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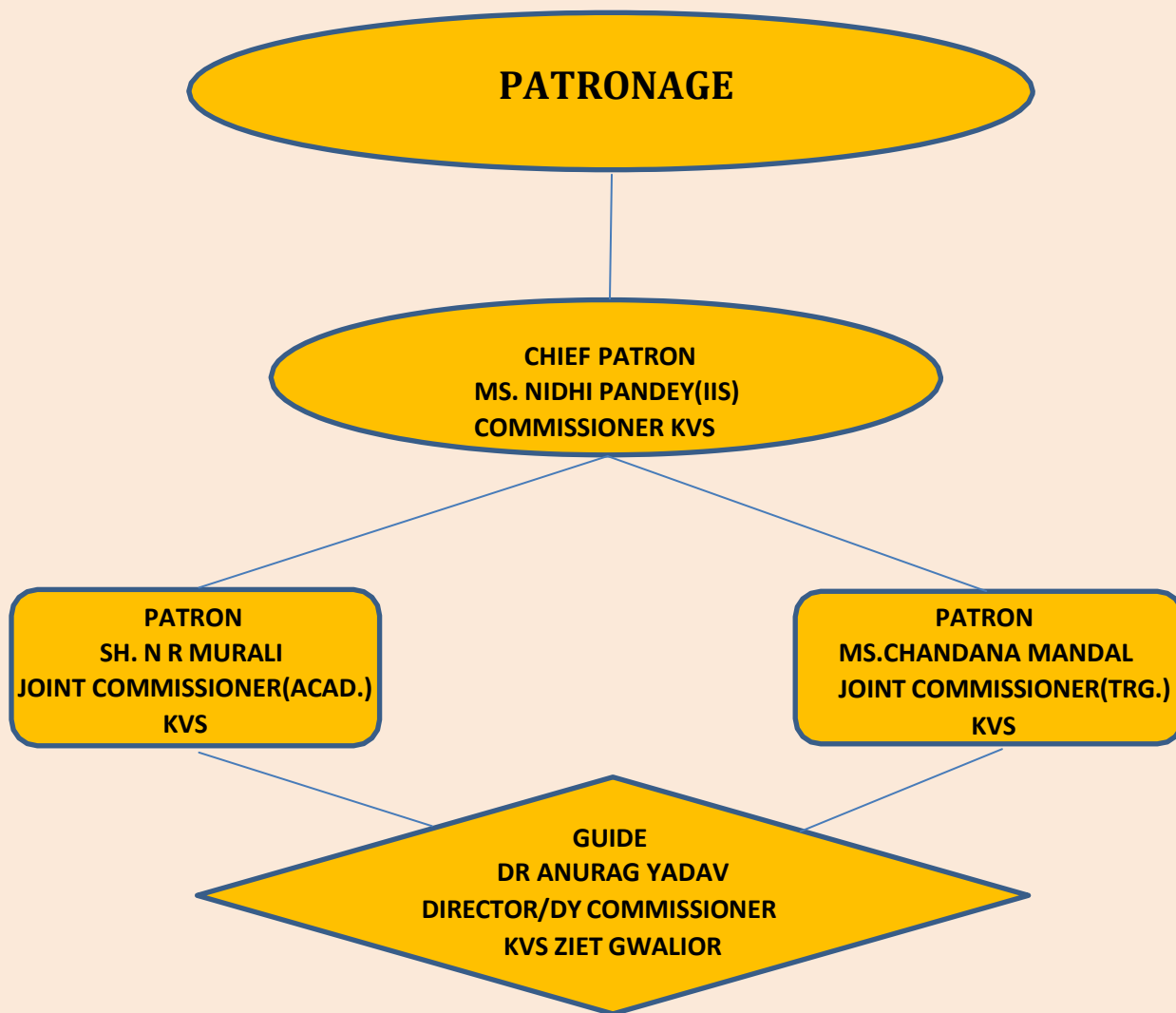


**ZONAL INSTITUTE OF EDUCATION AND
TRAINING, GWALIOR**

**INTERACTIVE STUDY
MATERIAL**

CHEMISTRY

CLASS XII 2022-23



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UNIT -1

SOLUTIONS

Points to Remember

1. The component that is having more number of moles is known as solvent. Solvent determines the physical state of the solution. Water is a universal solvent.
2. Mole fraction (X) is a unitless quantity.
3. Molality (m) and mole fraction are temperature independent quantities whereas molarity decreases with increase in temperature.
4. As the temperature increases Henry's law constant, K_H increases so the lower is the solubility of the gas in the liquid.
5. 11.7% w/w Helium is added to air used by scuba divers due to its low solubility in the blood.
6. Raoult's law becomes a special case of Henry's law in which K_H becomes equal to P_A^0 , i.e., vapour pressure of pure solvent.
7. Azeotropes having the same composition in liquid and vapour phase and boil at a constant temperature and therefore can't be distilled.
8. Azeotropes arise due to very large deviation from Raoult's law. Maximum boiling azeotropes form when solutions exhibit negative deviation from Raoult's law whereas minimum boiling azeotropes form when solutions exhibit positive deviation from Raoult's law.
9. Relative lowering in vapour pressure is a colligative property but lowering in vapour pressure is not.
10. Van't Hoff factor (i) is the ratio of the observed value of the colligative property in solution to the theoretically calculated value of the colligative property.
 - (a) A non-volatile solute undergoes dissociation, then $i > 1$.
 - (b) A non-volatile solute undergoes association, then $i < 1$.

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Some Important Formulae

1. Mole fraction (X)

If the number of moles of A and B are n_A and n_B respectively, the mole fractions of A and B will be

$$X_A = \frac{n_A}{n_A + n_B} \text{ and } X_B = \frac{n_B}{n_A + n_B}$$

$$X_A + X_B = 1$$

2. **Molarity (M)** = $\frac{\text{Moles of solute}}{\text{Volume of solution in liters}} \text{ mol L}^{-1}$

3. **Molality (m)** = $\frac{\text{Moles of solute}}{\text{Mass of solvent in kilograms}} \text{ mol kg}^{-1}$

4. Parts per million (ppm)

$$= \frac{\text{Number of parts of the compound}}{\text{Total number of parts of all components of the solution}} \times 10^6$$

5. Raoult's law for a solution of volatile solute in volatile solvent:

$$p_A = p_A^0 X_A$$

$$p_B = p_B^0 X_B$$

Where p_A and p_B are partial vapour pressures of component 'A' and component 'B' respectively in solution. p_A^0 and p_B^0 are vapour pressures of pure components 'A' and 'B' respectively.

6. Raoult's law for a solution of non-volatile solute and volatile solvent:

$$\frac{p_A^0 - p_A}{p_A^0} = i X_B = i \frac{n_B}{n_A} = i \frac{W_B \times M_A}{W_A \times M_B} \text{ (for dilute solutions)}$$

Where X_B is mole fraction of solute, i is Van't Hoff factor and $\frac{p_A^0 - p_A}{p_A^0}$ is relative lowering of vapour pressure.

VISUAL EXPLANATION

7. Elevation in boiling point (ΔT_b):

$$\Delta T_b = i \cdot K_b \cdot m$$

Where $\Delta T_b = T_b - T_b^0$ K_b = molal boiling point elevation constant

m = molality of solution

T_b = Boiling point of solution

T_b^0 = Boiling point of solvent

VISUAL EXPLANATION

8. Depression in freezing point (ΔT_f) :

$$\Delta T_f = i K_f m$$

Where $\Delta T_f = T_f^0 - T_f$

K_f = molal freezing point depression constant

m = molality of solution

T_f^0 = Freezing point of solvent

T_f = Freezing point of solution

VISUAL EXPLANATION

9. Osmotic pressure (π) of a solution:

$$\pi V = i nRT \quad \text{or} \quad \pi = i CRT$$

where π = osmotic pressure in bar or atm

V = volume in litres

i = van't Hoff factor

C = molar concentration in moles per litres

n = number of moles of solute

T = Temperature on Kelvin scale

$R = 0.083 \text{ L bar mol}^{-1} \text{ K}^{-1}$

$R = 0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}$

VISUAL EXPLANATION

10. Van't Hoff factor (i)

$$i = \frac{\text{Number of particles in solution after association or dissociation}}{\text{Number of particles actually dissolved in solution}}$$

$$i = \frac{\text{Observed colligative property}}{\text{Theoretically calculated colligative property}}$$

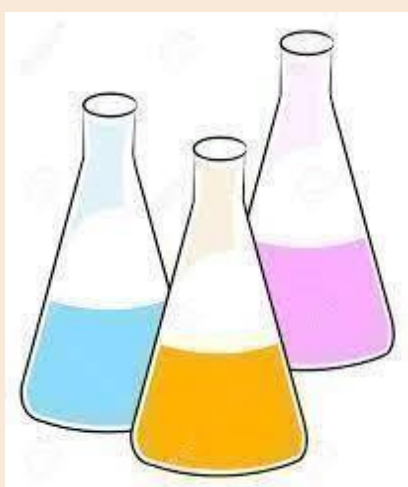
$$i = \frac{\text{Normal molar mass}}{\text{Abnormal molar mass}}$$

$i > 1$ For dissociation of solute

$i < 1$ For association of solute

$i = 1$ For ideal solution undergoing no association or dissociation

VISUAL EXPLANATION



UNIT -2

Electrochemistry

Points to Remember

Electrochemistry may be defined as the branch of chemistry which deals with the quantitative study of inter-relationship between chemical energy and electrical energy and inter-conversion of one form into other relationships between electrical energy taking place in redox reactions.

A cell is of two types:

- I. Galvanic cell
- II. Electrolytic cell

In Galvanic cell, the chemical energy of a spontaneous redox reaction is converted into electrical work.

In Electrolytic cell, electrical energy is used to carry out a non-spontaneous redox reaction.

1. Conductivity (k):

$$k = \frac{1}{\rho} = \frac{1}{R} \times \frac{l}{A}$$

where R is Resistance, l/A = cell constant (G^*) and ρ is resistivity.

2. Relation between k and Λ_m

$$\Lambda_m = \frac{1000 \times k}{C}$$

where Λ_m is molar conductivity, k is conductivity and C is molar concentration

VISUAL EXPLANATION.

Kohlrausch's law:

(a) In general, if an electrolyte on dissociation give y_+ cations and γ_- anions, then its limiting molar conductivity (Λ_m°) is given by

$$\Lambda_m^\circ = \nu_+ \lambda_+^\circ + \nu_- \lambda_-^\circ$$

Here, λ_+° and λ_-° are the limiting molar conductivities of cation and anion respectively and ν_+ and ν_- are the number of cations and anions furnished by one formula unit of the electrolyte.

(b) Degree of dissociation (α) is given by:

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^\circ}$$

Here, Λ_m^c is molar conductivity at the concentration C and Λ_m° is limiting molar conductivity of the electrolyte.

(c) Dissociation constant (K) of weak electrolyte:

$$K = \frac{\alpha^2 C}{1 - \alpha}$$

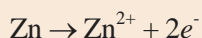
$$K = \frac{\left(\frac{\Lambda}{\Lambda_o}\right)^2 C}{1 - \frac{\Lambda}{\Lambda_o}} = \frac{\frac{\Lambda^2}{\Lambda_o^2} C}{\frac{\Lambda_o - \Lambda}{\Lambda_o}}$$

$$K = \frac{\Lambda^2 C}{\Lambda_o(\Lambda_o - \Lambda)}$$

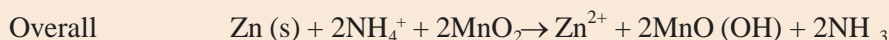
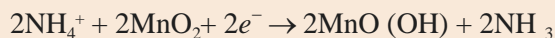
VISUAL EXPLANATION

Dry cell:

At anode (Oxidation)

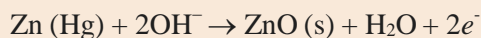


At cathode (Reduction)

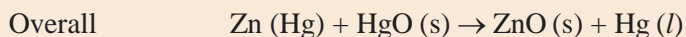
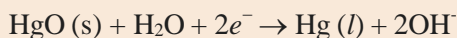


Mercury cell:

At anode (Oxidation)

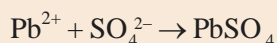
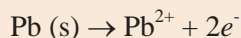


At cathode (Reduction)

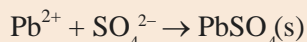
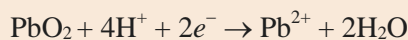


Lead storage cell

At anode (Oxidation)



At cathode (Reduction)



VISUAL EXPLANATION

3. Nernst Equation for electrode reaction:

$$E_{\text{cell}} \text{ or EMF} = E_{\text{cell}}^{\circ} - \frac{2.303RT}{nF} \log Q$$

where, n = total number of electrons lost or gained

$$1F = 96500 \text{ C, } T = 298 \text{ K}$$

$$R = 8.314 \text{ J/K}$$

$$Q = \text{reaction coefficient of overall reaction} = \frac{[\text{OS}]}{[\text{RS}]}$$

where, [OS] = concentration of oxidised state

[RS] = concentration of reduced state

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log Q$$

4. Relation between E_{cell}° and equilibrium constant (K):

$$\Delta G^{\circ} = -nFE_{\text{cell}}^{\circ} = -RT \ln K$$

$$\therefore nFE_{\text{cell}}^{\circ} = RT \ln K$$

$$\therefore E_{\text{cell}}^{\circ} = \frac{RT}{nF} \ln K$$

$$\text{OR } E_{\text{cell}}^{\circ} = \frac{2.303 RT}{nF} \log_{10} K$$

At 25°C,

$$\frac{2.303 \times RT}{F} = \frac{2.303 \times 8.314 \times 298}{96500} = 0.0592$$

$$\therefore E_{\text{cell}}^{\circ} = \frac{0.0592}{n} \log_{10} K$$

5. $\Delta G^0 = - nF E^0_{\text{cell}}$

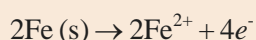
where ΔG^0 = standard Gibbs energy change and nF is the number of Faradays of charge passed. E^0_{cell} is standard cell potential.

$$\Delta G^0 = - 2.303 RT \log K_c$$

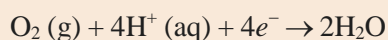
Corrosion of metals is an electrochemical phenomenon.

In corrosion, metal is oxidized by loss of electrons to oxygen and formation of oxides.

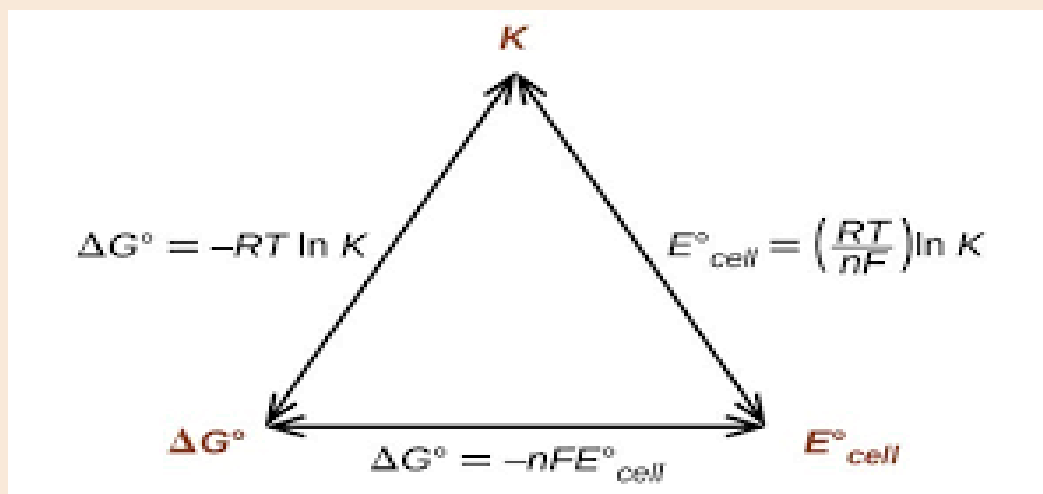
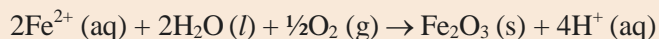
At anode (Oxidation) :



At cathode (Reduction) :



Atmospheric oxidation :



[CLICK HERE FOR DETAILED EXPLANATION](#)

UNIT -3

Chemical Kinetics

CONCEPTS

Chemical Kinetics : The branch of physical chemistry which deals with the study of rate of reaction and factors affecting rate.

Rate of chemical reaction : The change in concentration of any reactant or product per unit time is called rate of reaction.

Types of Rate of Reaction :

1. **Average rate of reaction** : The rate of reaction measured over the long time interval is called average rate of reaction.
2. **Instantaneous rate of reaction** : The rate of reaction measured at a particular time is called instantaneous rate of reaction.

Factors affecting Rate of Reaction

1. Concentration of reactant
2. Surface area
3. Temperature
4. Nature of reactant
5. Presence of catalyst
6. Radiation in photochemical reaction

VISUAL EXPLANATION

Rate constant (k) : It is equal to the rate of reaction when molar concentration of reactant is at unity.

Rate law : The rate of reaction is directly proportional to the product of concentration of reactant and each concentration is raised to the equal to no of moles actually participating in the reaction.



where powers p and q are determined experimentally.

Molecularity : The total number of reactants taking part in elementary chemical reaction is called molecularity.

Order of reaction : The sum of powers to which the concentration terms are raised in a rate law expression is called order of reaction.

For above case, Order = P + Q

Orders of reaction is determined experimentally.

VISUAL EXPLANATION

Half-life period : The time during which the concentration of the reactant is reduced to half of its initial concentration is called half-life period.

Activation energy : The minimum extra amount of energy absorbed by reactant molecules so that their energy becomes equal to the threshold energy is called activation energy.

Activation energy = Threshold energy – Kinetic energy

Temperature coefficient : The ratio of rate constant at two temperatures having difference of 10°C is called temperature coefficient.

Temperature coefficient = Rate constant at T + 10°C / Rate constant at T°C

Arrhenius Equation :

Arrhenius Equation

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

k	rate constant
A	"pre exponential factor"
E_a	Activation energy
R	Gas constant
T	Temperature

$$\log k_2 - \log k_1 = \frac{E_a}{2.303 R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \frac{T_2 \times T_1}{T_1 \times T_2}$$

1. **Integrated rate law equation for zero order reaction is given as below :**

$$(a) k = \frac{[R]_0 - [R]_t}{t}$$

Where k is rate constant and $[R]_0$ is initial molar concentration.

$$(b) t_{1/2} = \frac{[R]_0}{2k}, t_{1/2} \text{ is half-life period of zero order reaction.}$$

2. **Integrated rate law equation for first order reaction :**

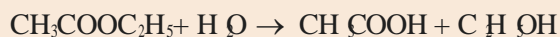
$$(a) k = \frac{2.303}{t} \log \frac{[R]_0}{[R]_t}$$

where k is rate constant, $[R]_0$ is initial molar concentration and $[R]_t$ is final concentration at time ' t '.

(b) Half-life period ($t_{1/2}$) for first order reaction :

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

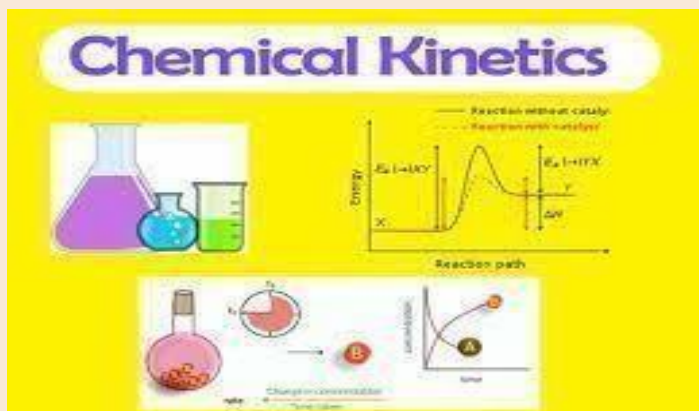
Pseudo chemical reaction : The chemical reaction which looks like higher order reaction but in real it follows lower order reaction.



$$\text{Rate} = k[\text{CH}_3\text{COOC}_2\text{H}_5]^1$$

Order = 1

[Click here for Visual Explanation of the Chapter](#)



UNIT -4

d and f block elements

1. Introduction

d-block elements are present from fourth period onwards. There are mainly three series of the transition metals – *3d* series (Sc to Zn), *4d* series (Y to Cd) and *5d* series (La to Hg, omitting Ce to Lu).

d-block elements are known as transition elements because their position in the periodic table is between the *s*-block and *p*-block elements. Electronic configuration of the *d*-block elements is $(n - 1)d^{1-10}ns^{0-2}$ but Cu^+ , Zn, Cd, Hg etc. $[(n - 1)d^{10}]$ are *d*-block elements, but not transition metals because these have completely filled *d*-orbitals.

Transition Metals of *d*-block Elements

3rd group ns^2	4th group $d^1ns^2d^2$	5th group ns^2d^3	6th group ns^2d^5	7th group ns^2d^5	8th group ns^2d^6	9th group ns^2d^7	10th group ns^2d^8	11th group ns^2d^{10}	12th group ns^2d^{10}
$(n - 1)$	$(n - 1)$	$(n - 1)$	$(n - 1)$	$(n - 1)$	$(n - 1)$	$(n - 1)$	$(n - 1)$	$(n - 1)$	$(n - 1)$
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg

VISUAL EXPLANATION

2. General Properties of the Transition Elements

(i) Atomic and Ionic Radii

In transition metals, left to right net nuclear charge increases due to poor shielding effect. Due to this, the atomic and ionic radii for transition elements for a given series show a decreasing trend for first five elements and then becomes almost constant for next five elements of the series.

(ii) Enthalpies of Atomisation

Transition elements exhibit higher enthalpies of atomization because of large number of unpaired electrons in their atoms. They have stronger interatomic interaction and hence, stronger bond.

(iii) Ionisation Enthalpies

- In a series from left to right, ionization enthalpy increases due to increase in nuclear charge.

- The irregular trend in the first ionization enthalpy of the 3d metals, though of little chemical significance, can be accounted for by considering that the removal of one electron alters the relative energies of 4s and 3d orbitals.

(iv) Oxidation States

- Transition metals shows variable oxidation state due to two incomplete outermost shells. Only stable oxidation states of the first row transition metals are

Sc(+ 3), Ti(+ 4), V(+ 5), Cr(+ 3, + 6), Mn(+ 2, + 7), Fe(+ 2, + 3), Co(+ 2, + 3), Ni(+ 2), Cu(+ 2), Zn(+ 2)

- The transition elements in their lower oxidation states (+ 2 and + 3) usually forms ionic compounds. In higher oxidation state compounds are normally covalent.

- Only Os and Ru show + 8 oxidation states in their compounds.
- Ni and Fe in Ni(CO)₄ and Fe(CO)₅ show zero oxidation state.

VISUAL EXPLANATION

(v) Trends in the Standard Electrode Potentials

- Transformation of the solid metal atoms to M²⁺ ions in solution and their standard electrode potentials.

- If sum of the first and second ionization enthalpies is greater than hydration enthalpy standard potential ($E_{M^{2+}/M}^{\circ}$) will be positive and reactivity will be lower and vice-versa.

(vi) Trends in Stability of Higher Oxidation States

The higher oxidation numbers are achieved in TiX₄, VF₅ and CrF₆. The + 7 state for Mn is not represented in simple halides but MnO₃F is known and beyond Mn no metal has a trihalide except FeX₃ and CoF₃ and increasing order of oxidizing power in the series VO₂⁺ < Cr₂O₇²⁻ < MnO₄⁻.

(vii) Magnetic Properties

- When a magnetic field is applied to substances, mainly two types of magnetic behavior are observed : diamagnetism and paramagnetism. Paramagnetism due to presence of unpaired electrons, each such electron having a magnetic moment associated with its spin angular momentum.

- The magnetic moment is determined by the number of unpaired electrons.

$$\text{Magnetic moment} = \sqrt{n(n+2)}$$

where, n = number of unpaired electrons.

If all electrons are paired, substance will be diamagnetic and magnetic moment will be zero.

(viii) Formation of Coloured Ions

• The d -orbitals are non-degenerated in presence of ligands. When an electron from a lower energy d -orbital is excited to a higher energy d -orbital, the energy of required wavelength is absorbed and rest light is transmitted out. Therefore, the colour observed corresponds to the complementary colour of the light absorbed.

• In V_2O_5 , V is in + 5 oxidation state. It is coloured due to defects in crystal lattice.

(ix) Formation of Complex Compounds

• Transition metals have small size high nuclear charge which facilitates the acceptance of lone pair of electron from ligands.

• They have vacant d -orbitals of appropriate energy in order to accommodate the lone pair of electrons.

(x) Catalytic Properties

• Transition metals have two outermost shells incomplete and ability to adopt multiple oxidation states and to form complexes, therefore used as a catalyst.

• Transition metals also provide larger surface area for the reactant to be adsorbed.

(xi) Formation of Interstitial Compounds

• Small size of non-metals (H, C, N) fit into the voids of crystalline solid of transition metals and form interstitial compounds.

• The principal physical and chemical characteristics of these compounds are as follows :

- (i) They have high melting points, higher than those of pure metals.
- (ii) They are very hard, some borides approach diamond in hardness.
- (iii) They retain metallic conductivity.
- (iv) They are chemically inert.

(xii) Alloy Formation

Alloy is the homogeneous mixture of two or more metals. Transition metals have approximate same size therefore, in molten form they can fit to each other crystalline structure and form homogeneous mixture and form the alloy.

E.g., Brass (copper-zinc) and bronze (copper-tin) etc.

VISUAL EXPLANATION

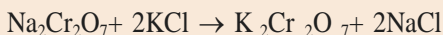
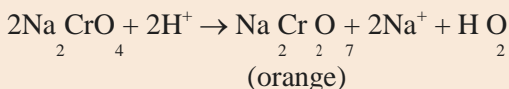
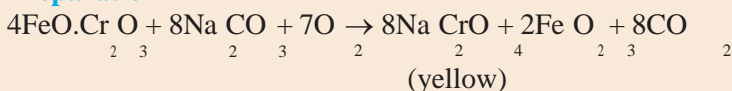
3. Some Important Compounds of Transition Elements

Potassium Dichromate ($K_2Cr_2O_7$)

(i) Ore

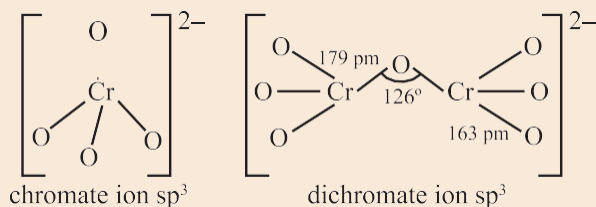
Ferrochrome or chromate ($FeO \cdot Cr_2O_3$) or ($FeCr_2O_4$)

(ii) Preparation



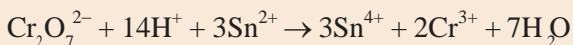
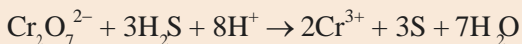
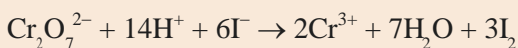
Sodium dichromate is more soluble than potassium dichromate.

- Chromates and dichromates are interconvertible in aqueous solution depending upon pH of the solutions.



(iii) Properties

Sodium and potassium dichromates are strong oxidizing agents, thus, acidified $K_2Cr_2O_7$ will oxidise iodides to iodine, sulphides to sulphur, tin (II) to tin (IV) and iron (II) salts to iron (III).



(iv) Uses

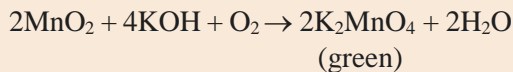
- $K_2Cr_2O_7$ is used as oxidizing agent in volumetric analysis.
- It is used in mordant dyes, leather industry, photography (for hardening of film).
- It is used in chromyl chloride test.
- It is used in cleaning glassware.

Potassium Permanganate (KMnO₄)

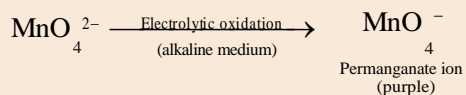
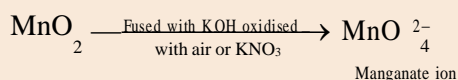
(i) Ore

Pyrolusite (MnO₂)

(ii) Preparation



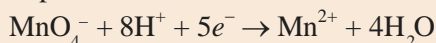
(iii) Commercial preparation



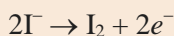
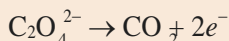
(iv) Properties

KMnO₄ acts as strong oxidizing agent.

(a) In presence of dilute H₂SO₄, KMnO₄ is reduced to manganous salt.

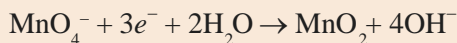


Acidic KMnO₄ solution oxidizes oxalates to CO₂, iron (II) and iron (III), nitrites to nitrates and iodides to iodine. The half reactions of reductants are



To acidify KMnO₄, only H₂SO₄ is used and not HCl or HNO₃ because HCl reacts with KMnO₄ and produce Cl₂ while HNO₃, itself acts as oxidizing agent.

(b) In alkaline medium, KMnO₄ is reduced to insoluble MnO₂.



Alkaline or neutral KMnO₄ solution oxidizes I⁻ to IO₃⁻, S O₂²⁻ to SO₄²⁻,

Mn²⁺ to MnO₂ etc.

(v) Uses

(a) In laboratory preparation of Cl₂.

(b) KMnO₄ is used as an oxidizing agent, disinfectant.

(c) In making Baeyer's reagent.

VISUAL EXPLANATION

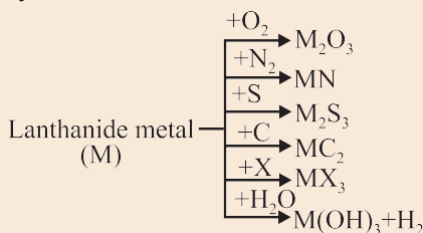
4. The Inner Transition Elements (*f*-Block)

The *f*-block consists of the two series, lanthanoids and actinoids. Lanthanoids are known as rare earth metals and actinoids are known as radioactive elements (Th to Lr).

Lanthanoids

General characteristics

- General configuration $[\text{Xe}] 4f^{1-14}, 5d^{0-1}, 6s^2$.
- Atomic and ionic size from left to right, decreases due to increase in nuclear charge. This is known as lanthanoid contraction.
- All the lanthanoids are silvery white soft metals and tarnish rapidly in air.
- Many trivalent lanthanoid ions are coloured both in the solid state and in aqueous solutions. Neither La^{3+} nor Lu^{3+} ion shows any colour but the rest do so.
- The lanthanoid ions other than the f^0 type (La^{3+} and Ce^{4+}) and the f^{14} type (Yb^{2+} and Lu^{3+}) are all paramagnetic. The paramagnetism arises to maximum in neodymium.
- Oxidation states $\rightarrow \text{Ce}^{4+}$; (Some elements) is favoured by its noble gas configuration, but it is a strong oxidant reverting to the common + 3 state. The E°_{value} for $\text{Ce}^{4+}/\text{Ce}^{3+}$ is + 1.74 V, the reaction rate is very slow and hence, Ce(IV) is a good analytical reagent. Pr, Nd, Tb and Dy also exhibit + 4 state but only in oxides. Eu^{2+} is formed by losing the two *s*-electrons and its f^7 configuration accounts for the formation of this ion. However, Eu^{2+} is a strong reducing agent changing to the common + 3 state. Similarly, Yb^{2+} which has f^{14} configuration is a reductant, Tb^{4+} has half-filled *f*-orbitals and is an oxidant.
- Lanthanoid are very reactive metals like alkaline earth metals.



- Misch metals, contain lanthanoids about 90-95% (Ce 40-5%, Lanthanum and neodymium 44%) iron 4.5%, calcium, carbon and silicon, used in cigarette and gas lighters, toys, tank and tracer bullets.

Actinoids

- General configuration $[\text{Rn}] 5f^{1-14}, 6d^{0-2}, 7s^2$.
- Actinoids exhibit a range of oxidation states due to comparable energies of 5*f*, 6*d* and 7*s* orbitals. The general oxidation state of actinoids is + 3.
- All the actinoids are strong reducing agents and very reactive.
- Actinoids are radioactive in nature and therefore, it is difficult to study their chemical nature

VISUAL EXPLANATION

UNIT -5

COORDINATION COMPOUNDS

1. Introduction

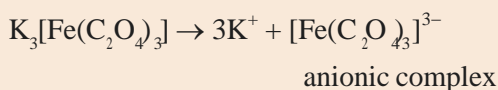
Complex compounds or coordination compounds are those molecular compounds which retain their identity in solid as well as in solution are known as complex compounds.

Example,

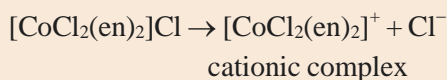


2. Types of Complex

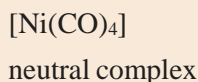
(i) Anionic complex



(ii) Cationic complex



(iii) Neutral complex



3. Ligands

VISUAL EXPLANATION

The ions or molecules bound to the central atom/ion in the coordination entity are called ligands.

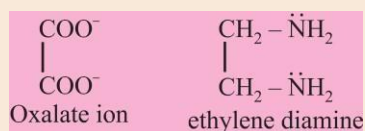
Types of Ligands

(i) Unidentate, a ligand which is bound to a metal ion through a single donor atom.

e.g., H₂O, NH₃, CO, Cl⁻, NH₂⁻ etc.

(ii) Didentate, a ligand which is bound to a metal ion through a two donor atoms.

e.g.,



(iii) Polydentate, a ligand which is bound to a metal ion through a several donor atoms.

e.g., ethylene diamine tetraacetate ion [EDTA]⁴⁻.

(iv) Ambidentate ligands, which can ligate through two different atoms.

e.g., – NO₂ – ONO, – SCN – NCS etc.

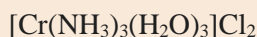
(v) Chelate ligands, these may be a di- or polydentate ligand which form closed ring with central metal ion. Closed ring is known as chelate ring. Number of more chelate ring in complex, complex will be more stable. The number of such ligating groups is called the denticity.

4. Homoleptic and Heteroleptic Complexes

Complexes in which a metal is bound to only one kind of donor groups *e.g.*, Co(NH₃)₆]³⁺ are known as homoleptic. Complexes in which a metal is bound to more than one kind of donor groups *e.g.*, [Co(NH₃)₄Cl₂]⁺, are known as heteroleptic.

5. Nomenclature of Coordination Compounds

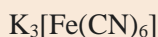
Cationic Complex



triamminetriaquachromium (III) chloride

- (i) Prefixes mono, di, tri, etc. are used to indicate the number of the individual ligands and ligands are named in an alphabetical order.
- (ii) Central metal atom and oxidation state indicated by Roman numeral in parenthesis.
- (iii) Name of ionisable anion.

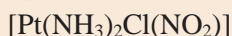
Anionic Complex



Potassium hexacyanoferrate (III)

- (i) Name of ionisable metal and oxidation state
- (ii) Name of ligand in an alphabetical order
- (iii) Central metal atom + ate and oxidation state

Neutral Complex



Diammine chloronitrito-N-platinum (II)

- (i) Name of ligands in an alphabetical order
- (ii) Central metal atom and oxidation state

VISUAL EXPLANATION

6. Isomerism in Coordination Compounds

Stereo isomerism and structural isomerism are the two principal types of isomerisms which are known among coordination compounds.

Stereo Isomerism

It occurs due to different arrangements of ligands around central metal atom. It is of two types : geometrical isomerism and optical isomerism.

Geometrical Isomerism

It arises in heteroleptic complexes due to different possible geometric arrangements of the ligands. Important examples of this behavior are found in square planar and octahedral complexes.

- (i) **Square planar complex of formula $[MX_2L_2]$ (X and L are unidentate)**, the two ligands X may be arranged adjacent to each other in a *cis* isomer, or opposite to each other in a *trans* isomer.

e.g., $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$

- (ii) **Square planar complex of the type $[MABXL]$ (where A, B, X, L are unidentates)** shows three isomers – **two *cis* and one *trans***. Such isomerism is not possible for tetrahedral geometry.

e.g., $[\text{Pt}(\text{NH}_3)(\text{Br})(\text{Cl})(\text{Py})]$

- (iii) **Octahedral complexes of formula $[MX_2L_4]$** in which the two ligands X may be oriented *cis* or *trans* to each other.

e.g., $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$

- (iv) **Octahedral complexes of formula $[MX_2A_2]$** where X are unidentates and A are didentate and form *cis* and *trans* isomers.

e.g., $[\text{CoCl}_2(\text{en})_2]$

- (v) **Octahedral coordination entities of the type $[Ma_3b_3]$** like $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$. If three donor atoms of the same ligands occupy adjacent positions at the corners of an octahedral face, we have the facial (*fac*) isomer. When the positions are around the meridian of the octahedron, we get the meridional (*mer*) isomer.

Optical Isomerism

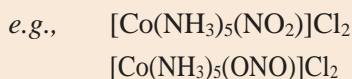
- It arises when mirror images cannot be superimposed on one another. These mirror images are called as enantiomers. The two forms are called *dextro* (*d*) and *laevo* (*l*).
- Optical isomerism is common in octahedral complexes but at least one didentate ligand should be present.

e.g., $[\text{Co}(\text{en})_3]^{3+}$, $[\text{PtCl}_2(\text{en})_2]^{2+}$ etc.

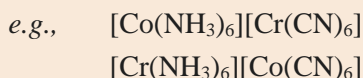
Structural Isomerism

In structural isomerism, isomers have different bonding pattern. Different types of structural isomerism is as follows :

(i) **Linkage isomerism**, arises in a coordination compound containing ambidentate ligand.



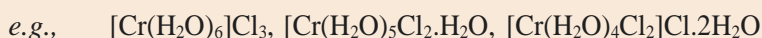
(ii) **Coordination isomerism**, arises from the interchange of ligands between cationic and anionic entities of different metal ions present in a complex.



(iii) **Ionisation isomerism**, when the ionisable anion exchange with anion ligand.



(iv) **Solvate isomerism**, is also known as 'hydrate isomerism'. In this case water is involved as a solvent.



VISUAL EXPLANATION

7. Bonding in Coordination Compounds

Werner's Theory

(i) In complex compounds, metal atom exhibit two types of valencies – primary valency and secondary valency.

(ii) Primary valencies are satisfied by anions only while secondary valencies are satisfied by ligands. Primary valency depends upon oxidation number of central metal atom while secondary valency represents coordination number of central metal atom.

(iii) Primary valencies are ionisable and are non-directional while secondary valencies are non-ionisable and directional. Therefore, geometry of complex is decided by secondary valencies.

Valence Bond Theory

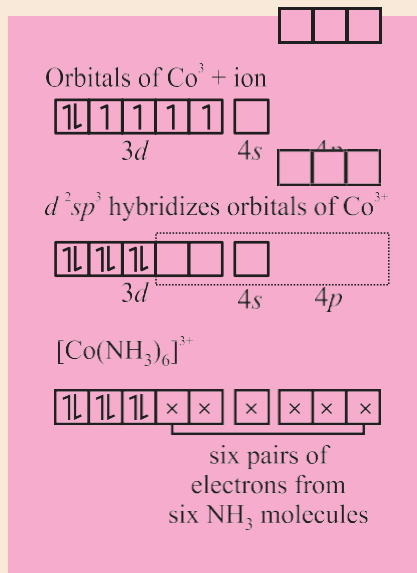
According to this theory, the metal atom or ion under the influence of ligands form inner orbital and outer orbital complex. These hybridized orbitals are allowed to overlap with ligand orbitals that can donate electron pairs for bonding.

(i) **Six ligands (unidentate) (octahedral entity)** Generally central atom belongs 3d series and ligands can be monodentate or didentate but coordination number should be six and shape of complexes will be octahedral and form two types of complexes.

(a) **Inner orbital complexes**, which are formed due to participation of $(n-1)d$ orbitals in hybridisation is (d^2sp^3) and shape of complex will be octahedral.

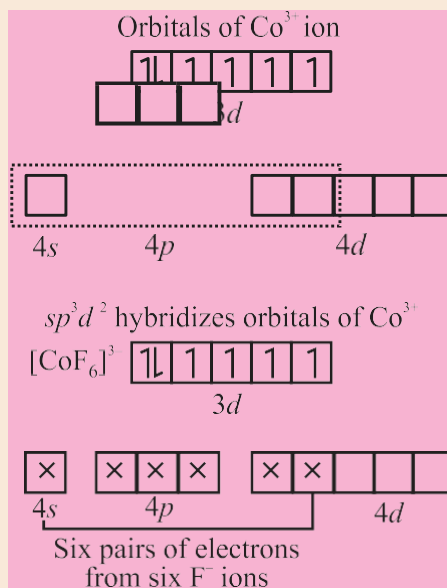
(b) **Outer orbital complexes**, which are formed due to participation of nd orbitals in hybridisation is (sp^3d^2) . Generally halides (F^- , Cl^- , Br^- , I^-), SCN^- , S^{2-} form outer orbital complexes and other ligands form inner orbital complexes.





All electrons are paired therefore, complex will be diamagnetic in nature.

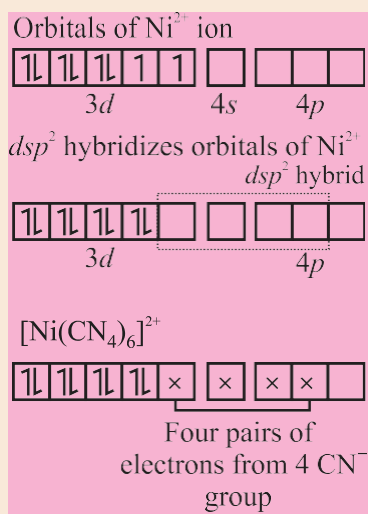
e.g., **Outer orbital complex**, $[\text{CoF}_6]^{3-}$



Complex has unpaired electrons, therefore, complex will be paramagnetic in nature.

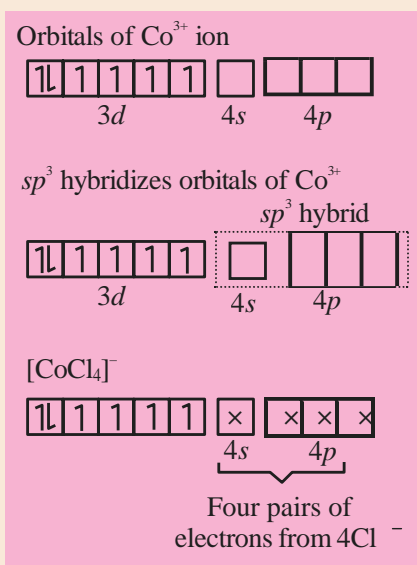
Complexes with coordination number : 4

1. $[\text{Ni}(\text{CN})_4]^{2-}$



All electrons are paired. Complex will be diamagnetic in nature.

2. $[\text{CoCl}_4]^-$



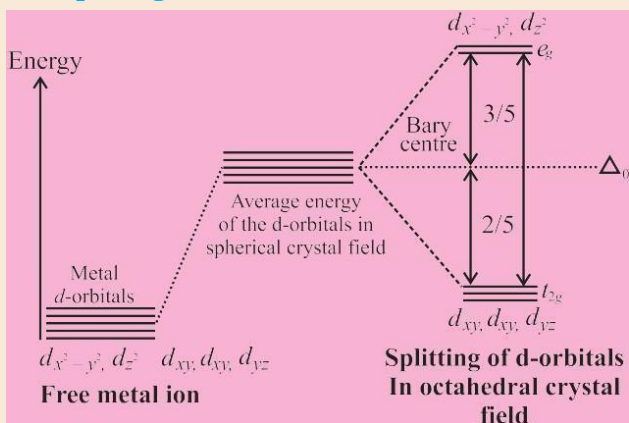
Complex has unpaired electrons. Complex will be paramagnetic in nature.

VISUAL EXPLANATION

Crystal Field Theory

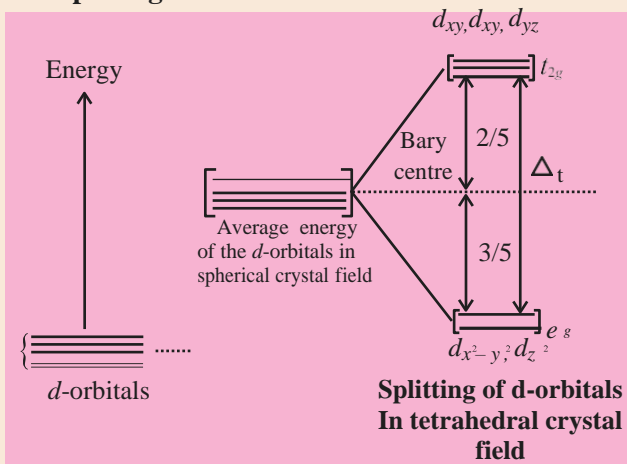
The five d -orbitals are split into lower and higher energy level due to approach of ligands is known as crystal field theory. The five d -orbitals in a gaseous metal atom/ion have same energy.

(i) Crystal field splitting in octahedral coordination entities.



- Energy separation is denoted by Δ (the subscript o is for octahedral).
- The energy of the two e_g orbitals (higher energy orbitals) will increase by $(3/5)\Delta_o$ and that of the three t_{2g} (lower energy orbitals) will decrease by $(2/5)\Delta_o$.
- If $\Delta_o < p$, the fourth electron enters one of the e_g orbitals giving the configuration $t_{2g}^3 e_g^1$. Ligands for which $\Delta_o < p$ are known as weak field ligands and form high spin complexes.
- If $\Delta_o > p$, it becomes more energetically favourable for the fourth electron to occupy a t_{2g} orbital with configuration t_{2g}^4 . Ligands which produce this effect are known as strong field ligands and form low spin complexes, where p represents the energy required for electron pairing in a single orbital.

(ii) Crystal field splitting in tetrahedral coordination entities.



- In tetrahedral coordination entities, $\Delta = (4/9)\Delta$. Consequently the orbital splitting energies are not sufficiently large for forcing pairing and, therefore, low spin configurations are rarely observed.

- Due to less crystal field stabilization energy, it is not possible to pair electrons and so all the tetrahedral complexes are high spin.

8. Colour in Coordination Compounds

- In complex compounds *d*-orbitals split in two sets t_{2g} and e_g . These have different energies. The difference in energies lies in visible region and electron jump from ground state t_{2g} level to higher state e_g level. This is known as *d-d* transition and it is responsible for colour of coordination compounds.

- *d-d* transition takes place in d^1 to d^9 ions, so the ions having d^1 to d^9 configuration are coloured. On the other hand, the ions d^0 and d^{10} configuration do not show *d-d* transition.

9. Importance and Applications of Coordination Compounds

- Hardness of water is estimated by simple titration with Na_2EDTA . The Ca^{2+} and Mg^{2+} ions form stable complexes with EDTA.

- Some important extraction processes of metals, like those of silver and gold make use of complex formation.

- Similarly, purification of metals can be achieved through formation and subsequent decomposition of their coordination compounds. For example, impure nickel is converted to $[\text{Ni}(\text{CO})_4]$, which is decomposed to yield pure nickel.

- Coordination compounds are used as catalysts for many industrial processes. Examples include rhodium complex, $[(\text{Ph}_3\text{P})_3\text{RhCl}]$, a Wilkinson catalyst, is used for the hydrogenation of alkenes.



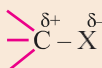
SELF TESTING CUM VISUAL EXPLANATION

UNIT -6

HALOALKANES AND HALOARENES

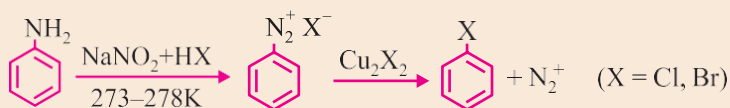
Points to Remember

1. Haloalkanes (Alkyl halides) are halogen derivatives of alkanes with general formula $[C_nH_{2n+1}X]$. (X = F, Cl, Br or I)
2. Haloarenes (Aryl halides) are halogen derivatives of arenes with general formula $Ar - X$.
3. Since halogen is more electronegative than C, hence C – X bond is polar.

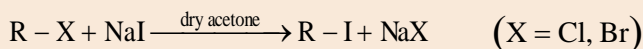


4. Named Reactions :

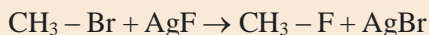
(a) Sandmeyer Reaction :



(b) Finkelstein Reaction :

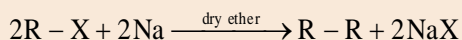


(c) Swartz Reaction :

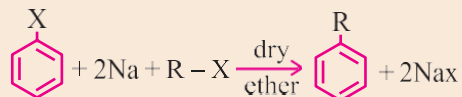


Instead of Ag – F, other metallic fluoride like Hg_2F_2 , CoF_2 or SbF_3 can also be used.

(d) Wurtz Reaction :

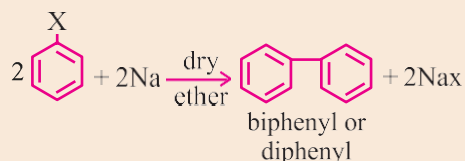


(e) Wurtz-Fittig Reaction :

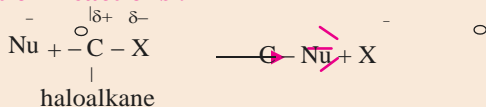


VISUAL EXPLANATION

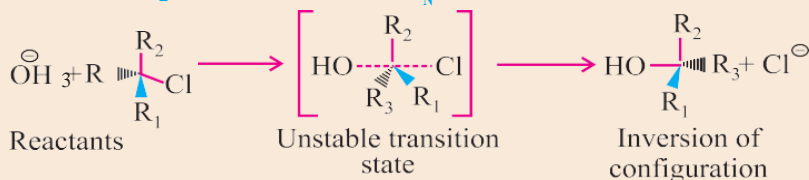
(f) Fittig Reaction :



5. Nucleophilic Substitution Reactions :



(a) Substitution nucleophilic bimolecular (S_N^2) :



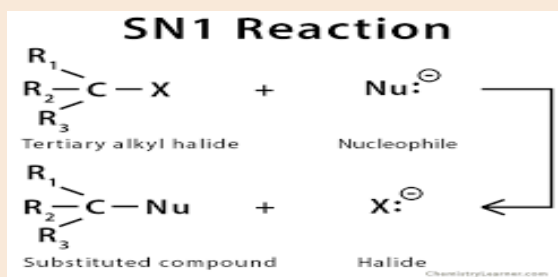
1. 1° haloalkane
2. Bimolecular, 2nd order
3. One step

Order of reactivity : $1^\circ > 2^\circ > 3^\circ$

Deciding factor : Steric hindrance

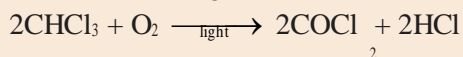
(b) Substitution nucleophilic unimolecular (S_N^1) :

1. 3° haloalkane
2. Unimolecular, 1st order
3. Two steps



Order of reactivity: $3^\circ > 2^\circ > 1^\circ$

6. Aryl halides are much less reactive towards nucleophilic substitution reactions than haloalkanes.
7. Halogen is deactivating but *o*, *p*-directing in electrophilic substitution reaction of haloarenes.
8. CHCl_3 is stored in dark bottles upto brim so that formation of poisonous gas phosgene in presence of air and light can be avoided.

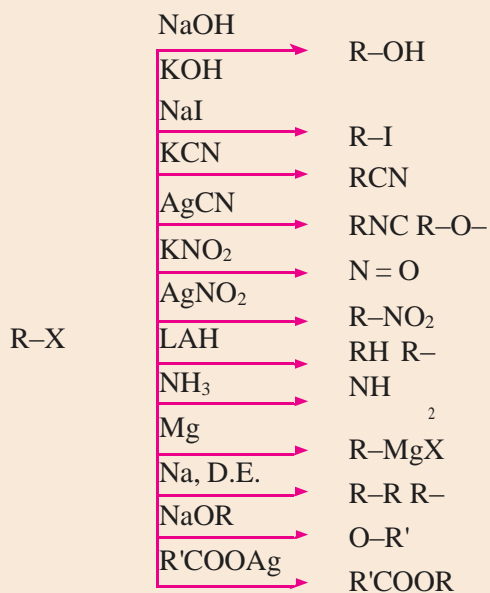


Chloroform

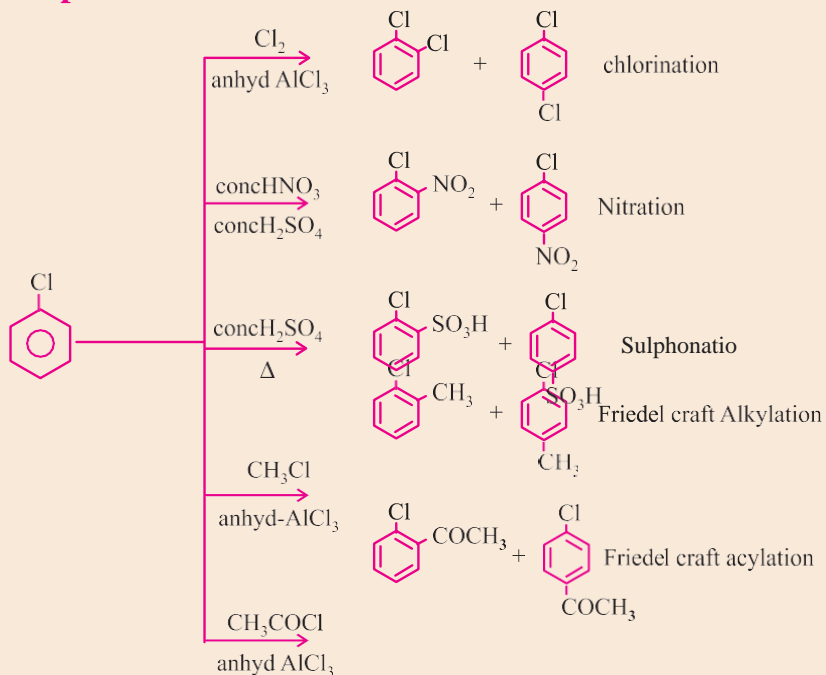
Carbonyl chloride (phosgene)

VISUAL EXPLANATION

9. Reaction of Haloalkanes :



10. Electrophilic Substitution Reaction of Haloarenes :



11. Elimination reaction: Two groups or atoms attached to two adjacent carbon atom and simultaneous formation of multiple bonds between these carbon atom.
[Reverse of addition]

Two types (i) β -Elimination \longrightarrow $E_1 \longrightarrow$ Two step eliminate
(ii) α -elimination $E_2 \longrightarrow$ One step eliminate

Saytza's Rule

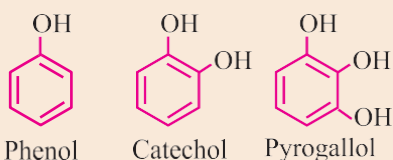
VISUAL EXPLANATION

UNIT -7

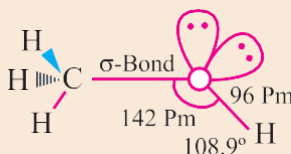
ALCOHOLS PHENOLS AND ETHERS

Points to Remember

1. Hydroxyl (– OH) derivatives of alkane are called alcohols.
2. Alcohols are classified as 1°, 2° and 3°.
3. –OH group is attached to sp^3 hybridized carbon. Alcohols further may be monohydric, dihydric and polyhydric on the basis of OH group.
4. **Phenols** : Compounds containing – OH group bound directly to benzene ring.



5. **Structure** : Oxygen atom is sp^3 hybridised and tetrahedral geometry of hybrid atomic orbitals ROH bond angle depends upon the R group. R – O – H angle for $\text{CH}_3 - \text{OH}$ is 108.9° .



6. **Isomerism** :
 - (i) Functional isomerism
 - (ii) Chain isomerism
 - (iii) Positional isomerism

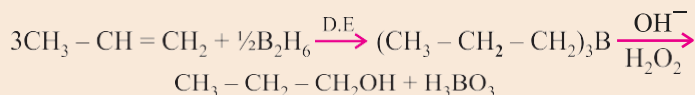
VISUAL EXPLANATION

7. **General Methods of Preparation** :

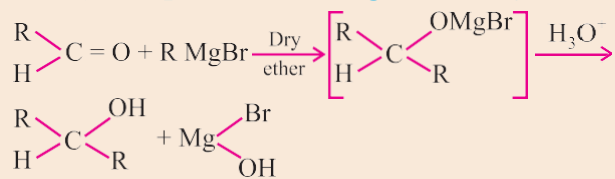
(i) Acid catalysed hydration of alkenes :



(ii) Hydroboration oxidation :

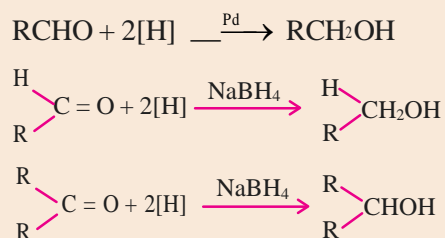


(iii) From carbonyl compounds with Grignard's reagent :



Formaldehyde gives 1° alcohol and ketones gives tertiary alcohol.

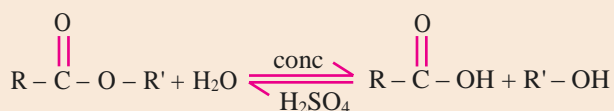
(iv) By reduction of carbonyl compounds :



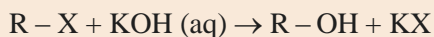
(v) By reduction of esters with LiAlH₄ or Na/C₂H₅OH :



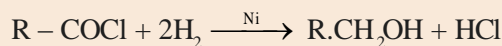
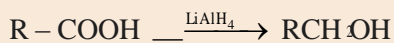
(vi) By hydrolysis of esters :



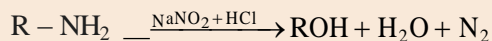
(vii) From alkyl halides :



(viii) By reduction of acids and their derivatives :



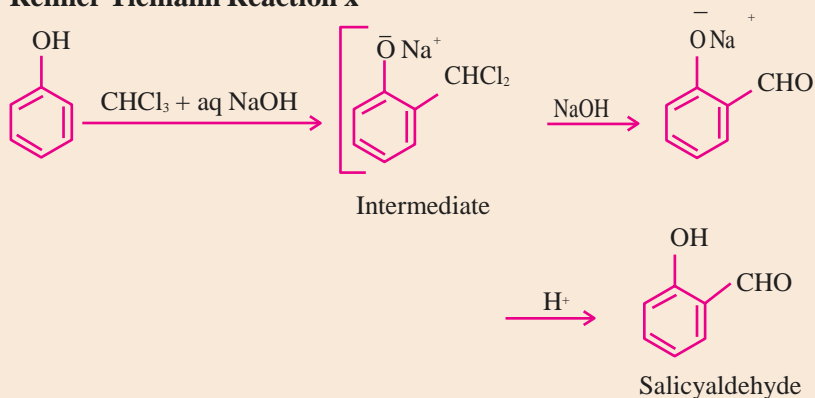
(ix) From 1° amines :



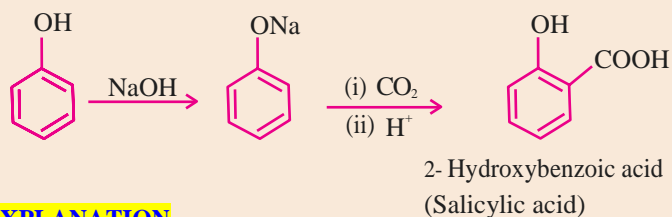
VISUAL EXPLANATION

NAME REACTIONS

1. Reimer Tiemann Reaction

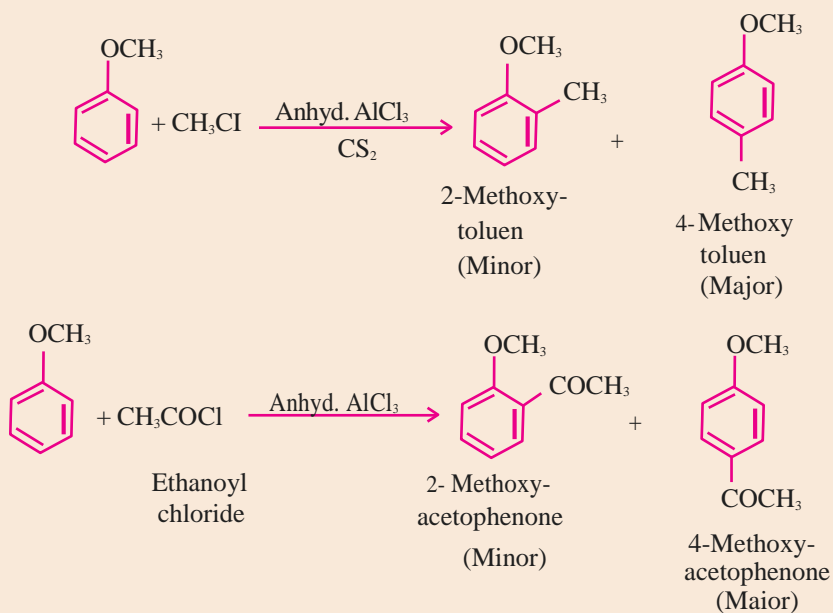


2. Kolbe reaction

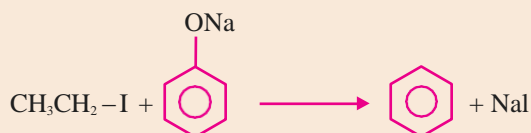


VISUAL EXPLANATION

3. Friedel craft reaction



4. Williamson synthesis: Reaction with alkyl halide with sodium alkoxide or sod. Phenoxide is called Williamson synthesis.

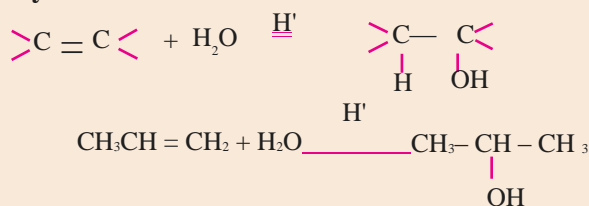


Both simple and mixed ether can be produced.

Depending upon structure and cleavage of unsymmetrical ethers by halogen acid may occur either by SN^2 or SN^1 mechanism.

MECHANISMS

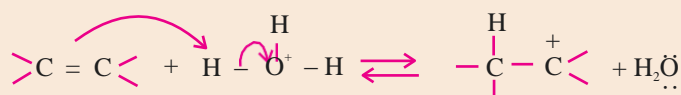
1. Hydration of Alkene :



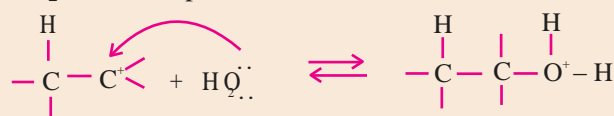
Mechanism

The mechanism of the reaction involves the following three steps:

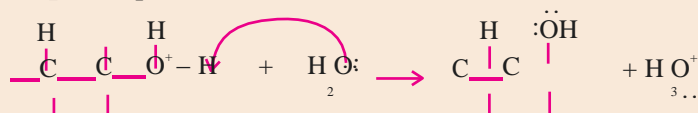
Step 1: Protonation of alkene to form carbocation by electrophilic attack of H_3O^+ .



Step 2: Nucleophilic attack of water on carbocation.

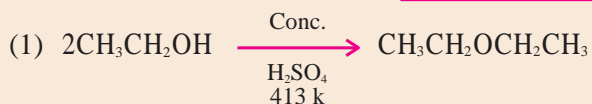
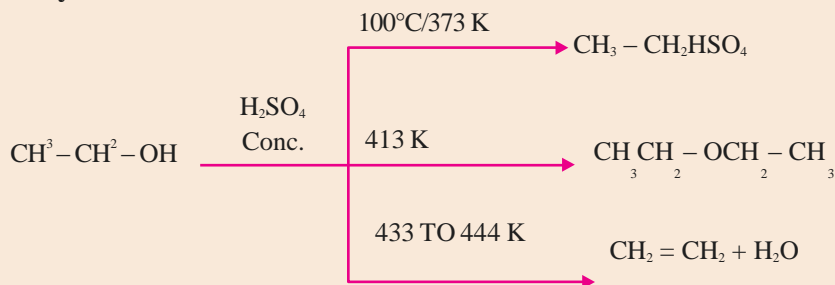


Step 3: Deprotonation to form an alcohol.

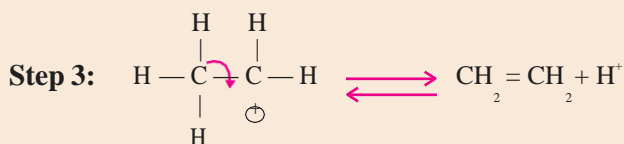
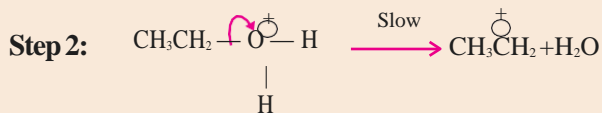
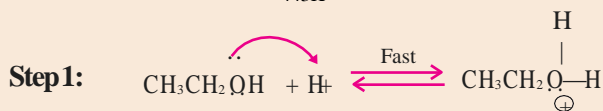
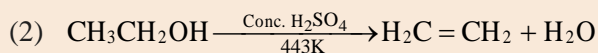
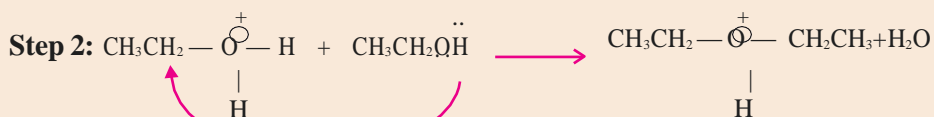
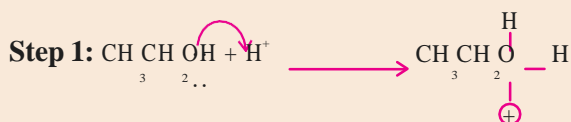


VISUAL EXPLANATION

2. Dehydration Reaction



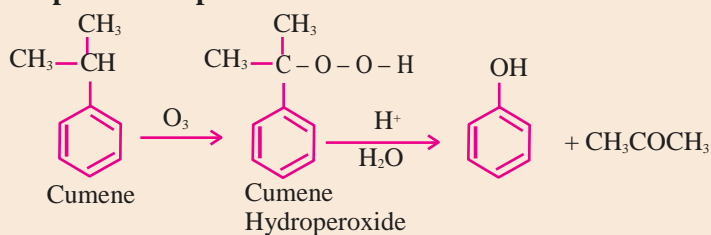
Mechanism:



[CLICK HERE FOR POWER POINT PRESENTATION](#)

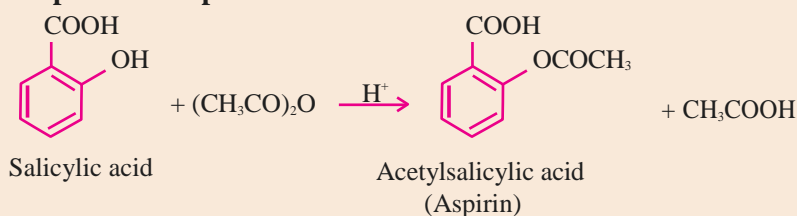
IMPORTANT PREPARATIONS

(1) Preparation of phenol from Cumene

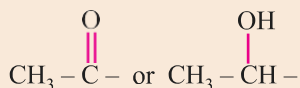


VISUAL EXPLANATION

(2) Preparation of Aspirin



8. Ethers are dialkyl derivatives of water or monoalkyl derivatives of alcohols with formula R – O – R'
9. Lucas test can be used to distinguish primary, secondary and tertiary alcohols (ZnCl₂ + HCl).
(3° turbidity – instant, 2° - 5 minutes, 1° - heating for 60 minutes)
10. Ethers are relatively inert and hence are used as solvents.
11. 100% ethanol is known as absolute alcohol.
12. 95% ethanol is called rectified spirit.
13. A mixture of 20% ethanol and 80% gasoline is known as power alcohol.
14. Iodoform test is used for distinguishing compounds having the groups



15. Presence of EWGs increase the acid strength of phenols while EDG decrease the acid strength.

EWG : – NO₂, – X, – CN, – COOH etc.

EDG : – R, – OR, – OH, – NH₂ etc.

16. 3° alcohols are resistant to oxidation due to lack of α-hydrogen.
17. Intermolecular H-bonds of *p*- and *m*-nitrophenol increases water solubility/acid strength while intramolecular H-bonds in *o*-nitrophenol decreases these properties.
18. In the reaction of alkyl aryl ether (anisole) with HI, the products are always alkyl halide and phenol because O – R bond is weak than O – Ar bond which has partial double character due to resonance.
19. C – O – C bond in ether is bent and hence the ether is always polar molecule even if both alkyl groups are identical.

UNIT -8

ALDEHYDES KETONES AND CARBOXYLIC ACIDS

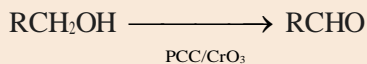
Points to Remember

1. Aldehydes and ketones, are commonly called as carbonyl compounds.
2. In Rosenmund's reduction, poisoning of Pd with BaSO₄ prevent reduction of R – CHO to R – CH₂OH.
3. In the reaction of toluene with CrO₃, acetic anhydride is used to protect benzaldehyde by forming benzylidenediacetate to avoid its oxidation to benzoic acid.
4. Order of reactivity of aldehydes and ketones towards nucleophilic addition is :
 - (i) HCHO > CH₃CHO > CH₃CH₂CHO.
 - (ii) HCHO > RCHO > R CO R.
 - (iii) ArCHO > Ar COR > Ar CO Ar.
5. Benzaldehyde does not reduce Fehling's reagent.
6. Aldehydes and ketones with atleast one α-H atom get condensed in presence of a base. This is known as Aldol condensation.
7. Aldol condensation involves carbanion as intermediate.
8. Aldehydes with no α-H atoms under Cannizzaro's reaction.
9. Ketones react with dihydric alcohols to form cyclic ketals.
10. Monocarboxylic acids having (C₁₂–C₁₈) carbon atoms, are called fatty acids.
11. Boiling points of carboxylic acids is greater than corresponding alcohols.
12. Presence of EWGs enhances the acidic character of carboxylic acids.
13. –COOH group is *m*-directing in electrophilic substitution reactions.
14. Compounds containing – CHO group are named as carbaldehydes if – CHO groups are three or more.
15. Isomerism : Chain, position and functional.
16. Structure of –CHO group *sp*² hybridised.



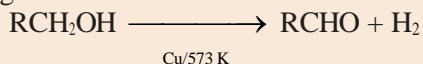
17. General Methods of Preparation:

(i) Controlled oxidation of 1° alcohols :

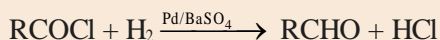


(Collin's reagent)

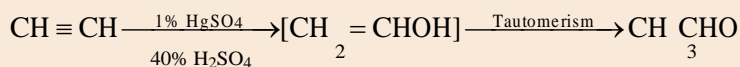
(ii) Dehydrogenation of 1° alcohols :



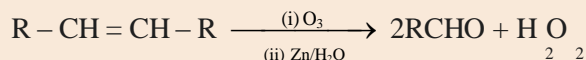
(iii) From Rosenmund reaction/reduction :



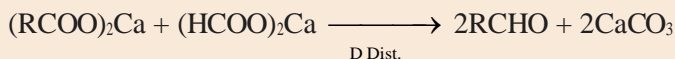
(iv) Hydration of alkynes :



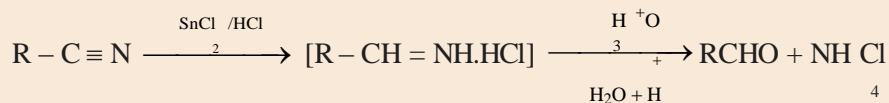
(v) Reductive ozonolysis of alkenes :



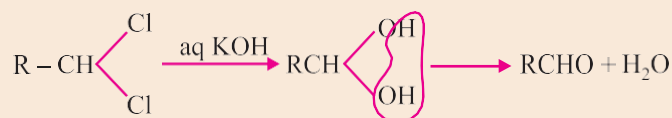
(vi) From salts of fatty acids :



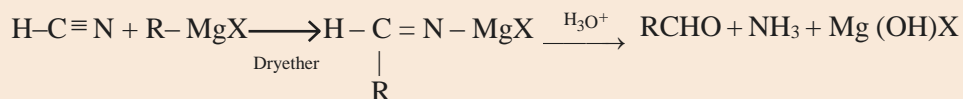
(vii) Stephen's reduction of nitrile compounds :



(viii) Hydrolysis of geminal halides :

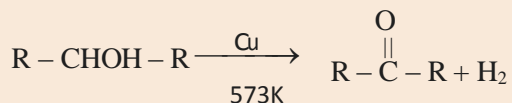


(ix) From Grignard's reagent :

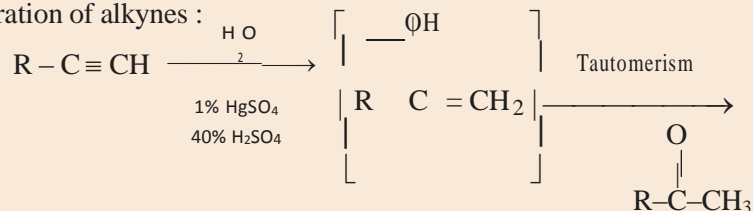


General Methods of Preparation of Ketones only

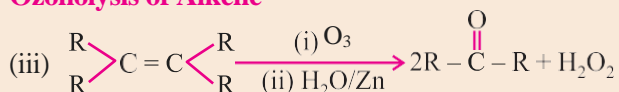
(i) Dehydrogenation of 2° alcohols :



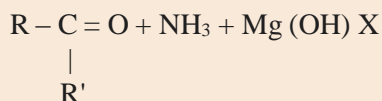
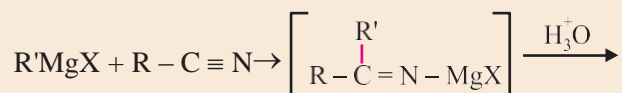
(ii) Hydration of alkynes :



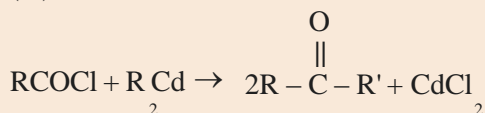
Ozonolysis of Alkene



(iv) From Grignard's reagents :



(iv) From acid chlorides :



Physical Properties:

HCHO is a gas at normal temperature. Formalin is 40% as solution of HCHO. Due to polarity they have high values of boiling point. Solubility in water is only for lower members.

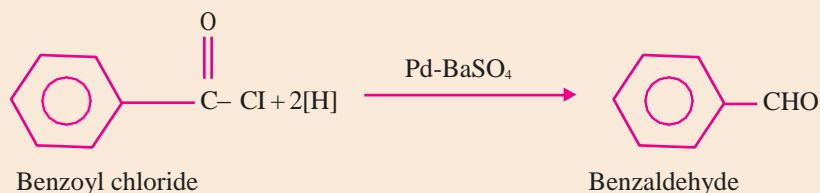
Reactivity :

- (i) + I effect of alkyl groups decreases the +ve charge on carbonyl carbon.
- (ii) Steric hindrance : Bulky group hinder approach of nucleophile.
- (iii) α -hydrogen atom is acidic due to resonance.

[CLICK HERE FOR PRESENTATION](#)

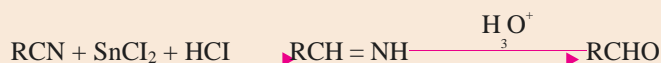
1. ROSENMUND REDUCTION:

Acyl chlorides when hydrogenated over catalyst, palladium on barium sulphate yield aldehydes



2. STEPHEN REACTION

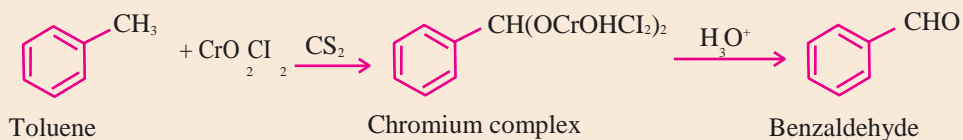
Nitriles are reduced to corresponding imines with stannous chloride in the presence of Hydrochloric acid, which on hydrolysis give corresponding aldehyde.



3. ETARD REACTION

On treating toluene with chromyl chloride CrO_2Cl_2 , the methyl group is oxidized to a chromium complex, which on hydrolysis gives corresponding benzaldehyde.

OR

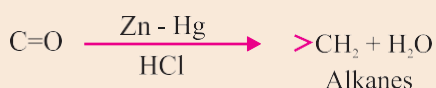


This reaction is called Etard reaction

4. CLEMMENSEN REDUCTION

VISUAL EXPLANATION

The carbonyl group of aldehydes and ketone is reduced to $-\text{CH}_2$ group on treatment with zinc amalgam and conc. Hydrochloric acid.



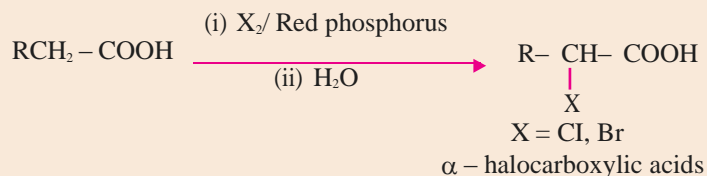
5. WOLFF-KISHNER REDUCTION

On treatment with hydrazine followed by heating with sodium or potassium hydroxide in high boiling solvent like ethylene glycol

CARBOXYLIC ACID

1. HELL-VOLHARD-ZELINSKY REACTION (HVZ)

Carboxylic acids having an α - hydrogen are halogenated at the α -position on treatment with chlorine or bromine in the presence of small amount of red phosphorus to give α -halocarboxylic acids.



2. ESTERIFICATION

Carboxylic acids react with alcohols or phenols in the presence of a mineral acid such as conc. H_2SO_4 as catalyst to form esters.



18. Vinegar is 8 to 10% solution of CH_3COOH .
19. α -hydrogen atoms in carboxylic acid are acidic in nature and can be easily replaced by halogen atoms in HVZ reaction.
21. Relative acid strength of $\text{RCOOH} > \text{HOH} > \text{ROH} > \text{HC} \equiv \text{CH} > \text{NH}_3$. It is because a strong acid has weak conjugate base.
22. Some dicarboxylic acids bearing general formula $\text{HOOC} - (\text{CH}_2)_n - \text{COOH}$ where $n = 0, 1, 2, \dots$ etc.

$\text{HOOC} - \text{COOH}$ Oxalic acid 1, 2 ethanedioic acid

$\text{HOOC} - \text{CH}_2 - \text{COOH}$ Malonic acid 1, 3 propanedioic acid

$\text{HOOC} - (\text{CH}_2)_2 - \text{COOH}$ Succinic acid 1, 4 butanedioic acid

$\text{HOOC} - (\text{CH}_2)_3 - \text{COOH}$ Glutonic acid 1, 5 pentamdioic acid

$\text{HOOC} - (\text{CH}_2)_4 - \text{COOH}$ Adipic acid 1, 6 hexanedioic acid

23. Melting points : Higher : Even carbon atoms than next lower or higher homologues containing even number of carbon atoms due to symmetry and closer packing of molecules in the crystal lattice.

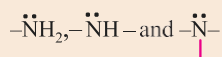
VISUAL EXPLANATION

UNIT -9

AMINES

Points to Remember

1. Amines are alkyl and/or aryl derivatives of NH_3 .
2. Functional groups of 1° , 2° and 3° amines are respectively as given below :

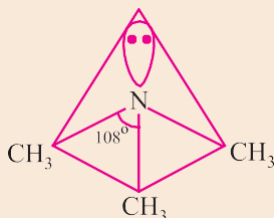


3. Gabriel phthalimide synthesis can't be used for the preparation of 2° and 3° amines. It gives aliphatic primary amine only.
4. Hoffmann's bromamide reaction gives 1° amines having one carbon atom less than parent primary amide.
5. The order of basic strength of aliphatic amines is :
 - (i) Aliphatic amines are more basic than $\ddot{\text{N}}\text{H}_3$.
 - (ii) In aqueous solution medium, the order is $2^\circ > 1^\circ > 3^\circ$ (for $-\text{CH}_3$ group) and $2^\circ > 3^\circ > 1^\circ$ for $-\text{C}_2\text{H}_5$ group.
 - (iii) In non-aqueous medium or gaseous phase, the order is $3^\circ > 2^\circ > 1^\circ$.
6. Basic strength of aromatic amines :
 - (i) Aromatic amines are weaker bases than $\ddot{\text{N}}\text{H}_3$.
 - (ii) ERGs like $-\text{CH}_3$, $-\text{OR}$, $-\text{NH}_2$ etc. increase basic strength while EWGs like $-\text{NO}_2$, $-\text{CN}$ etc. decrease the basic strength. The effect of substituents is more at para positions and less at meta position.

VISUAL EXPLANATION

7. Basic strength of amines is expressed in terms of K_b or $\text{p}K_b$.
8. 1° , 2° and 3° amines can be distinguished by Hinsberg's test.
9. Hinsberg's reagent is benzenesulphonyl chloride ($\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$).
10. 3° amines like trimethylamine are used as insect attractants.
11. Diazonium salts are represented by the general formula $[\text{Ar N} \equiv \text{N}]^+ \text{X}^-$.

12. **Structure of amines :** Pyramidal for trimethyl amine $(\text{CH}_3)_3\text{-}\bar{\text{N}}$. They are Lewis bases.



13. Carbylamine test only given by 1° amines.
14. Manich reaction involves the reaction of ketones with HCHO and NH₃ (or amine) in acidic medium to form Manich bases.
15. 1° amines give effervescence with HNO₂.
16. –NH₂ group in aniline is *o*- and *p*- directing and is highly activating in nature.
17. Acylation of aniline is done before subjecting it to nitration or halogenation.
18. Aliphatic diazonium salts are very unstable and do not exist while aromatic salts are relatively stable.
19. These salts are prepared from 1° aryl amines by diazotization reactions.
20. Diazotised salts (diazonium salts) are used to prepare a variety of aromatic compounds.
21. R – C ≡ N have generally pleasant odours but alkyl isocyanides have highly unpleasant odours.
22. Alkyl isocyanides have lower boiling points than that of isomeric alkyl cyanides due to lower dipole moments.
23. Arenediazonium salts are highly reactive compounds and reactivity is due to excellent leaving ability of diazo group as N₂ gas.

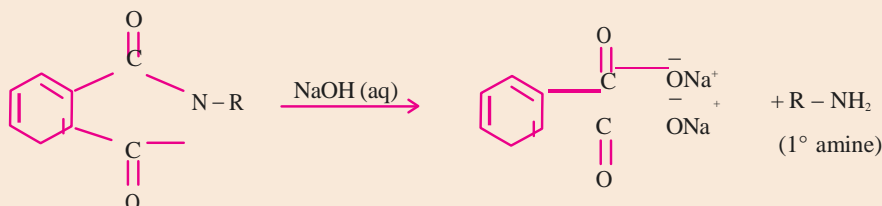
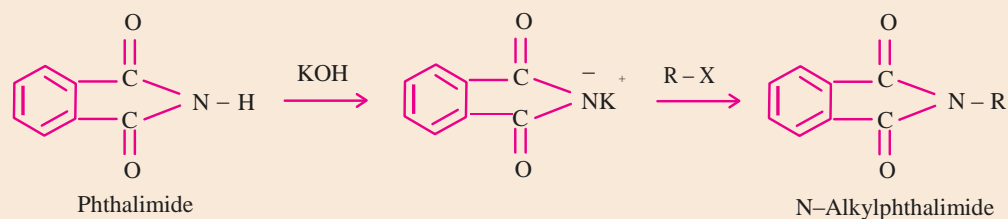
VISUAL EXPLANATION

NAME REACTIONS

1. Gabriel phthalimide synthesis

Gabriel synthesis is used for the preparation of primary amines. Phthalimide on treatment with ethanolic potassium hydroxide forms potassium salt of phthalimide which on heating with alkyl halide followed by alkaline hydrolysis produces the corresponding primary amine. Aromatic primary amines cannot be prepared

by this method because aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide.



2. Hoffmann bromamide degradation reaction

Hoffmann developed a method for preparation of primary amines by treating an amide with bromine in an aqueous or ethanolic solution of sodium hydroxide. The amine so formed contains one carbon less than present in the amide.



3. Carbylamine reaction

Aliphatic and aromatic primary amines on heating with chloroform and ethanolic potassium hydroxide form isocyanides or carbylamines which are foul smelling substances. Secondary and tertiary amines do not show this reaction. This reaction is known as carbylamine reaction or isocyanide test and is used as a test for primary amines.

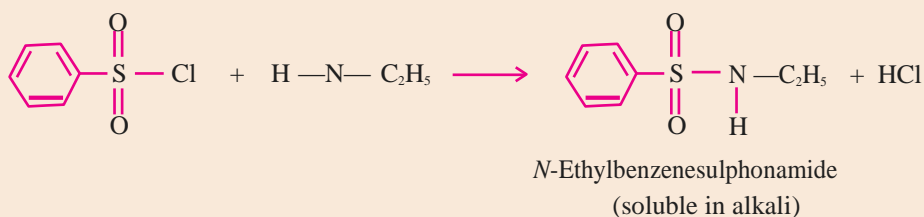


VISUAL EXPLANATION

4. Hinsberg Test:

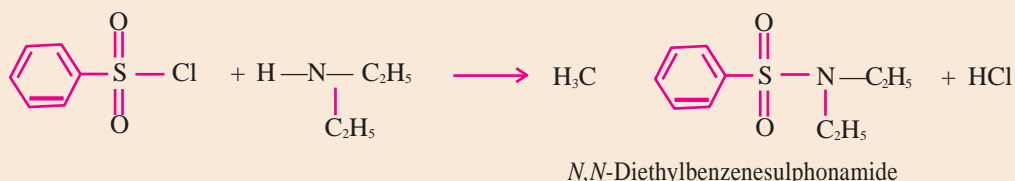
Benzenesulphonyl chloride ($\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$), which is also known as Hinsberg's reagent, reacts with primary and secondary amines to form sulphonamides.

- (a) The reaction of benzenesulphonyl chloride with primary amine yields N-ethylbenzenesulphonyl amide.



The hydrogen attached to nitrogen in sulphonamide is strongly acidic due to the presence of strong electron withdrawing sulphonyl group. Hence, it is soluble in alkali.

- (b) In the reaction with secondary amine, N, N-diethylbenzenesulphonamide is formed.

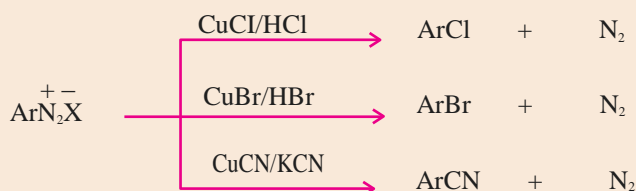


Since N, N-diethylbenzene sulphonamide does not contain any hydrogen atom attached to nitrogen atom, it is not acidic and hence insoluble in alkali.

- (c) Tertiary amines do not react with benzenesulphonyl chloride. This property of amines reacting with benzenesulphonyl chloride in a different manner is used for the distinction of primary, secondary and tertiary amines and also for the separation of a mixture of amines.

5. Sandmeyer Reaction

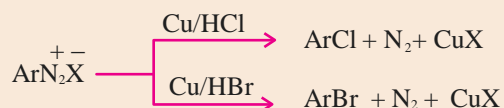
The Cl⁻, Br⁻ and CN⁻ nucleophiles can easily be introduced in the benzene ring of diazonium salts in the presence of Cu(I) ion.



VISUAL EXPLANATION

6. Gatterman Reaction

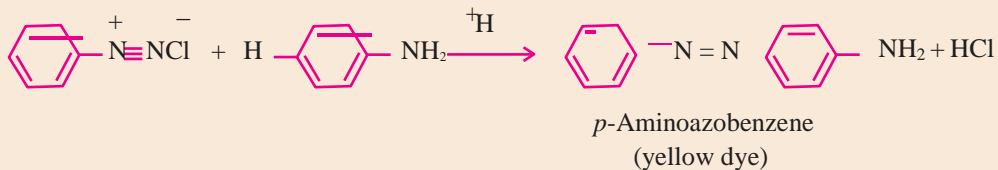
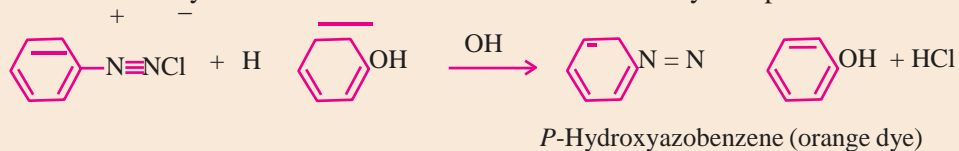
Chlorine or bromine can be introduced in the benzene ring by treating the diazonium salt solution with corresponding halogen acid in the presence of copper powder.



7. Coupling reactions

The azo products obtained have an extended conjugate system having both the aromatic rings joined through the -N=N- bond. These compounds are often coloured and are used as dyes. Benzene diazonium chloride reacts with phenol in which the phenol molecule at its para position is coupled with the diazonium salt to form p-hydroxyazobenzene. This type of reaction is known as coupling reaction.

Similarly the reaction of diazonium salt with aniline yields p-aminoazobenzene.



VISUAL EXPLANATION

DISTINCTION BETWEEN PAIRS OF COMPOUNDS

Give one chemical test to distinguish between the following pairs of compounds.

- (i) Methylamine and dimethylamine
- (ii) Secondary and tertiary amines
- (iii) Ethylamine and aniline



UNIT -10

BIOMOLECULES

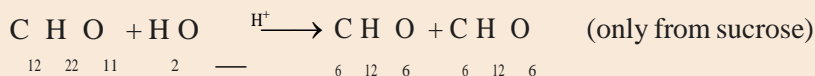
Points to Remember

1. **Carbohydrates :** These are optically active polyhydroxy aldehydes or ketones or the compounds which produce these on hydrolysis.
2. **Classification :**
 - (i) **Monosaccharides :** Those carbohydrates which cannot be hydrolysed into further simpler carbohydrates. *E.g.*, glucose, fructose, galactose etc.
 - (ii) **Disaccharides :** Those carbohydrates which produces two monosaccharides on hydrolysis. *E.g.*, sucrose, maltose and lactose.
 - (iii) **Oligosaccharides :** Those carbohydrates which give two to ten monosaccharides on hydrolysis.
 - (iv) **Polysaccharides :** Those carbohydrates which on hydrolysis give large number of monosaccharides hydrolysis. *E.g.*, starch, cellulose, glycogen.
3. **Sugar :** Carbohydrates which are sweet in taste.
 - (i) **Reducing sugars :** Those which reduce Fehling's or Tollen's reagent due to availability of free aldehydic groups. *E.g.*, glucose, fructose, galactose.
 - (ii) **Non-reducing sugars :** Those which do not reduce Fehling's or Tollen's reagent. They do not have free aldehydic group. *E.g.*, sucrose.
4. **Glucose :** It is a monosaccharide with molecular formula $C_6H_{12}O_6$

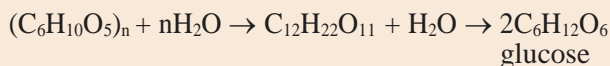
VISUAL EXPLANATION

Preparation :

(i) **From sucrose :**

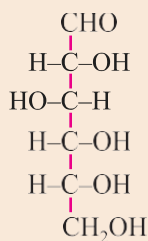


(ii) **From starch :**



5. **Structure :**

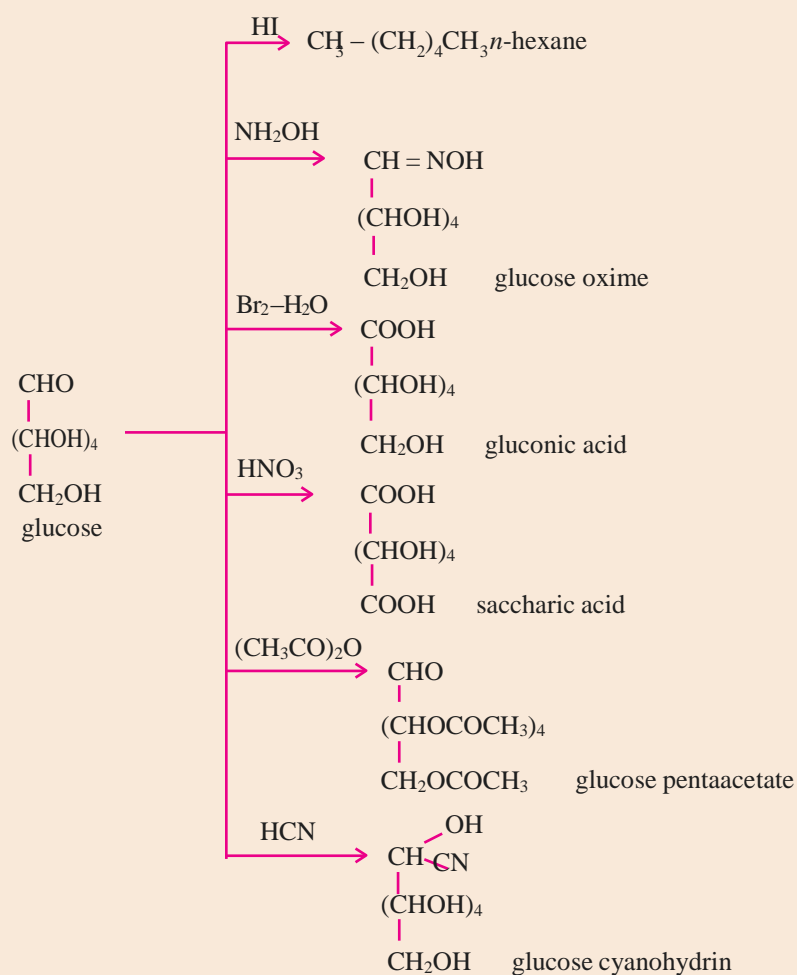
Fischer structure : (+) glucose has 'D' configuration as shown



D-(+)-glucose

'D'- means – OH group on first chiral 'C' from the bottom is on right hand and (+) means it is dextrorotatory *i.e.*, it rotates plane polarized light towards right.

Reactions of glucose :



Objections against open chain structure of glucose

The open chain structure was unable to explain the following reactions :

- (a) It does not give the 2, 4-DNP test, Schiff's test and does not form the hydrogensulphite product with NaHSO_3 .
- (b) The pentacetate of glucose does not react with NH_2OH , indicating the absence of free aldehydic group.
- (c) Glucose exist in 2 different crystalline forms α and β forms. These are called anomers. They differ in optical rotation, they also differ in melting point.

After which a close chain (cyclic) structure of glucose was proposed by Haworth.

* Anomers are isomers which have a different configuration at C-1 functional group c-atom

- 6. **Glycosidic linkage** : The linkage between two monosaccharide units through oxygen is called the glycosidic linkage.

VISUAL PRESENTATION

- 7. **Proteins** : These are macro molecules made up of amino acids joined by amide linkage $[-(-\text{CONH}-)-]$ is here called as peptide linkage. These are required for growth and development of the body.
- 8. **Amino acids** : These contain an amino ($-\text{NH}_2$) and an acidic ($-\text{COOH}$) group and are therefore amphoteric in nature. In solution they exist in the form of zwitter ion (a dipolar ion).
- 9. **Classification**

Fibrous Protein	Glubular Protein
(i) Polypeptide chains run par`allel or anti-parallel and held together by hydrogen and disulphide bonds.	(i) Chains of polypeptide coil around to give a spherical shape.
(ii) Generally insoluble in water <i>e.g.</i> , keratin, collagen, myosin, fibroin.	(ii) Usually soluble in water, <i>e.g.</i> , insulin, thyroglobin, albumin, haemoglobin and fibrinogen gets converted into fibrous protein fibroin on clotting of blood.

10. Structure and shape of protein (Ref. page no. 416 NCERT Book)

Primary structure	Secondary structure	Tertiary structure	Quaternary structure
The specific sequence of amino acids in the polypeptide chain. Change in amino acids sequence changes the protein completely. They have covalent bonds.	It is the shape in which the long polypeptide chain can exist. It is of two types : α -helix and β -pleated. These structures arise due to regular folding of the backbone of the polypeptide chain due to H-bonding between the C = O and -NH - groups of the peptide bond.	Represents overall folding of the polypeptide chain. It gives rise to the fibrous or globular molecular shapes. Forces stabilizing the 2° and 3° structures are hydrogen bonds, disulphide linkages, van der Waal's and electrostatic forces of attraction.	Protein can be composed of two or more polypeptide chains called sub-units. The spatial arrangement of these sub-units with respect to each other is quaternary structure of the protein.

- Native state of protein :** The parental state or the natural state in which the protein is found.
- Denaturation of protein :** Destruction of the native state of protein is denaturation. It can be brought by physical and chemical methods. The 2° and 3° structures are destroyed, only 1° structure is retained.

VISUAL EXPLANATION

Enzymes : These are biocatalyst and generally globular proteins *e.g.*, invertase, zymase, phenylalanine hydroxylase, urease etc.

Main characteristics of enzymes :

- It speed up the biological reaction upto million times.
 - It is highly specific and work on lock and key theory.
 - It is highly sensitive to pH and temperature.
- Vitamins :** They are organic compounds required in the diet in small amounts to perform specific biological functions for maintenance of optimum growth and health of the organism. They are classified as follows :
 - Fat soluble vitamins :** Vitamin A, D, E and K. They are stored in liver and adipose tissues.

- (ii) **Water soluble vitamins** : B group vitamins and vitamin C. They need to be supplied regularly in diet as they are excreted in urine and cannot be stored (except vitamin B₁₂) in our body.

Their deficiency causes diseases. (Ref. table in page no. 418 of NCERT Book)

Biotin (Vit H) is however neither fat nor water soluble. Its deficiency leads to loss of hair.

14. **Nucleic acids** : These are biomolecules which are long chain polymers of nucleotides. They are of two types :

(i) **Deoxyribonucleic acid (DNA)**

(ii) **Ribonucleic acid (RNA)**

15. Vitamin	Deficiency disease
A	Xerophthalmia (eye fails to produce tears), night blindness
B ₁	Beri-beri(severe lethargy)
B ₂	Ariboflavinosis, cheilosis, burning sensation of skin
B ₁₂	Pernicious anaemia(gradual loss of RBCs), inflammation of tongue and mouth
C	Scurvy
D	Rickets & osteomalacia(softening of bones)
E	Increased fragility of RBC and muscular weakness
K	Increased blood clotting time
H	Loss of hair

VISUAL EXPLANATION

16. Hormones are chemical substances which are produced in ductless glands in the body.
17. Nucleoside = Base + Sugar
Nucleotide = Base + Sugar + Phosphoric acid

18. DNA	RNA
(i) Double helical.	(i) Single stranded.
(ii) Sugar is 2-deoxyribose.	(ii) Sugar is ribose.
(iii) Bases : A, T, G, C.	(iii) Bases : A, U, G, C.
(iv) Property of replication.	(iv) Do not replicate.
(v) It is responsible for transmission of heredity character.	(v) Helps in protein biosynthesis.