Ketals**



$$CH_3CHO + CH_3OH \xrightarrow{\text{Dry HCl}} H_3C-\overset{H}{\underset{OCH_3}{C}}-OH$$

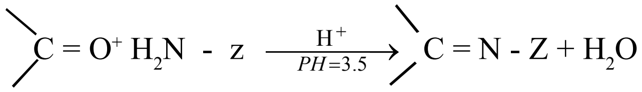
Hemi acetal



$$H-\overset{CH_3}{\underset{OCH_3}{C}}-OCH_3 \xleftarrow[-H_2O]{CH_3OH/HCl}$$

Acetal

- Nucleophile addition followed by loss of water
- Reaction with ammonia derivatives (NH_2-2)



$$>C = O^+ H_2N - z \xrightarrow[PH=3.5]{H^+} >C = N - Z + H_2O$$

where z=OH, NH_2, - NHC_6H_5M - $NHCONH_2$ etc

- Oxidation of aldehyde and ketones
- Oxydation of aldehydes
- Aldehydes can be oxidised to carboxylic acids having same number of carbon atoms.

$RCHO + 2[Ag(NH_3)_2]^+ \quad 3OH^- \rightarrow RCOO^- + 4NH_3 + 2H_20 + 2Ag$ (Silver mirror)

(Tollen's reagent)

$RCHO + 2Cu^{2+} + 3OH- \rightarrow RCOO- + Cu^+ + 2H_2O$

From fehling or

Benedict's soln.

- Oxidation of Ketones
- Yields acids with lesser number of carbon atoms.

$CH_3COCH_2CH_2CH_3 \rightarrow CH_3COOH + CH_3CH_2COOH$

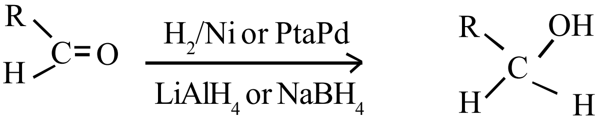
- Oxidation with sodium hypohalite

$CH_3CHO + 3I_2 \xrightarrow{NaOH} Cl_3\text{-}CHO \xrightarrow{NaOH} CHI_3 + HCOONa$

Iodoform Sodium Formate

Reduction

- Reduction to alocohols
- Catalytic reduction with complex metal hydrides



$$\begin{matrix} R \\ H \end{matrix}\!\!>C=O \xrightarrow[LiAlH_4 \text{ or } NaBH_4]{H_2/Ni \text{ or } PtaPd} \begin{matrix} R & & OH \\ & C & \\ H & & H \end{matrix}$$

Aldehydes → 1° alcohol

Ketones 2° → alcohol

Reduction to hydrocarbons

Clemmensen Reduction

$$RCHO + 4[H] \xrightarrow{Zn\text{-}Hg/HCl} R-CH_3 + H_2O$$

- **Wolf - Kishner reduction**

$$R-CH=O \xrightarrow[-H_2O]{NH_2NH_2} R-CH=NNH_2$$

Hydrazone

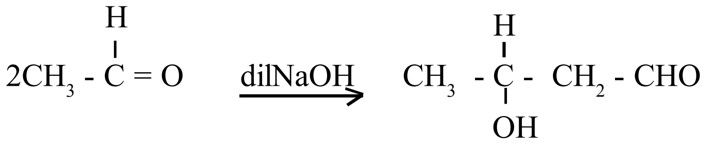
$$\xrightarrow{KOH\ glycol} R-CH_3 + NH_2$$

Acidity of α - hydrogen

- The α hydrogen of aldehyde and ketones are weakly audic due to I effect of the C=O which reduces the electron density in the C - H bond
- The carbanion on the enolate ion left after the removal of the proton is stabilized by resonance.

Other reactions

- Aldol condensation - given by only those aldehydes and ketones which contain α - H atoms



$$2CH_3-\overset{\overset{H}{|}}{C}=O \xrightarrow{dilNaOH} CH_3-\underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{C}}-CH_2-CHO$$

(Aldol)

$$\xrightarrow[-H_2O]{H+} CH_3CH = CHCHO$$

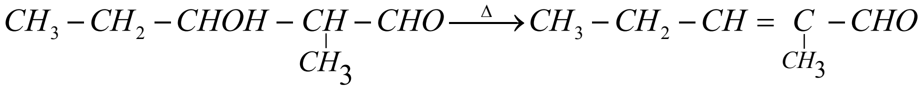
Cross Aldol Condensation

$$\begin{matrix}CH_3CHO\\+\\CH_3-CH_2-CHO\end{matrix}\xrightarrow[\Delta]{NaOH}$$

1) $CH_3CHOH-CH_2CHO\xrightarrow{\Delta}CH_3-CH=CH-CHO$

$But-2-enal$

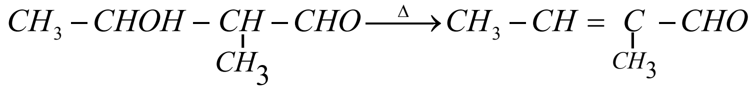
2)



$$CH_3-CH_2-CHOH-\underset{\underset{CH_3}{|}}{CH}-CHO\xrightarrow{\Delta}CH_3-CH_2-CH=\underset{\underset{CH_3}{|}}{C}-CHO$$

$2-Methylpent-2-enal$

3)

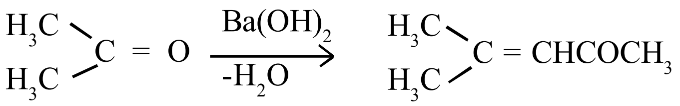


$$CH_3-CHOH-\underset{\underset{CH_3}{|}}{CH}-CHO\xrightarrow{\Delta}CH_3-CH=\underset{\underset{CH_3}{|}}{C}-CHO$$

$2-Methylbet-2-enal$

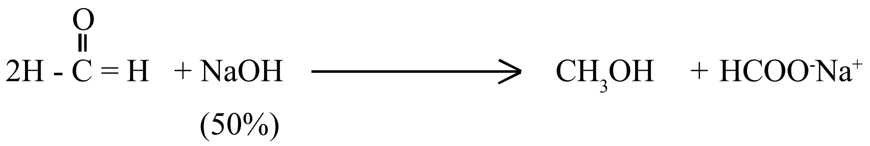
4) $CH_3-CH_2-CH\ OH\ CH_2CHO\xrightarrow{\Delta}CH_3-CH_2-CH=CH-CHO$

$Pent-2-enal$



4 methylpent 3en zone

- Cannozzaro reaction : Given by those aldehyde whih do not conatain α H atoms



$$2H-\overset{\overset{O}{\|}}{C}=H \;+\; \underset{(50\%)}{NaOH} \longrightarrow CH_3OH \;+\; HCOO^-Na^+$$

Disfinction between aldehyde and ketones

- **Tollen reagent -** Both aliphatic and aromatic aldehydes give silver mirror but ketones do not.
- **Fehling's solution** - Aliphatic aldehydes reduce Fehling's solution to give red ppt of Cu_2O while aromatic aldehydes and ketones do not.
- **Schiff's reagent test**: Aldehydes restore the pink colour of schiff's reagent (magnenta or resontine hydrochloride dissolved in water and its pink colour decolourins by passing SO_2 or H_2SO_3)
- **Iodoform test** : Methyl Ketones (CH_3COCH_3, $CH_3COCH_2CH_3$, $C_6H_5COCH_3$ etc) on treatment with I_2 / NaOH give yellow ppt of iodoform.

Carboxylic Acids

- Organic compound containing COOH group are known as carboxylic acids.
- Formula $C_nH_{2n}O_2$

Nomenclature

- Carbon chain is numbered from the carboxylic acid group.
- The longest chain containing the carboxylic group -COOH is selected
- While writing IUPAC name of carboxylic acid 'e' of alkane is replaced by oic acid.
  Eg $CH_3CH_2CHCOOHBr$ - 2 Bromo Butanoic Acid

Structure

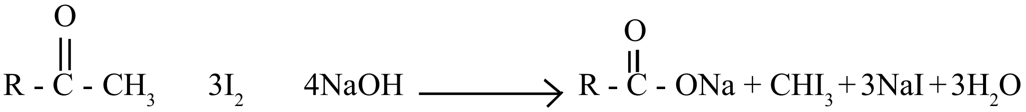
- Carbon atom of carboxyl group is sp^2 hybridised and form one one σ bond with each oxygen atom and one σ bond with hydregen or carbon atom depending upon the structure of carboxylic acid.
- Half filled p orbital of each oxygen atom and unhybridised p orbital of carbon atom lies in the same plane and overlap to form a bond which is localised between three atoms one carbon and two oxygen atom.

General method of preparation

- **From 1° alcohol and aldehydes :** Oxidation of primary alcohols and aldehydes with neutral acid or alkaline $KMnO_4$ or acidic $K_2Cr_2O_7$ gives corresponding carboxylic acid.

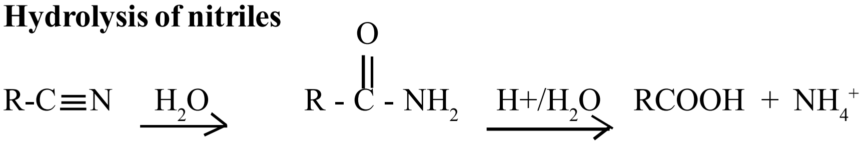
$$RCH_2OH \xrightarrow{[O]} RCHO \xrightarrow{[O]} R\text{-}COOH$$

- **Oxidation of methyl Ketones**



$$R - \overset{\overset{O}{||}}{C} - CH_3 \quad 3I_2 \quad 4NaOH \longrightarrow R - \overset{\overset{O}{||}}{C} - ONa + CHI_3 + 3NaI + 3H_2O$$

- **Hydrolysis of nitriles**

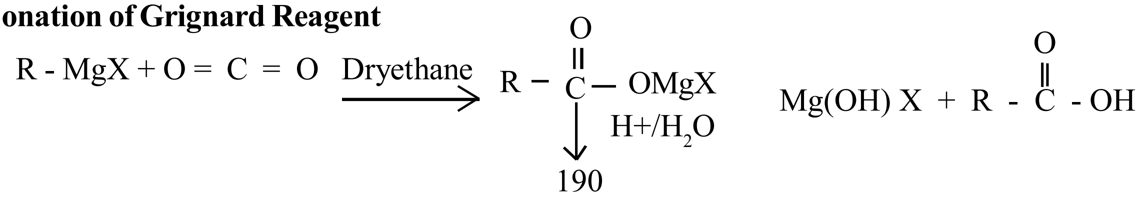


$$R\text{-}C{\equiv}N \xrightarrow{H_2O} R - \overset{\overset{O}{||}}{C} - NH_2 \xrightarrow{H+/H_2O} RCOOH + NH_4^+$$

- **KOH reaction [Carboxylation of olefins]**

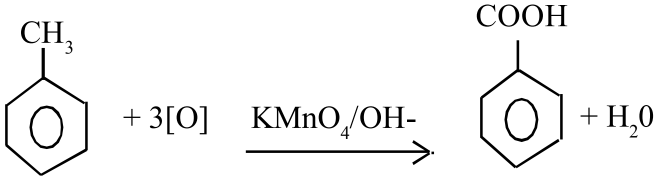
$$H_2C = CH_2 + CO{+}H_2O \xrightarrow[300\text{-}400^{o}C]{H_3PO_4} CH_3CH_2 - COOH$$

Carbonation of Grignard Reagent



$$R - MgX + O = C = O \xrightarrow{Dryethane} R - \overset{\overset{O}{||}}{C} - OMgX \;\; \xrightarrow[\;190\;]{H+/H_2O} \;\; Mg(OH)\,X + R - \overset{\overset{O}{||}}{C} - OH$$

- **Oxidation of alkyl benzene**



Physical Properties

Physical Properties

- Lower acids up to C_{10} are colour less liquids while higher ones are colourless waxy solids
- Solubility decreases as the molecular mass increases.
- Boiling point of aliphatic mono carboxylic acids are much higher than those of hydrocarbon and some what higher than those of alohols of comparable molecular mass due to stronger H bond
- Melting point of an acid with even number of C atom is higher

Acidic Stength

- Carboxylic acid ionize in acqueous solution and exist in equilibrium with carboxylate ion.
- Carboxylate ion is stabilised by resonance.

Effect of Substituent on acidic strength

- If an electron with drawing group is present then there will be dispersion of negative charge on the carboxylate ion as a result it will be more stable than those acids which do not have electron withdrawing groups.
- More the effect of electron withdrawing group the compount will be more acdic. Thus fluoroacitic acid is more acidic than chloroacetic and finally acetic acid.
- More the number of halogen atom, greater would be the dispersion of the negative charge and hence more will be stabilization of anion and the compound will be more acidic. Thus

$CCl_3COOH > Cl_2CHCOOH > ClCH_2COOH > BrCH_2COOH > ICH_2COOH$

Number of substituents

$Cl_3CCOOH > Cl_2\text{-}CH\text{-}COOH > ClCH_2COOH$

Position of substituents

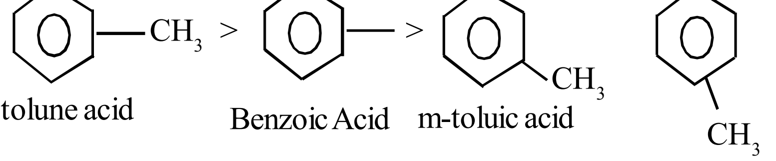
$CHCl\text{-}COOH > CHCl\text{-}CH_2COOH > CHCl\text{-}CH_2CH_2COOH$

relative acidic strenght of substitued aromatic acids

- Electron donatong substituens(+I effect) decreases the acidic strength where as electron with drawing groups (-I effect) increases the acidic strenght of substituted benzoic acids.
- Benzoic acid is less acidic than formic acid because of +I effect of Phenyl Group.
- The +I effect of Phenyl is less than that of methyl group hence

$H\text{-}COOH > C_6H_5\text{-}COOH > CH_3COOH$

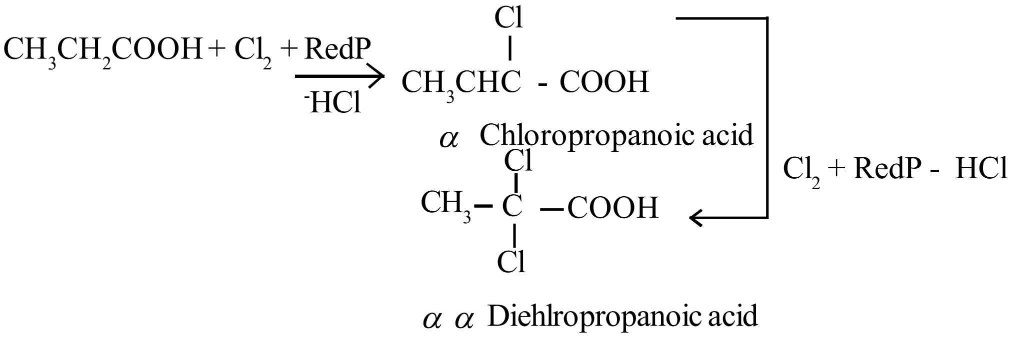
- Ortho substituted benzoic aicd are more acidic among the three isomers.
- This is called ortho effect and it arises due to combined effect of steric and electronic factors.



O-tolune acid Benzoic Acid m-toluic acid p-toluic acid

Chemical Properties

- Hell Volhard Zelnsky reaction



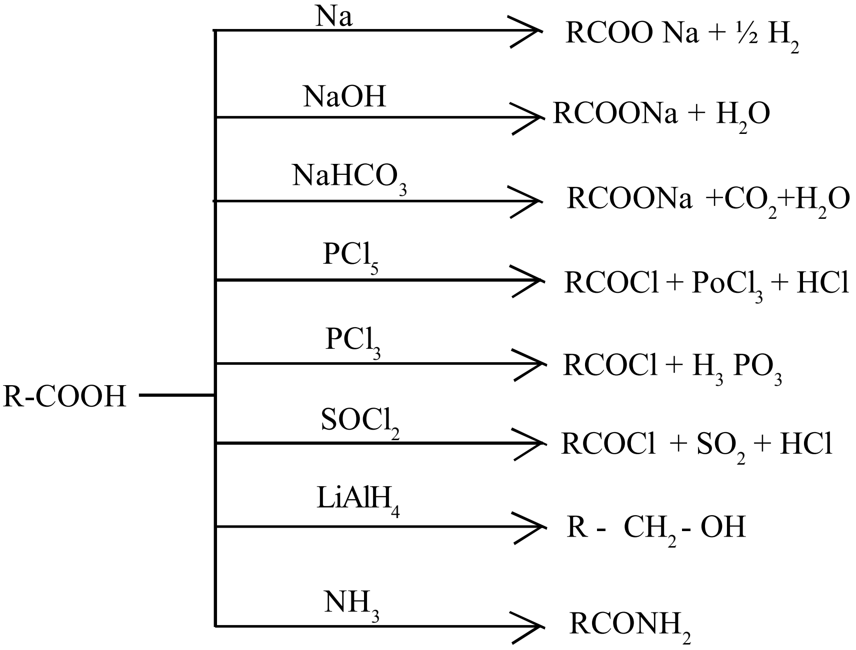
$$CH_3CH_2COOH + Cl_2 + RedP \xrightarrow[-HCl]{} CH_3CH\overset{Cl}{\overset{|}{C}} - COOH$$

α Chloropropanoic acid

$$\xrightarrow{Cl_2 + RedP - HCl} CH_3 - \underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{C}} - COOH$$

α α Diehlropropanoic acid

- **Electrophilic aromatic substitution reaction**



$$R\text{-}COOH \xrightarrow{Na} RCOO\,Na + ½\,H_2$$
$$R\text{-}COOH \xrightarrow{NaOH} RCOONa + H_2O$$
$$R\text{-}COOH \xrightarrow{NaHCO_3} RCOONa + CO_2 + H_2O$$
$$R\text{-}COOH \xrightarrow{PCl_5} RCOCl + PoCl_3 + HCl$$
$$R\text{-}COOH \xrightarrow{PCl_3} RCOCl + H_3\,PO_3$$
$$R\text{-}COOH \xrightarrow{SOCl_2} RCOCl + SO_2 + HCl$$
$$R\text{-}COOH \xrightarrow{LiAlH_4} R - CH_2 - OH$$
$$R\text{-}COOH \xrightarrow{NH_3} RCONH_2$$

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Chapter XIII

AMINES

- Amines are the derivatives of NH_3 in which one or more H atom have been replaced by alkyl or aryl group.
- These are classified as primary (1°), secondary (2°) and tertiary (3°) depending on whether one, two or all the three H atoms have been replace by alkyl or aryl group.

Nomenclature

- In the common system, amenes are called alkyl amlnes or amino alkanes but in the IUPAC systems, these are called alkanamines.

Eg: $CH_3CH_2NH_2$,	CH_3CH_2-NH-CH_3
Ethanamine (1°)	N- methylethanaamine(2°)

Structure of amino group

- Nitrogen atom of amino group is sp^3 hybridised. Three of these orbitals get involved in sigma bond formation with other atoms where as fourth orbital contain lone pair of electrons. Thus amines are pyramidal in shape.

General method of Preparation

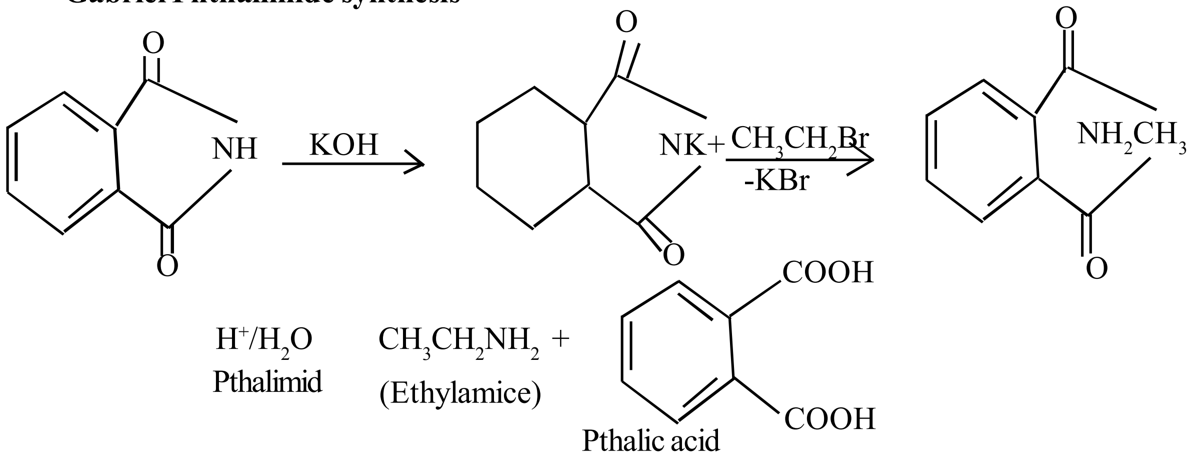
- **from alcohols**

$$CH_3CH_2OH \xrightarrow[H_2O]{NH_3\Delta} \overset{\text{primary}}{CH_3CH_2NH_2} \xrightarrow[H_2O]{CH_3CH_2OH/\ \Delta} [CH_3CH_2]_2NH((2^{o}\text{amine})$$

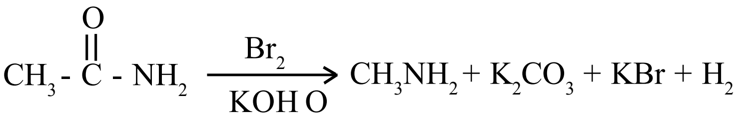
$$\xrightarrow[-H_2O]{CH_3CH_2OH/\ \Delta} (CH_3CH_3)_3N$$

(Tertiary amine)

- **Gabriel Phthalimide synthesis**



- **Hofman bromamide reaction**
- For converting amide to primary amines having one carbon atom less.



$$CH_3-\overset{\overset{O}{||}}{C}-NH_2 \xrightarrow[KOH\ O]{Br_2} CH_3NH_2 + K_2CO_3 + KBr + H_2$$

- Reduction of N containing compound

$CH_3CH_2NO_2 \xrightarrow{Sn/HCl\ or\ H_2/Pt} CH_3CH_2CH_2NH_2$

Primary amine

$CH_3CH_2CN \xrightarrow{LiAlH_4\ or\ Na\ /\ Alcohol} CH_3CH_2CH_2NH_2$

(Ethylcyanide) Primary amine

$CH_3CONH_2 \xrightarrow{LiAlH_4} CH_3CH_2NH_2$

(Ethanamide) Primary amine

- By hydorlysis of N containing compounds

$CH_3CH_2NC \xrightarrow{H^+/H_2O} CH_3CH_2NH_2 + HCOOH$

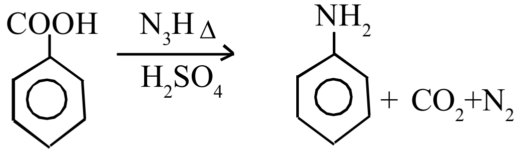
Ethyl isocyanide Ethanamine

$CH_3CH_2N = C = O \xrightarrow{KOH} CH_3CH_2NH_2 + HCOOH$

Ethyl isocyanate Ethanamine

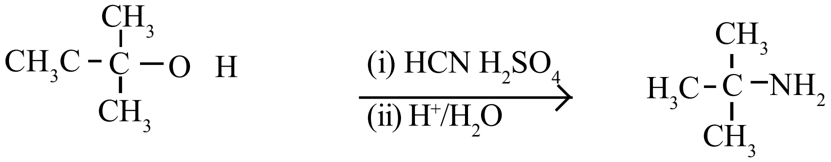
- Schmidt Reaction
- To convert carboxylic acid to amines having one carbon atom less

$$CH_3COOH \xrightarrow[H_2SO_4]{N_3H\ \Delta} CH_3NH_2 + CO_2 + N_2$$



Benzoic Acid Anilene

- **Ritter Reaction**



$$CH_3C-\underset{CH_3}{\overset{CH_3}{C}}-O\ H \xrightarrow[(ii)\ H^+/H_2O]{(i)\ HCN\ H_2SO_4} H_3C-\underset{CH_3}{\overset{CH_3}{C}}-NH_2$$

Ammonolysis of alkyl halides

$NH_3 + R - X \longrightarrow R - N^+H_3X^-$ (Substituted ammonium salt)

(Nucleophile)

Physical Properties

- Lower amines are gases and liquid but higher amines are solids
- Primary and secondary amines have higher boiling points than other organic compounds due to hydrogen bonding.
- Primary and secondary amines are soluble in water due to hydrogen bonding between and H_2O.

Basic Character

$$CH_3NH_2 + HCl \rightarrow CH_3NH^+_3Cl^-$$

- Due to the presence of lone pair of electron on nitrogen atom, amines are basic in nature.
- Basic character of amines can be compared on the basic of inductive effect of alkyl groups, steric effect and resonance involvements of lone pair of electrons.

Aliphatic Amines

- Among aliphatic amine +I effect of alkyl groups pushes the electron towards nitrogen atom an so increase the basic character.

- In a acqeous solution , the following order is observed.

  2°Amine >1°Amine > 3°Amine > Ammonia (aq. soln)
- This can be explained on the basis of solvation effect

  In tertiary amines after accepting a proton there is no hydrogen to stabilize the positive ion by hydrogen bonding.

Aromatic Amines

- Aromatic amines are less basic than aliphatic amines, because of the involvement of lone pair of electron in resonance with the aromatic ring which now becomes less available for donation.
- Also sp^2 hybridised carbon of the aromatic ring is more electron withdrawing than sp^3 hybridisid carbon of aliphatic amines and exerts a stronger withdrawing effect resulting in less tendency to donate lone pairs.

Substituted atomatic amines

- In substituted aromatic amines, generally electron withdrawing groups, decrease the basic character and electron releasing group increases the basic character of amines.

- A group present at ortho position to amino group always decreases the basic character whether it is electron releasing or electron withdrawing and this phenomonon is known as the ortho effect.

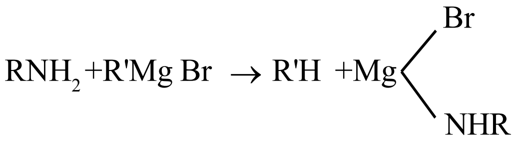
Chemical Properties

- **Carbylamine reaction**

  $RNH_2 + CHCl_3 + 3KOH(alc) \rightarrow R\text{-}N \overset{\rightarrow}{=} C + 4KCl + 3H_2O$

  Only by 1^0 amines

- **Reaction with grignard reagent**



$$RNH_2 + R'MgBr \rightarrow R'H + Mg\begin{cases} Br \\ NHR \end{cases}$$

- **Oxidation of amines**
- **Oxidation with potassium permanganate**

  $R - CH_2 - NH_2 \xrightarrow{KMnO_4} R - CH{=}NH$

  $\rightarrow R - CH{=}O + NH_3$

Oxidation of aniline

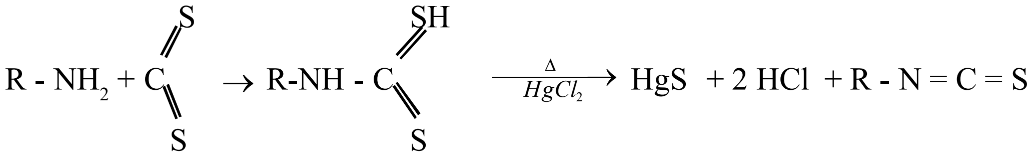
$\text{Aniline} \xrightarrow{K_2Cr_2O_7\ /\ H_2SO_4} \text{A black dye}$

(aniline black)

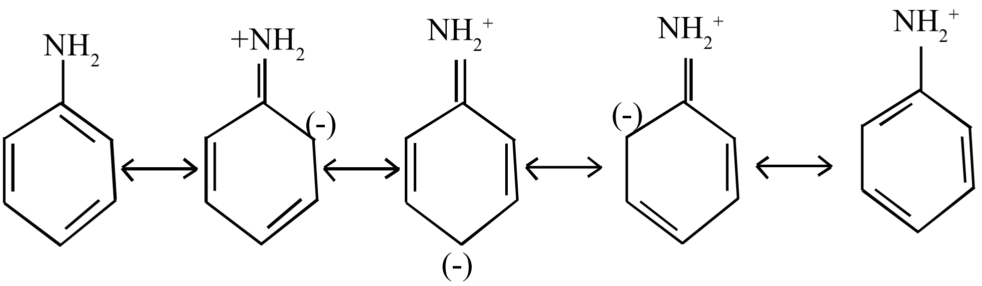
- **Acylation of amines**

  $R - NH_2 \xrightarrow{CH_3COCl} RNHCOCH_3 + HCl$

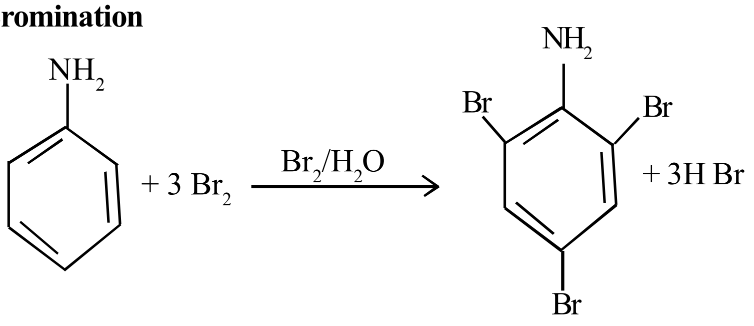
- **Hoffmann mustard oil reaction**



- **Ring substitution on aniline**

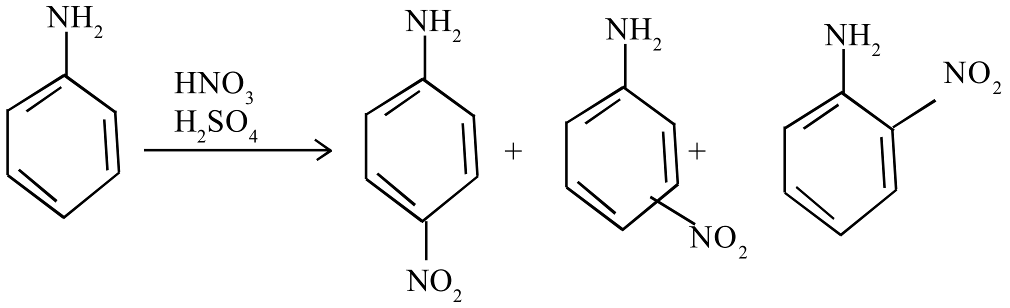


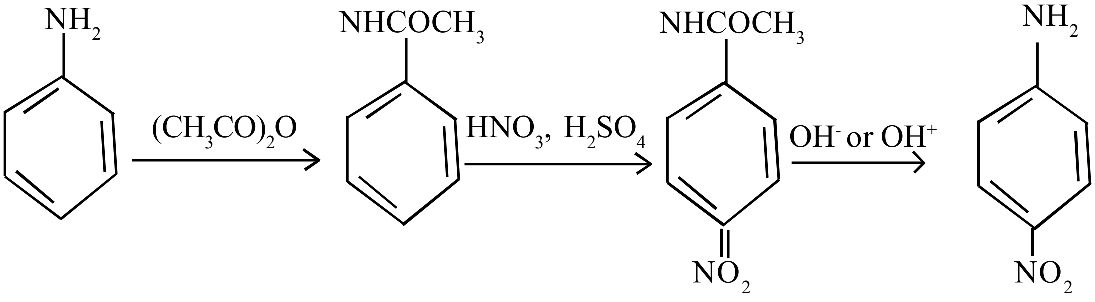
- **Bromination**



2, 4, 6 - Hibromo ancline

- **Nitration**

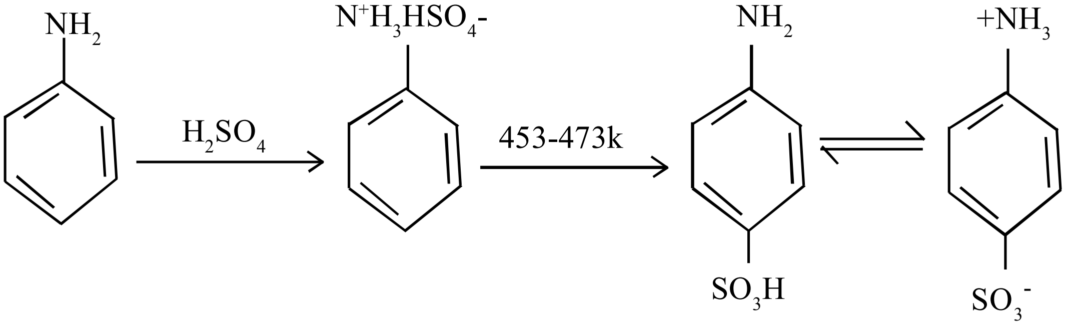




p - nitroacetanilide

p - nitro aniline

- **Sulphonation**



Aniline hydrogensulphide

Zwitter ion

- **Reaction with nitrous acid**

  $NaNO_2 + HCl \rightarrow NaCl + HNO_2$

  $R\text{-}NH_2 + HNO_2 \rightarrow R\text{-}OH + N_2 + H_2O$

  $R_3N + HONO \rightarrow [R_3NH]^+NO_2^- \rightarrow R\text{-}OH + R_2N\text{-}N{=}O$ (Nitrosamine)

- **Diazonium Salts (ArN_2X)**

  The diasonium salt have the general formula (ArN_2X) where X may be an anion like Cl^-Br^- HSO_4^- etc and the group N_2^+ is called diazonium ion group.

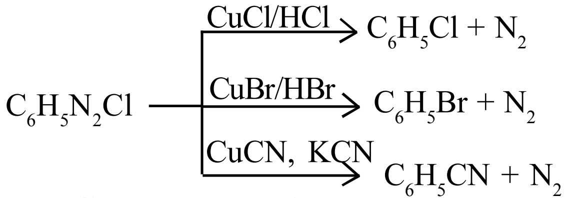
  $C_6H_5N_2Cl$ is called benzene diazonium chloride.

  $$C_6H_5NH_2 + NaNO_2 + HCl \xrightarrow{273-278k} C_6H_5Cl + NaCl + H_2O$$

  The conversion of primary aromatic amines into diazonium salts is known as **diazotisation.**

Reaction of benzenediazonium chloride

- **Sandmeyers reaction**

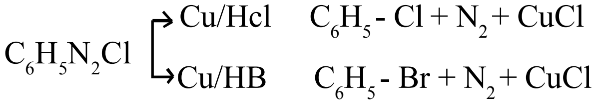


$$C_6H_5N_2Cl \xrightarrow{CuCl/HCl} C_6H_5Cl + N_2$$

$$C_6H_5N_2Cl \xrightarrow{CuBr/HBr} C_6H_5Br + N_2$$

$$C_6H_5N_2Cl \xrightarrow{CuCN,\ KCN} C_6H_5CN + N_2$$

- **Gatterman reaction**



$$C_6H_5N_2Cl \xrightarrow{Cu/Hcl} C_6H_5\text{-}Cl + N_2 + CuCl$$

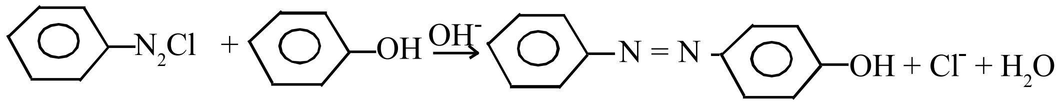
$$C_6H_5N_2Cl \xrightarrow{Cu/HB} C_6H_5\text{-}Br + N_2 + CuCl$$

- **Other reactions**

  1) $C_6H_5N_2Cl + KI \rightarrow C_6H_5I + KCl + N_2$
  2) $C_6H_5N_2Cl + H_3PO_2 + H_2O \rightarrow C_6H_6 + N_2 + H_3PO_3 + HCl$
  3) $C_6H_5N_2Cl + H_2O \rightarrow C_6H_5\text{-}OH + N_2 + HCl$
  4) $C_6H_5N_2Cl \xrightarrow[2)\ NaNO_2,Cu]{1)\ HBF_4} C_4H_5NO_2 + N_2 + NaBFu$

Coupling Reaction

1)



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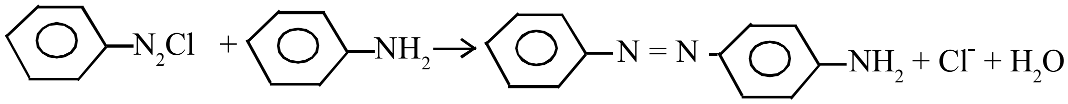

(yellow dye)

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Chapter XIV

BIOMOLECULES

Biochemistry

The brach of Chemistry which deals with study of chemical composition and structure of living organisation and chemical changes taking place in them.

Biomolecules

The complex organic molecules which build up organisam and form the basis of life.

Carbohydrates

These are polyhydroxy aldehydes or ketones or the compounds wich can provide them on hydrolysis.

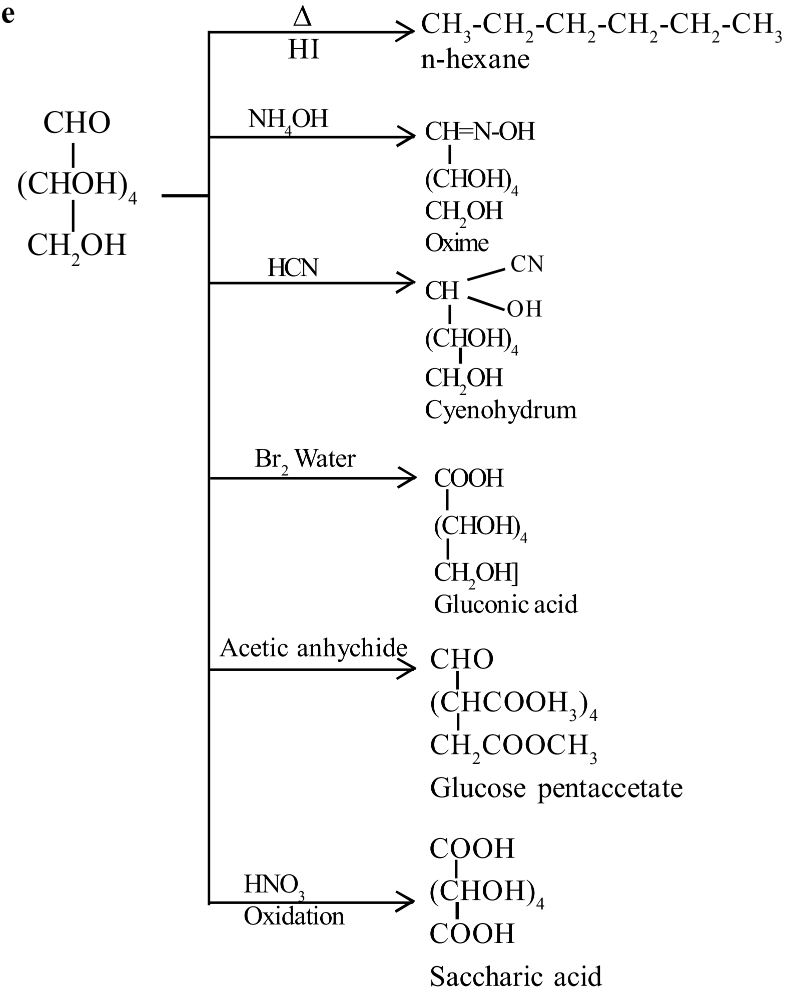
Classification of Carbohydrates

a) **Monosacharides :** Simple carbohydrates which can not be hydrolysed further.
eg: Glucose & Fructose

b) **Oligo Scacharides :** Carbohydrates which on hydrolysis give two to nine mono sacharides.
eg: Sucrose, Maltose and Lactose

c) **Polysaccharides :** Carbohydrates which on hydrolysis give large number of monosacharides.
eg : Starch, Cellulose and glycogen

Glucose



Starch : It is a polymer of glucose and consists of 15-20% water souble Amylose and 80-85% water insoluble Amylopectin.

* Sucros is a non reducing sugar

* Maltose and Lactose are reducing sugars.

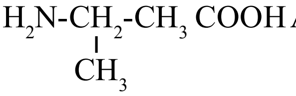
Functions of carbohydrates

1) They act as biofuels to provide energy for functioning of living organism
2) They act as constituents of cell membrane.

Anomer : A Stereo isomer which differ in configuration about a carbon atom

amino acids : The organic compound containing - COOH and an NH_2(Amino) group at the same carbon atom (α - carbon)

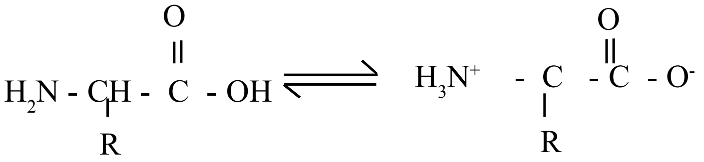
eg: H_2N-CH_2-COOH Glycine



$H_2N-\underset{\underset{CH_3}{|}}{CH_2}-CH_3\ COOH$ Alamine

Zwitter ion

It is a neutral species carries both positive and negative charges. In the formation of a zwitter ion a proton form -COOH part of the molecule is released and attaches itself to $-NH_2$ part to form a dipole ion.



$$H_2N-\underset{\underset{R}{|}}{CH}-\overset{\overset{O}{||}}{C}-OH \rightleftharpoons H_3N^+-\underset{\underset{R}{|}}{C}-\overset{\overset{O}{||}}{C}-O^-$$

Proteins : These are polymers of amino acids which are essential for the growth and maintenance of life.

Structure of Protein

1) **Primary Structure :** The sequence in which amino acids are arranged in proteins.
2) **Secondary Structure :** The manner in which the polypeptile chains are folded.
3) **Tertiary Structure :** This gives the overall shape of proteins
4) **Quarternary Structure :** The special arrangement of two or more peptile chains.

Denaturation of Protein

The proces that brings about changes in physical and biological properties of the proteins. Denaturation does not change the primary structure but changes the secondary and tertiary structure of proteins.

eg : When the egg is boiled hard, the soluble globular proteins present in it denatures resulting in the formation of soluble fibrous proten.

Nucleic Acids

Bio molecules present in the living cell which play significant role in synthesis of proteins in living organism

Difference between DNA X RNA

DNA	RNA
1) DNA has 2 deoxy ribose as sugar unit	1) RNA has ribose as as sugar unit
2) The bases in DNA are Adenine(A), Thymine(T), Guanine(G), Cytosine(C)	2) The bases in RNA areadrenine (A), Guanine(G), Uracil & Cystome (C)
3) DNA has double standard structure	3) RNA has single standard structure

Functions of Nucleic Acids

1) For Protein synthesis
2) for Replication

Vitamins

The organic compounds, other than carbohydrates, proteins and fats that are necessary to maintain normal health and growth

a) Water soluble vitamins: B group vitamis and Vitamins C

b) Fat soluble vitamins : Vitamins which are soluble in fat and oils but insoluble in water
eg:- Vitamins A, D, E and K

Name and Vitamin	Sources	Deficiency Deseases
Vitamin A	Carrots, Butter and Milk	Night Blindness
Vitamin B1	Milk, Green Vegetables	Beri Beri
Virtamin C	Citrus Fruits Green leafy vegetables	Scurvy
Vitamin D	exposure to sunlight	Rickets
Vitamin K	Green Leafy vegetables	Increased blood clottiong time

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Chapter XV

POLYMERS

Polymers are macrosized, high molecular mass compounds formed by the combination of simple units called monomers and the process is called polymerization. A polymer formed from one type of monomers is called a **homopolymer**

Eg: Polyethene, PVC, Polystyrene etc

A polymer formed from two or more different monomers is called **copolymers.**

Eg: Nylon 66, Bakelite

Classification of Polymers

I Based on source / Origin

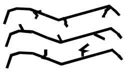
i) Natural Polymers - Eg: Starch, Cellulose, Proteins Nucleic Acids

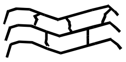
ii) Synthetic Polymers(Manmade Polymers)
Eg: PVC, Polythene, Polysterene, Teflon, Nylon

iii) Semi synthetic polymers
Eg: Cellulose nitrate, vulcanised rubber etc.

II Based on Structure

i) Linear Polymers  Eg : Polythene, Nylon, Polyester

ii) Branched Chain Polymers  Eg: Starch, Glycogen

iii) Cross linked Polymers or three dimensional network polymers
Eg: Bakelite, Melamine etc 

III Based on Molecular forces

i) **Elastomers :** Having weak inter molecular forces and elastic character can be stretched easily
Eg: Vulcanised rubber

ii) **Fibres :** Have strong inter molecular forces of attraction between chains [Hydrogen bonding or dipole dipole interaction]
Eg : Nylon 66

iii) **Thermoplastics :** Intermolecular forces in between those of elastomers and fibres. They can be easily moulded on heating ie., soften on heating and become hard on cooling,
eg: PVC, Polystyrene, Polyethane

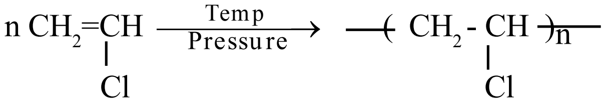
iv) **Thermosetting Polymers :** Have extensive cross linking formed between polymers chains on heating. They become hard, infusible mass upon heating and is a permenant change.
Eg: Bakelite, Melamine

IV Based on Synthesis

i) **Addition Polymers :** Polymers formed by the repeated addition of monomer units. These are also called Chain growth Polymers.
Eg: Polythene, PVC, Polystyrene etc

$$n\,CH_2{=}CH_2 \xrightarrow[\text{Pressure}]{\text{Temp}} -\!\!\left(CH_2-CH_2\right)\!\!-_n$$

Ethene Polyethene



$$n\,\underset{\displaystyle Cl}{CH_2{=}\overset{}{\underset{|}{CH}}} \xrightarrow[\text{Pressure}]{\text{Temp}} -\!\!\left(CH_2-\underset{\underset{\displaystyle Cl}{|}}{CH}\right)\!\!-_n$$

Vinylchloride PVC

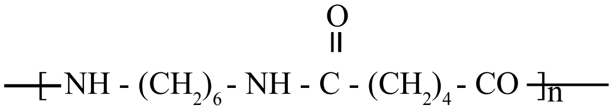
ii) Condensation polymers or step growth polymers

Polymers formed by the condensation of two or more monomers with the elimination of simple molecule like H_2O, NH_3, Alcohol etc are called condensation polymers.

Eg: Nylon -66, Terylene, Bakelite etc.

n Hexamethylene diamine + nAdipic acid $\xrightarrow[-nH_2O]{}$ Nylon - 66

$nNH_2\text{-}(CH_2)_6\text{-}NH_2 + nHOOC\text{-}(CH_2)_4\text{-}COOH \xrightarrow[-nH_2O]{}$



$$-\!\!\left[NH-(CH_2)_6-NH-\overset{\overset{\displaystyle O}{\|}}{C}-(CH_2)_4-CO\right]\!\!-_n$$

Nylon - 66

2) n Ethylene glycol + n dimethyl terephalate $\xrightarrow[CH_3OH]{}$ Terylene

Some commercially important polymers

1) Polythene $-\!\!\left[(CH_2\text{-}CH_2)\right]\!\!-_n$
   a) Low density Polyethene(LDPE)
   b) High Density Polyethene(HDPE)
2) Polytetra fluoro ethene (Teflon) (PTFE)

$$n\,CF_2{=}CF_2 \xrightarrow[\text{High Pressure}]{\text{Catalyst}} -\!\!\left[(CF_2\text{-}CF_2)\right]\!\!-_n$$

Tetrafluoroethene

It is used for making oil seals, Gaskets, Teflon & Handle for non stick utensils.

3) Polyacrylonitrite (PAN) (ORLON or ACRILIN)

$$n\,CH_2=\overset{\overset{CN}{|}}{C}H \xrightarrow{\text{Polymerisation}} -\!\!\left[CH_2-\overset{\overset{CN}{|}}{C}H \right]_n\!\!-$$

Poly acrylonitrile (PAN)

It is a substitute for wool in making commercial fibres

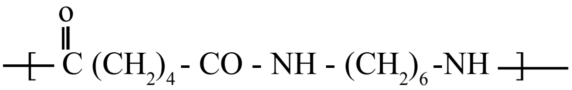
II Polyamides

Polymers possessing amide $-\!(-CO\text{-}NH-)\!-$ linkage, Important examples of synthetic fibres termed as Nylons.

1. **Nylon 66:** It is a condensation polymer of hexamethylene diamine and adipic acid

$$n\,HOOC-(CH_2)_4-COOH + n\,NH_2-(CH_2)_6-NH_2 \xrightarrow[\text{High Pressure}]{553K}$$

Adipic acid Hexamethylene diamine



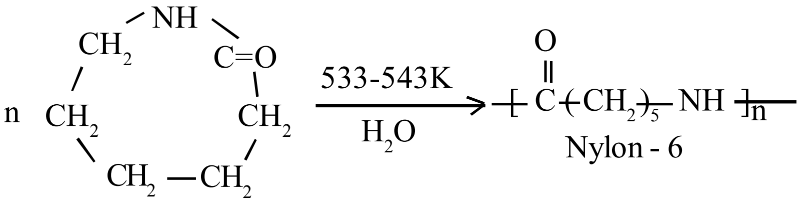
$$-\!\!\left[\overset{\overset{O}{\|}}{C}(CH_2)_4-CO-NH-(CH_2)_6-NH \right]\!\!-$$

(Nylon 66)

They possess strong intermolecular force [Hydrogen bonding] between the chains.

Used in making sheets, bristles for brushes and in textile industry.

2. **Nylon 6:** It is obtained by the polymerisation of coprolactam with water at 543K



$$\xrightarrow[H_2O]{533\text{-}543K} -\!\!\left[\overset{\overset{O}{\|}}{C}-(CH_2)_5-NH \right]_n\!\!-$$

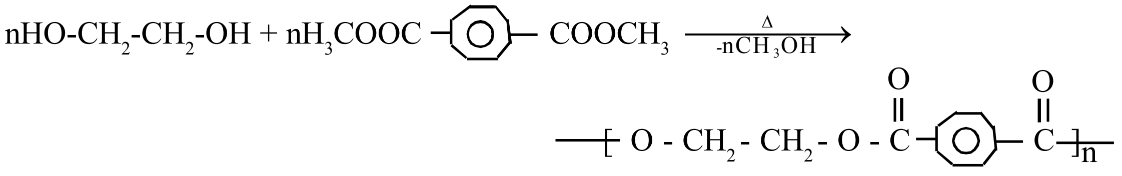
Caprolactam

Nylon - 6

Uses: For the manufacture of tyre cords , fabrics & ropes]

III Polysters : Poly condensation products of dicarboxylic acids and diols

Eg: Dacron or Terylene

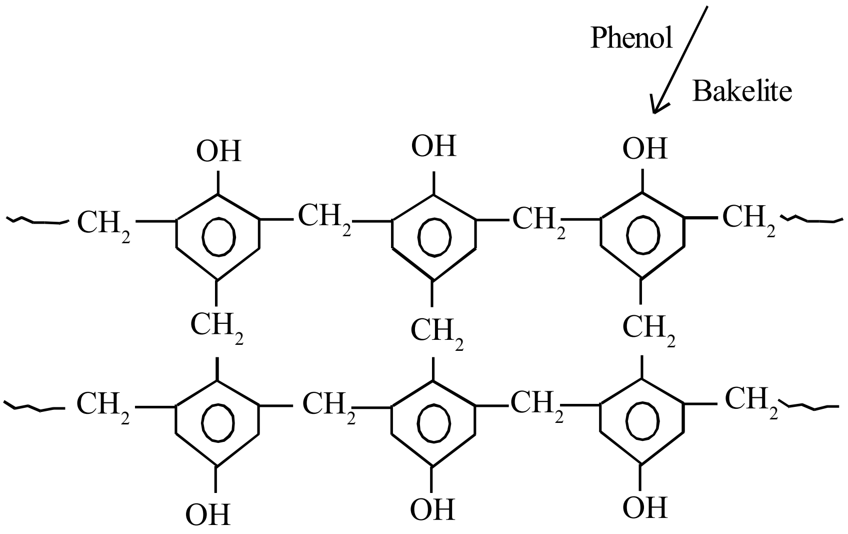


$$nHO-CH_2-CH_2-OH + nH_3COOC-C_6H_4-COOCH_3 \xrightarrow[-nCH_3OH]{\Delta} -\!\!\left[O-CH_2-CH_2-O-\overset{\overset{O}{\|}}{C}-C_6H_4-\overset{\overset{O}{\|}}{C} \right]_n\!\!-$$

Terylene

Phenol - formaldehyde resin (PF resin) - Bakelite

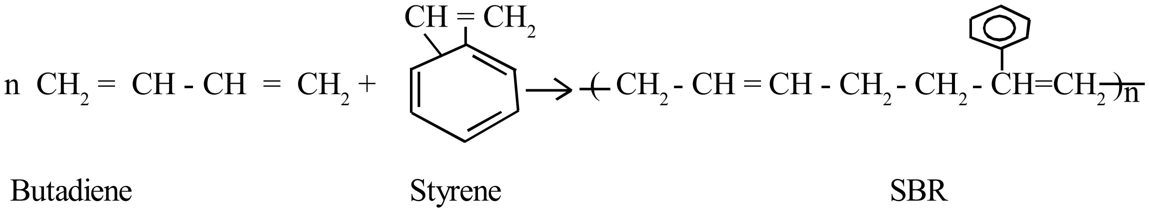
nPhenol + nFormaldehyde $\xrightarrow{H^+ \text{ or } {}^-OH}$ O or P - hydroxymethylol phenol



Melamine formaldehyde resin

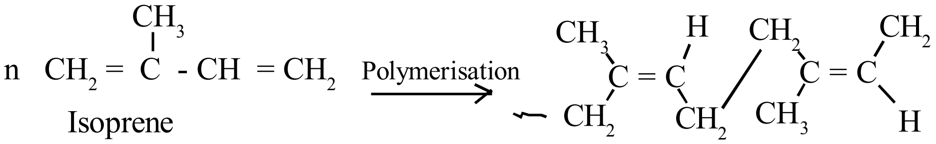
Co polymer :- A polymers formed from two or more different monomeric species.

Eg: Styrene - butadiene (SBR) rubber, Bakelite etc.



Rubber :- Natural rubber is a linear polymer of isoprene

[cis -1,4-Polyisoprene-Natural rubber]



Natural rubber consists of variuos chains held together by weak Van der Waal's forces and has a coiled structure and thus exhibits low elastic properties.

Vulcanization : It is a process of treating natural rubber with sulphur and an appropriate additive at a temperature range of 373 to 415K to modify its physical and mehanical properties, On vulcanization, sulphur forms cross links at the reactive sites of the double bonds and gives mechanical strength to the rubber.

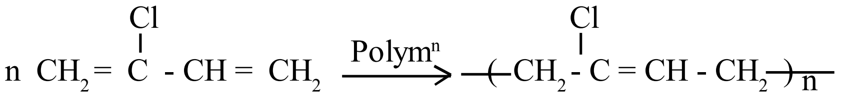
Molecular mass of polymers

i) Number average molecular mass ($\overline{M}$n)

i) Weight average molecular mass ($\overline{M}$w)

Synthetic Rubber

i) Neoprene : It is a polymer of chloroprene(2 Chloro - 1,3 Butadiene)

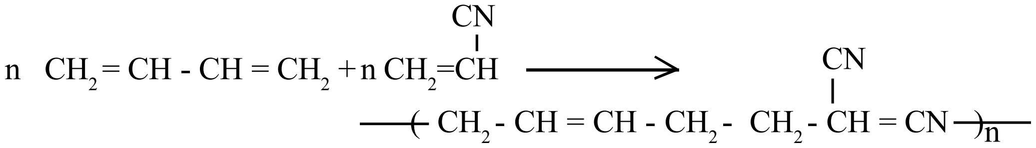


$$n\ CH_2=\overset{Cl}{C}-CH=CH_2 \xrightarrow{Polym^n} -(CH_2-\overset{Cl}{C}=CH-CH_2)_n-$$

Chloroprene Polychloroprene

- Resistant to oils.
- Used for the manufacture of Belts and Hoses

ii) Buna N: It is a co-polymer of 1,3 Butadiene and acrylonitrile



$$n\ CH_2=CH-CH=CH_2+n\ CH_2=\overset{CN}{CH} \longrightarrow -(CH_2-CH=CH-CH_2-CH_2-\overset{CN}{CH}=CN)_n-$$

Buna - N

Biodegradable Polymers

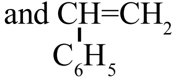
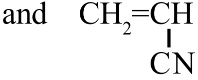
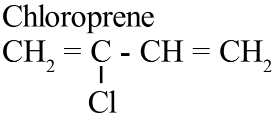
- Undergo environmental degradation
- Functional group very similar to that present biopolymers

Eg: i) Poly β - hydroxybutyrate - co - β hydroxy valerate (PHBV)

- It is a polymer of 3- hydroxy butanoic acid and 3- hydroxy pentanoic acid. It is used in speciality packaging, orthopaedic devices and controlled release of drugs

2) **Nylon 2, Nylon 6 :-** It is an alternating copolymer of glycine and amino caproic aicd.

	Polymer	Monomers	Uses
1.	Polytetrafluoroethene (Teflon) $-(CF_2-CF_2)_n-$	Tetrafluoroethene $CF_2=CF_2$	Making oil seals and gaskets. Used for non-stick surface coated utensils.
2.	Polyacrylouitrile $-(CH_2-\underset{CN}{CH})_n-$	Acrylonitrile $CH_2=CHCN$	As a substitue for wool in making commercial fibres as orlon or acrilan.

3.	**Poly amides** Nylon 6,6 $\left(HN - (CH_2)_6 - NH - CO - (CH_2)_4 - CO \right)_n$	Adipic acid $HOOC\text{-}(CH_2)_4\text{-}COOH)$ and Hexamehytene diamine $(NH_2\text{-} (CH_2)_6 - NH_2)$	Making sheets, bristles for brushes and in textile industry.
4.	Nylon 6 $\left(CO - (CH_2)_5\text{-} NH \right)_n$	Caprotactum	For the manufacture of tyre cords fabric and ropes.
5.	Polyesters Dacron (Terylene)	Ethylene glycol and terephthalic acid	It is used in blending with cotton and wool fibres and also as glass reinforcing materials in safety helmets.
6.	Glyptal Phenol-fomal dehyde polymer	Ethylene glycol and phthalic acid	Manufacture of paints and lacquers
7.	Noolac	Linear polymers of phenol and fomal dehyde	Used in paints
8.	Bakelite	Cross linked polymer of phenol and form aldehyde	For making combs, phonograph records, electrical switches and handles of various utensils.
9.	**Synthetic rubber** Buna - S  $\left(CH_2\text{-}CH{=}CH\text{-}CH_2\text{-}\underset{C_6H_5}{CH}\text{-}CH_2 \right)_n$	1,3 Butadiene and Styrene $CH_2{=}CH\text{-}CH{=}CH_2$  and $\underset{C_6H_5}{CH}{=}CH_2$	For the manufacture of autotyres, floortiles, footwear components, cable insullation etc.
10.	Bana - N	1,3 Butadience and acrylonitrile $CH_2{=}CH\text{-}CH{=}CH_2$  and $CH_2{=}\underset{CN}{CH}$	Making oil seals, tank lining etc
11.	Neoprene $\left(CH_2 - C = CH - CH_2 \right)_n$	Chloroprene  $CH_2 = \underset{Cl}{C} - CH = CH_2$	For manufacturing conveyor belts, gas kets and hoses.

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Chapter XVI

CHEMISTRY IN EVERYDAY LIFE

- **Medicins** are chemicals used in diagnosis, prevention and treatment of diseases.
- **Chemotherapy:** Means use of chemicals for therapeutic effect.
- **Enzyme inhibitors :** Are drugs which inhibit the active site of enzyme.
- **Receptors:** Are proteins that are involved in the body's communication system.
- **Antacids** are drugs used in the treatment of hyper acidity
  eg : $NaHCO_3$,$Al(OH)_3$, $Mg(OH)_2$
- **Metal hydroxides** are better antacids than $NaHCO_3$ as they are insoluble and hence do not increase the pH above 7
- **Cemetidine and Ranitidine** are antacids which reduce the production of acids by preventing the interation of histemine with receptors in stomach wall
- **Antihistamines** are anti allergic durgs. They inhibit the action of histamines
  eg: Bromopheniramine, ferfenadine (seldane)
- **Tranqilizers** are neurilogically active drugs used for relieving anxiety, stress and mental deseases They are present in sleeping pills

Types :

i) **Antidepresant** drugs for reducing depression
   eg:- Iproniazid, Phenelzine
ii) **Mild tranquilizers :**
   eg: Equanil, meprobamate etc
iii) **Barbiturates** are present in sleeping pills
   eg : Veronal, Valium etc

Analgesics are drugs used for reducing pain

Types

i) **Non narcotic analgesics** are non addictive. eg: Aspirin
ii) **Narcotic analgesics** are (Additive) eg: Morphine, Heroin)

Anti microbials prevent the action of microbes (Bacteria, Virus)

eg : Antibacterial drugs, Antifungal durgs, Antiviral drugs, anti parasitic drugs)
Antibiotics, Antiseptics etc.

Antibiotics : Inhibits the growth or destroys microorganism

eg: Salvarsen (for the treatment of syphilis), Sulphapyridine, protosil.

1) **Broad spectrum antibiotics** effective against a wide range of gram positive and gram negative bacteria. Eg:- Ampicillin, Amoxycillin
2) **Narrow spectrum antibiotics** affective against either gram posetive or gram negative becteria, eg; Pencillin G
3) **Limited spectrum antibiotics** effective against a single bacteria.

Important Antibiotics :

- **Pencilin G** is developed from fungus by Alexander Fleming.
- **Ampicilline and Amoxycilline** are synthetic modification of pencilline. They are broad spectrum antibiotic.
- **Chloram Phenical** is a broad spectrum antibiotic for typhoid, dysentery, acute fever, pneumonia etc

- **Vancomycin** ,ofloxacin and disidazirine are antibiotics.
- **Antiseptics and Disinfectants** are chemicals which kill or prevent the growth of micro organisam.
- **Antiseptics** are safe to living tissues (Cuts, ulcers etc)
  Eg : Dettol is (Chloroxylenol +Terpinol)
  Bithional used in antiseptic soaps.
  Iodoform and tincture of iodine are antiseptics for wounds
  Aiqueous solution of boric acid for wounds in eyes.
  Disinfectants are applied to inanimate objects such as floors, drainages etc. Same substance can act as antisceptic as well as disinfectant by varying its concentratio; for example 0.2% solution of phenol is an antiseptic while its 1% solution is disinfectant.

- **Tincture of Idodine** is an antiseptic containing 2-3% I_2 in alcohol - water mixture.
  Cl_2 and SO_2 in very low concentration are used as disinfectants.
- **Antifertility drugs** used for family planning or birth control. They are mixture of synthetic estrogenes and progestrone derivatives
  eg:- Norethindorne, Novelstrol etc

Chemicals in food

- **Natural sweeteners** are caloric intake eg: Sucrose,
- **Aritificial sweetening agent** is non claroric intake which can be used by diabetic patients
  eg: Sacharin, Aspartame, Sucralose, Alitame etc
- **Food presenvatives** prevent spoilage of food due to microbial growth
  eg: Table salt(NaCl), Sugar(Sucrose), Vegetable oils, Sodium Benzoate, Salts of Sorbic Acid and propanoic Acid.
- **Soaps** are cleansing agents used in softwater. They are not suitable for hard water. They are Sodium or Potassium Salts of Long Chain fatty acids
  Fat or oil + NaOH $\rightarrow$ Soap + Glycerol
  (This reaction is known as saponification)
  Potassium soaps are soft to skin.
  Transparant soap is made by dissolving the soap in ethanol.

- **Synthetic Detergents** are cleansing agents with out any soap. They are effectve both in soft and hard water and even in ice cold water.

Types : **Anionic Detergents** are sodium salts of sulphonated long chain alcohols or hydrocarbons, The anionic part act as cleansing agent. They are mostly used for household works and are also present in tooth pastes.

Cationic Detergents are quarternay ammonium slats amines with acetates, chlorides or bormides as anion. The cationic part act as cleansing agent eg : Cetyl trimethyl ammonium bromide
(In hair conditioner)

Non ionic or neutral detergents have polar groups which can form hydrogen bonding with water. They are present in liquid dish washing detergents, Stearic acid reacts with Poly ethylene glycol to give a non ionic detergents.

Bio degradables detergents have straight chain hydrocarbon eg Sodium lauryl sulphate; Sodium dodecyl benzene sulphonate
Non biodegradable detergents have branched chain hydrocarbon, They accumulate in soil and in water. They cause pollution
eg : Sodium tetramethyl octyl benzene sulphonate

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Model Questions

Score : 60
Time : 2 Hrs

CHEMISTRY

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1. a. A unit cell of a cubic crystal consists of anions B at each corner of the cub and cations A at the centre of alternate faces of the cube. What is the simplest formula of the compound? (1)

   b. "Ionic solids which have anionic vacancies due to metal excess defect developes colour". Substantiate the statement with suitable example. (1½)

   c. Schematic alignment of magnetic moments of ferromagnetic, antiferromagnetic and ferriomagnetic substances are given below. Identify each of them. (1½)

   (i) ↑↓↑↓↑↓↑↓ (ii) ↑↑↓↑↑↑↓↑ (iii) ↑↑↑↑↑↑↑↑

2. a. Soda water is prepared by treating water with CO_2 under high pressure. Which law is involved in the process? State the law? (2)

   b. What is the osmotic pressure of 0.5M. Solution of glucose at 25^0C? $R=0.0821L\ atm\ K^{-1}mol^{-1}$ (2)

3. Leclanche cell, lead storage cell and fuel cell are galvanic cells having different uses.

   a. Among these Leclanche cell is a primary cell and Lead storage cell is a secondary cell Write any two differences between primary cell and secondary cell (2)

   b. Write the overall cell reaction in H_2-O_2 fuel cell. (1)

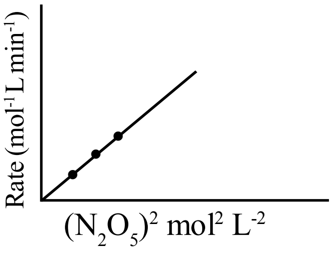
   c. State Kohlrausch's law. Give one application (2)

4. A relation connecting rate constant and temperature is called Arrhenius equation.

   a. Write Arrhenius iquation (1)

   b. The rate of the chemical reaction doubles for an increase of 10K in absolute temperature from 298K.
   Calculate activation energy (Ea) (1½)

   c. Observe the graph given below
   Is the graph for a second order reaction? Justify your answer (1½)



5. Adsorption of gases on solids depend on the pressure applied

   a. What is the effect of pressure on the adsorption of a gas on a solid (1)

   b. Briefly explain Freundlich adsorption isotherm (1)

   c. Suggest a method to prepare ferric hydroxide sol. (1)

6. Match the following

A	B	C
Mond's process	Zone refining	Calcination
Sulphide ore	Vapour phase refining	Semi conductor
Germanium	$ZnCO_3$	Froth floatation
Calamine	Zinc blend	Nickel

(3)

7. a. Nitrogen and phosphorous belong to gp 15 of the periodic table.
   Phosphorous can form 2 series of halids of the type PX_3 and PX_5.
   Nitrogen does not form pentahalides (NX_5). Why? (1)
   b. What is oleum? Write the chemical equation for the conversion of oleum sulphuric acid (2)
   c. Which is the most acidic oxoacidic of chlorine? Give its structure (2)

8. a. Write the steps involved in the preparation of potassium dichromate from chromite ore (2)
   b. What is lanthanide contraction? What is it due to? (2)

9. Co-ordination compounds are those compounds which retain their identity even in solution and it is essential for all living matter.
   a. Name a co-ordination compound containing Magnesium, which is essential for plants (½)
   b. When we co-ordinate EDTA with any metal we get a ring structure.
   What is this process called? (½)
   c. Name the co-ordination compounds. (2)
   (i) $K_3[Cr(C_2O_4)_3]$ (ii) $[Pt(NH_3)_2Cl_2]$

10. a. Which one of the following is more reactive towards SN^1 reaction.
    Pentan - 3- o1 ; Pental - 1 - o1 (1)
    b. What happens when chlorobenzene is treated with a mixture of conc HNO_3 and conc H_2SO_4?
    (1)
    c. An organic compound A reacts with metallic sodium in other medium to form ethane.
    A also reacts with magnesium in either medium to give B. Identify A and B. Give the Chemical equations for the reactions involved. (2)

11. Consider the three alcohols given below.
    Butan - 2-o1, butan - 1 - o1 and methyl propan - 2 - o1
    a. Which of them will give a ketone on heating with acidified potassium dichromate?
    Write the structure of the ketone that would be formed? (2)
    b. Arrange them in the decreasing order of reactivity towards Lucas reagent. (1)
    c. The bondangle $\mathrm{C}\overset{\mathrm{O}}{\wedge}\mathrm{H}$ in alcohols, is slightly less than tetrahedral angle.
    Give reason for the difference in bond angle in alcohol. (1)

12. a. Give chemical test to distinguish between propanal and propanone (1)

b. Show how acetaldehyde reacts with the following reagent.

(i) $H_2NNH\ CONH_2$ (semi carbazide)

(ii) Zinc amalgam and conc. HCl. (2)

c. Account for the following

(i) Carboxylic acids are stronger acids than phenols.

(ii) $H_2CCl\ COOH$ is a stronger acid than CH_3COOH (2)

13. You are given $C_6H_5NH_2$, alcoholic KOH, $CHCl_3$, $NaNO_2$ and dil. HCl. How will you get the following products from these? Give the name of the reaction.

a. C_6H_5NC (1½)

b. $C_6H_5N^+_2Cl^-$ (1½)

14. a. What is Zwitter ion? Give the Zwitter on structure of α - amino acid. (2)

b. Give any one point of difference between DNA & RNA (1)

15. a. What are the monomers of Nylon 66. Give the preparation of it (2)

b. Give 2 examples synthetic rubbers (1)

16. a. Allosteric site is a term related to drug - encyme interaction. Explain (1)

b. Write the therapeutic action of the following drugs in our body

(i) Analgesics (ii) Tranquilizers (2)

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