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പ്രിയപ്പെട്ട കുട്ടികളോട്,

കോവിഡ് മഹാമാരിമൂലം 2020-21 അധ്യയനവർഷം ജൂണ് 1ന് ആരംഭിച്ചത് ഓൺലൈൻ പ്രക്രിയയിലൂടെയാണല്ലോ. എന്നാൽ + 2 ക്ലാസുകൾക്ക് മുഖാമുഖമുള്ള പഠനമാരംഭിച്ചത് 2021 ജനുവരി ഒന്നിനാണ് - അതും സാമൂഹികഅകലം പാലിച്ച് ഒരു ക്ലാസിലുള്ള കുട്ടികളുടെ എണ്ണം ക്രമീകരിച്ചുകൊണ്ട്. പുതിയ ഒരു ശീലത്തിലേക്ക് മാറിയതുകൊണ്ട് പല കുട്ടികള്ക്കും പൊതുപരീക്ഷക്ക് തയ്യാറെടുക്കുന്നതിന് വിഷമമുണ്ടാകും. അതുകൊണ്ട് ഈ മഹാമാരിക്കാലത്തും മികച്ചരീതിയിൽ കുട്ടികളെ പരീക്ഷക്കായ് തയ്യാറാക്കുന്നതിനും ആത്മവിശ്വാസം നൽകുന്നതിനുമുള്ള ഒരു ഉപാധിയായാണ് ഈ കൈപ്പുസ്തകം നിങ്ങളുടെ മുന്നിലേക്കെത്തിക്കുന്നത്. ഈ വർഷം വിദ്യാഭ്യാസവകുപ്പ് പ്രസിദ്ധീകരിച്ച ഫോക്കസ് ഏരിയയെ കേന്ദ്രീകരിച്ച്, ലഘുനോട്ടുകളും, മാതൃകാചോദ്യങ്ങളുമായാണ് ഈ കൈപ്പുസ്തകം തയ്യാറാക്കിയിട്ടുള്ളത്. കൈപ്പുസ്തകത്തിനുപരിയായി ടെക്സ്റ്റ് ബുക്ക് കൂടി ആധാരമാക്കി കുട്ടികൾ പഠനം ക്രമീകരിക്കേണ്ടതാണ്.അങ്ങനെ ശരിയായ രീതിയിൽ ഈ പുസ്തകം പ്രയോജനപ്പെടുത്തിയാൽ ആത്മവിശ്വാസത്തോടെ പരീക്ഷയെ നേരിടാനാവുമെന്ന് പ്രതീക്ഷിക്കുന്നു.

റിസോഴ്സ് അധ്യാപകർ

CONTENTS

1. THE SOLID STATE

Based on structural features solids are classified into two. Crystalline solids and amorphous solids.

Crystalline solids

- Long range order
- Sharp melting point
- Anisotropic in nature (Physical properties are different in different directions.)

Amorphous solids

- Short range order
- No sharp melting point
- Isotropic in nature (Physical properties are same in all directions)

Crystal lattice : The three dimensional arrangement of constituent particles in a crystal is called crystal lattice or space lattice.14 types of crystal lattices are possible called **Bravais lattices.**

Unit cell : The smallest repeating unit in a crystal lattice is called unit cell.

(a) **Primitive unit cell** (simple unit cell): In this unit cell, the constituent particles are present at the corners only.

(b) **Centred unit cell:** In this unit cell, the constituent particles are present at the corners and other positions

These are of three types.:

(i) **Face-Centred unit cell**: In this unit cell, the constituent particles are present at the corners and centres of each faces.

(ii) **Body-Centred unit cell:** In this unit cell, the constituent particles are present at the corners and centre of the body.

(iii) **End-Centred unit cell:** In this unit cell, the constituent particles are present at the corners and any two opposite faces.

Number of atoms in different cubic unit cells:

i) Primitive (or simple) cubic unit cell – 1 (particles at all the corners)
ii) Face centred cubic unit cell – 4 (particles at all corners and centre of each faces)
iii) Body centred cubic unit cell – 2 (particles at all corners and at the centre)

Close packing

In the formation crystals, the packing of constituent particles take place in such a way that the available space is used most economically. This type of packing is called close packing.

Coordination number

It is the number of nearest neighbours of a particle in a crystal.

Interstitial void

The vacant space present in close packing is called interstitial void. These are two types.

(a) Tetrahedral void: The void surrounded by four spheres is called tetrahedral void.

(b) Octahedral void: The void surrounded by six spheres is called octahedral void.

If 'N' is the number of close packed particles(spheres),

The number of tetrahedral voidsgenerated = 2N

The number of octahedral voidsgenerated = N

Close packing in three dimensions:

(i) Hexagonal close packing (hcp): The AB, AB ...pattern of arrangement of constituent particles in crystal. Zn, Cd etc possess hcp structure.Its co.ordination number is12

ii) Cubic close packing (ccp) or face centred cubic (fcc) : The ABC, ABC. .pattern of arrangement of particles in crystal. Cu, Ni etc possess ccp structure. Its co.ordination number is12

Imperfections or defects in crystals

Any deviation from perfectly ordered arrangement of atoms or ions in crystals is called defects or imperfection. These are of two types. (i) Line defect (ii) Point defect

Point defects are three types : 1. Stoichiometric point defects 2.Non stoichiometric point defects and 3. Impurity defects

1.Stoichiometric point defect (Thermodynamic point defect / intrinsic point defect)

The defect which do not disturb the stoichiometry of the solid is called stoichiometric point defect.

Two types of stoichiometric point defects shown by ionic solids are:

(i) **Schottky defect**:- This defect is due to the missing of equal number of anions and cations from lattice site. It is also a vacancy defect. Due to this defect density of the crystal decreases.

Examples:- NaCl, KCl, CsCl, AgBr, etc.

(ii) **Frenkel defect** (Dislocation defect):-

This defect is due to the dislocation of the cations from the lattice site to the interstitial site. It is an interstitial defect and vacancy defect.During this defect density of the crystal remains unchanged.

Examples:- AgCl, AgBr, AgI, ZnS etc

2.Non stoichiometric point defect

The defect which disturb the stoichiometry of the solid is called non-stoichiometric point defect

(a) *Metal excess defect due to anion vacancies*:-

In this defect, the anion is missing from lattice site.To maintain electrical neutrality, electron is occupied in the anionic vacancies. This centre is called F-centre (Colour centre). Due to the formation of F-centre, the crystals become coloured.Examples:- Heating of NaCl in an atmosphere of Na develops yellow colour. ie, excess of Na in NaCl gives yellow colour. Similarly, Excess of K in KCl gives violet colour and excess of Li in LiCl gives pink colour.

(b) *Metal excess defect due to extra cation at interstitial site*

In this defect, extra cations are present at the interstitial site. To maintain electrical neutrality, electron is also present at the neighboring interstitial site.

Examples:- When ZnO is heated, it loses oxygen and turns yellow in colour.

Here excess Zn^{2+} formed present at the interstitial site and equivalent number of electrons are also accommodated in the neighbouring interstitial site.

(c) *Metal deficiency defect due to cation vacancy*

In this defect, some cations are missing from lattice site. To maintain electrical neutrality an adjacent metal atom acquires extra positive charge. Examples:- FeO.

FeO is mostly found with a composition of $Fe_{0.95}O$

3.Impurity Defects: It is the defect arising due to the presence of foreign particles in a crystal.

Eg. when molten NaCl is crystallised in presence of small amount of $SrCl_2$, some Na + ions are replaced by Sr^{2+} ions and some cationic vacancies are formed. The no. of cationic vacancies produced is equal to the number of Sr^{2+} ions occupied. Another example is a solid solution of $CdCl_2$ and AgCl.

Properties of solids

1) **Electrical properties**:

Conduction of Electricity in metals, semi-conductors and insulators - Band Model

According to band model, in metal there are two types of bands – valence band and conduction band. Valence band is the lower energy electron occupied band and conduction band is the higher energy unoccupied band.

In metals, the valence band is either partially filled or it is overlapped with the conduction band.

So electron can easily flow from the valence band to the conduction band.

In semi-conductors, there is a small energy gap between the valence band and conduction band and only a few electrons can enter into the conduction band. So they conduct only partially.

In insulators, the gap between the valence band and the conduction band is large and so they do not conduct electricity.

Magnetic properties of Solids

1. Paramagnetic substance:- The substance which is weakly attracted by magnetic field is called paramagnetic substance. It can be magnetised in a magnetic field in the same direction. It loses its magnetism in the absence of magnetic field. Paramagnetism is due to the presence of unpaired electrons.

Example:- O_2 , Cu^{2+}, Fe^{3+}, Cr^{3+}

2. Diamagnetic substance: The substance which is weakly repelled by magnetic field is called diamagnetic substance. It can be weakly magnetised in a magnetic field in the opposite direction. Diamagnetism is due to the absence of unpaired electrons. Example:- NaCl, H_2O , benzene

*3. Ferromagnetic substance:-*The substance which is strongly attracted by magnetic field is called ferromagnetic substance. It retains magnetism even in the absence of magnetic field. ie, It can be permanently magnetised. Ferromagnetism is due to the spontaneous alignment of magnetic moments (domains) in the same direction. These substances are used for making peramanent magnet.

Example:- Fe, Co, Ni, CrO_2 , Gd (Gadolinium)

4. Antiferromagnetic substance: The substance which are expected to have high magnetic moments but actually it possess zero magnetic moments are called antiferromagnetic substance. It is due to the alignments of magnetic moments in the opposite direction alternatively.

Example:- MnO

5. Ferrimagnetic substance: The substance which are expected to have high magnetic moments but actually it possess small magnetic moments are called ferrimagnetic substance. Here some of the magnetic moments arecancelled each other and remaining exhibit magnetic properties.

Example:- Fe_3O_4 (magnetite), $ZnFe_2O_4$ (Zinc ferrite), $MgFe_2O_4$ (Magnesium ferrite)

On heating ferrimagnetic substance, it becomes paramagnetic.

Model Questions

1. Defects are found even in crystals prepared very carefully.

(i) Which stoichiometric defect can cause decrease in density of solid ?

(ii) Frenkel defect is not found in Sodium Chloride. Why ?

(iii)KCI crystal is colourless. But on heating it in an atmosphere of potassium vapour, it becomes violet in colour. Account for this.

Hint:(i) Schottky defect (ii) Size of Na^+ is larger (iii) F-Centre

2.(a)A compound formed by P and Q crystallises in the cubic structure. The P atoms present at corners of a cube while Q atoms are at face centres. What is the formula of the compound ? (b) Give reason for the following: ZnO on heating become yellow. Why?

Hint: (a) PQ_3 (b) Metal excess defect due to interstitial cation.

3.Differentiate ferromagnetic and ferrimagnetic substance.

Hint: Refer note given above

4.Differentiate tetrahedral voids and octahedral voids.

Hint: Refer note given above

5.In terms of band theory, what is the difference between a conductor and semiconductor?

Hint: Refer note given above

6.Draw the unitcell of copper which crystallises in fcc lattice and calculate the number of atoms in its unit cell.

Hint: 4

7.a) What type of substance could make better permanent magnets – ferrimagnetic or ferromagnetic? Justify your answer.

b) In terms of band theory, write the difference between conductor and insulator.

Hint: a) Ferromagnetic – Domains aligned in one directions (b) Refer note given above.

8. The smallest repeating structural unit of a crystal is called

(a) Lattice point (b) Bravais lattice (c) Space lattice (d) Unit cell Hint: Unit cell

9.From the following choose the incorrect statement about crystalline solids.

i) Melt at sharp temperature ii) They have definite heat of fusion

iii) They are isotropic iv) They have long range order Hint: They are isotropic

10.A metal crystallises into a lattice containing a sequence of layers ABAB. What is the type of packing in the element known as ?

Hint: Hexagonal Close Packing

11.Identify the following as p-type or n-type semiconductor.

a) Si doped with Ga (b) Germanium doped with Arsenic

Hint: a) p -type (b) n- type

12.Classify the following based on their magnetic properties : C_6H_6, O_2, Fe, Cu^{2+},Co, TiO_2,MnO_2, Fe_3O_4

Hint : Diamagnetic:C_6H_6, TiO_2, Paramagnetic : O_2, Cu^{2+}, Ferromagnetic: Fe, Co, Antiferromagnetic: MnO_2 Ferrimagnetic: Fe_3O_4

2. SOLUTIONS

Solution is a homogeneous mixture of two or more components- mainly solute and solvent

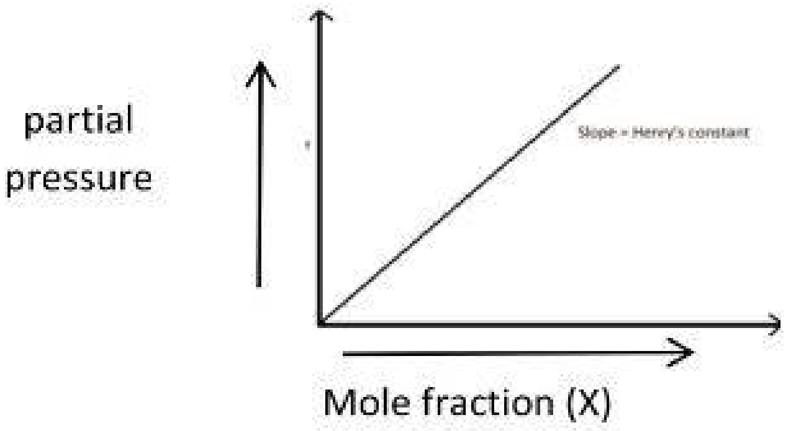
Solubility of gas in liquid

The solubility of a gas in a liquid depends pressure applied which is explained by Henry's law

Henry's law: " Partial pressure (p) of the gas in vapour phase is proportional to the mole fraction (X) of the gas in the solution. ie. $\mathbf{P = K_H.X}$ (K_H is Henry's constant)

K_H value is inversely proportional to solubility of a gas in a liquid

Graph of Henry's law



Applications of Henry's law:

(i) To increase the solubility of CO_2 in **soft drinks** or **soda**.

(ii) **Bend** experienced by Scuba divers. (Medical condition created by solubility of nitrogen in the blood). To avoid bends, oxygen taken in oxygen cylinder is diluted with less soluble **Helium**

(iii) **Anoxia** experinced by peoples at high altitude where the partial pressure of oxygen is less than the ground level .

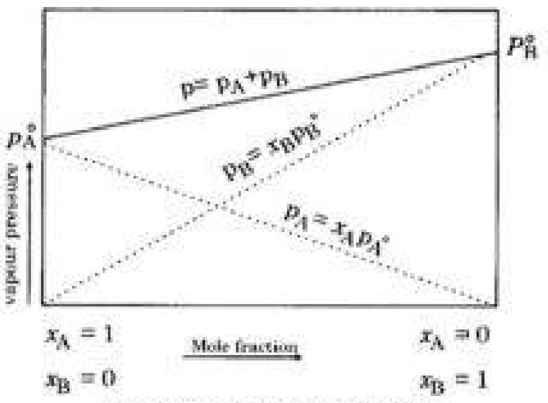
Effect of temperature the solubility of a gas in a liquid

When temperature increases, the value of K_H is increases . Therefore solubility of the gas in liquid decreases. **Therefore aquatic life is more comfortable in cold water.**

Vapour pressure of Liquid-Liquid solution

Raoult's Law: For a solution of volatile liquids, the partial vapour pressure of each component in the solution is directly proportional to its molefraction.

ie, $\mathbf{P_A = P^o_A . X_A}$ **&** $\mathbf{P_B = P^o_B . X_B}$



Graph for an ideal solution

Ideal solution:

The ideal solution will satisfy the follwing conditions.

(i) obey's Raoult's law.

ie, $\mathbf{P_A = P^o_A . X_A}$ **&** $\mathbf{P_B = P^o_B . X_B}$

(ii) $\mathbf{\Delta H_{mix} = 0}$

(iii) $\mathbf{\Delta V_{mix} = 0}$

Examples of ideal solution:

(1) solution of n-hexane and n-heptane

(2) solution of bromoethane and chloromethane

(3) benzene and toluene

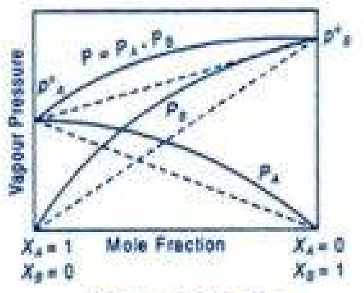
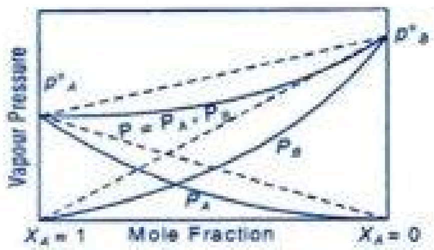
Note: Consider a binary solution contains two components A (solvent) and B (solute).

In ideal solution, A-A (solvent-solvent) and B-B(solute-solute) interactions are equal to the A-B (solvent-solute) interactions.

Non ideal solution

(i) Does not obey Raoult's law, **(ii)** $\mathbf{\Delta H_{mix} \neq 0}$, **(iii)** $\mathbf{\Delta V_{mix} \neq 0}$.

The total vapour pressure of such solution is either **higher** or **lower** than predicted by Raoult's law. Therfore non ideal solution divided into **two**

Non ideal solution showing **Positive deviation**	**Non ideal solution showing** **Negative deviation**
 Positive deviation from Raoult's law behaviour	 Negative deviation from Raoult's law behaviour
Shown by liquid pairs for which A-B interaction is **weaker** than A-A and B-B interactions.	Shown by liquid pairs for which A-B interaction is **stronger** than A-A and B-B interactions.
Eg : (i) Water and Alcohol (weaken H-bond) (ii) Acetone and Alcohol (weaken H-bond)	eg : (i) Water and Nitric acid (strengthen H-bond) (ii) Phenol and Aniline (strengthen H-bond
Form **minimum boiling azeotropes**	Form **maximum boiling azeotropes**

Azeotropic mixtures (Azeotropes) or Constant boiling mixture

Liquid mixtures which distill without change in composition are called azeotropic mixtures.they are two types-minimum boiling azeotropes & maximum boiling azeotropes.

Colligative Properties

Colligative property is the property which depend upon the **number of solute particles** and

does not depend upon their nature.

Examples (1) Relative lowering of vapour pressure (2) Elevation of boiling point

(3) Depression of freezing point (4) Osmotic pressure

Osmosis and Osmotic Pressure

Osmosis is the flow of solvent molecules from lower concentration side to a higher concentration side through a **semi-permeable membrane**

Eg. for semi-permeable membrane are egg membrane, all animal and plant membrane, Cellulose acetate. **Osmotic pressure is defined as the excess pressure that must be applied on solution side to stop osmosis.**

Applications of Colligative Properties

Used to determine molar mass of non volatile solute (M_2) using the following equations

Colligative Properties	**Equation**	**Equation to calculate M_2**
Relative lowering of VP	$\frac{P^o_S - P_S}{P^o_S} = X_{solute}$	$M_2 = \frac{P^o_1 . W_2 . M_1}{W_1 (P^o_1 - P_1)}$
Elevation of BP	$\Delta T_b = K_b.m$	$M_2 = \frac{K_f . W_2 . 1000}{\Delta T b . W_1}$
Depression of FP	$\Delta T_f = K_f.m$	$M_2 = \frac{K f . W_2 . 1000}{\Delta T f . W_1}$
Osmotic pressure	$\pi = CRT$	$M_2 = \frac{W_2 . R . T}{\pi V}$

Note:

(i) Osmotic pressure is used to measure **molecular mass of proteins, polymers** and other macromolecules because of two reasons : (a) osmotic pressure is measured at room temperature

(b) molarity is used instead of molality.

(ii) Anti freeze solutions (eg. Glycol) are used in automobile radiators to prevent the freezing of water (depression of freezing point).

(iii) NaCl and $CaCl_2$ is used **to remove ice from road** because it depress the freezing point of water.

(iv) The osmotic pressure of fluid inside the blood cell and that of 0.9% (mass/volume) NaCl solution are equal. ie, they are **isotonic** (solutions having sameosmotic pressure). Therefore, 0.9% (mass/volume) NaCl solution is used in **intravenous injections.**

Reverse osmosis

The direction of osmosis can be reversed if a pressure larger than osmotic pressure is applied to the solution side. Here solvent is flowing from lower concentration to higher concentration through **semi permeable membrane**. This process is called **reverse osmosis**. Reverse osmosis is used in **desalination of sea water** and in water purifiers.

Abnormal molecular mass

Molecular mass calculated on the basis of colligative properties may be lower or higher than the normal value. Such molecular mass is called **abnormal molar mass**. Abnormal molecular mass is due to the following reasons.

(i) Dissociation of particles

(ii) Association of particles.

Due to dissociation of particles, the number of particles increases. Therefore colligative property increases. Hence molecular mass decreases.

Eg:- KCl solution (Here KCl dissociated in to K + and Cl - . Therefore number of particles increases.)

Due to association of particles , the number particles decreases. Therefore colligative property decreases and hence molecular mass increases.

Eg:- Acetic acid (ethanoic acid) in benzene. (In benzene, acetic acid dimerises due to hydrogen bonding. Therefore number of particles decreases).

Model questions:

Q1. *What will happen if a pressure greater than osmotic pressure is applied on the solution separated by a semipermeable membrane from the solvent? Explain.* **(Hint: Reverse osmosis)**

Q2. *What type of deviation is shown by a mixture of acetone and chloroform? Justify on the basis of strength of intermolecular interactions that develop in the solution. What type of azeotropic mixture will be formed by the above solution?* **(Hint: Non ideal solution showing negative deviation, molecular interaction btw acetone and chlorofom increases through H-bond than....)**

Q3. Calculate the osmotic pressure exerted by a solution prepared by dissolving 1.5 g of a polymer of molar mass 185000 in 500 ml of water at 27 ^{0}C. (R = 0.0821 L atm K -1 mol -1)

(Hint: $\pi = \frac{W2RT}{M2V}$ **;** W_2**= 1.5g ,** M_2 **= 185000, V = 500 ml =0.5 L , T = 300K)**

Q4. Write down any **four** examples for osmosis which are shown in daily life ?

Answer: **a) Raw mango placed in concentrated salt solution loses water and shrink.**

b) Wilted flowers revive when placed in fresh water

c) Blood cells collapse when suspended in saline water.

d) The preservation of meat by salting and fruits by adding sugar protect against bacterial action.

3. ELECTROCHEMISTRY

The **Nernst equation** is often used to relate the electrode potential of an electrode with the electrolytic concentration. The electrode potential of the equation $Mn^{+} + ne^{-} \rightarrow M$ can be given by:

$\mathbf{E_{cell} = E^0_{cell} + 2.303RT/n \log [M^{n+}]/[M]}$; Where E^0 is the standard electrode potential, R is the gas constant (8.314 JK^{-1} mol^{-1}), F is Faraday constant (96500 C mol^{-1}), T is temperature in Kelvin and $[M^{n+}]$ is the concentration of the species, M^{n+}.

For ***Daniel cell,*** Nernst equation can be written as:

$$E_{cell} = E^0_{cell} + \frac{0.0591}{2} \log \frac{[Cu^{2+}]}{[Zn^{2+}]}$$

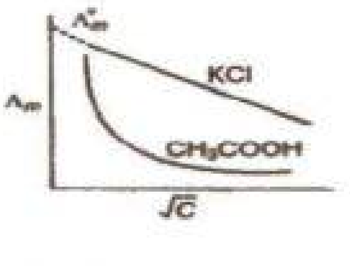
Variation of conductivity and Molar conductivity with concentration: ***Conductivity*** *always decreases with dilution*, as the number of ions per unit volume that carry the current in a solution decrease on dilution.

Molar conductivity of a solution at a given concentration is the conductance of volume V of a solution containing one mole of electrolyte kept between two electrodes with an area of cross-section A and unit length distance. $\Lambda_m = K\ V$

V = Volume, K = specific conductivity, Λ_m = molar conductivity.

Molar conductivity *increases with decrease in concentration* as the total volume, V, of a solution containing one mole of electrolyte also increases. Upon dilution, the concentration decreases. When the concentration approaches zero, the molar conductivity of the solution is known as limiting molar conductivity (λ^0_m). Variation of molar conductivity with concentration is different for strong and weak electrolytes. For strong electrolytes, the relation between λ_m and concentration can be given by:

$$\lambda_m = \lambda^0_m - A\sqrt{c}$$



Where, λ_m is the molar conductivity at a particular concentration, λ^0_m is the molar conductivity at infinite dilution, 'c' is the concentration and A is a constant depends on the nature of the electrolyte.

For weak electrolytes*, as dilution increases, the degree of dissociation increases*. So the number of ions and hence the molar conductivity increases. For strong electrolytes, the value of λ^0_m can be determined by the extrapolation of the graph. But for weak electrolytes, it is not possible since the graph is not a straight line. So their λ^0_m values are calculated by applying Kohlrausch's law of independent migration of ions.

Kohlrausch's law of independent migration of ions: *The law states that the limiting molar conductivity of an electrolyte at infinite dilution is equal to the sum of the conductivities of the anions and cations.*

Applications of Kohlrausch's law:

1) Determination of λ^0_m of weak electrolytes:

2) Determination of degree of dissociation of weak electrolytes:

Batteries: *A battery/cell is a galvanic cell in which the chemical energy of a redox reaction is converted to electrical energy.*

Two types **a) Primary cells:** *These are cells which cannot be recharged or reused.* Here the reaction occurs only once and after use over a period of time, they become dead E.g. Dry cell, mercury button cell etc.

1. Dry Cell. It is a compact form of Leclanche cell. It consists of a zinc container as anode and a carbon (graphite) rod surrounded by powdered manganese dioxide (MnO_2) and carbon as cathode. Electrolyte is a moist paste of ammonium chloride (NH_4Cl) and zinc chloride ($ZnCl_2$).

At anode: $Zn \rightarrow Zn^{2+} + 2e^-$

At Cathode: $MnO_2 + NH_4^+ + e^- \rightarrow MnO(OH) + NH_3$

Ammonia produced in this reaction forms a complex with Zn^{2+} and thus corrodes the cell. The cell has a potential of nearly 1.5 V.

2. Mercury cell: Here the anode is zinc – mercury amalgam and cathode is a paste of HgO and carbon. The electrolyte is a paste of KOH and ZnO. The electrode reactions are:

Anode reaction: $Zn/(Hg) + 2OH^- \rightarrow ZnO + H_2O + 2e^-$

Cathode reaction: $HgO + H_2O + 2e^- \rightarrow Hg + 2OH^-$

The cell has a constant potential of 1.35 V.

b) Secondary cells: *These are cells that can be recharged after use by passing current through the electrodes in the opposite direction, i.e. from the negative terminal to the positive terminal.*

Example is lead storage cell, which is used in automobiles and invertors. Anode is lead and a grid of lead packed with lead dioxide (PbO_2) as the cathode. The electrolyte is 38% H_2SO_4 solution.

At anode: $Pb + SO_4^{2-} \rightarrow PbSO_4 + 2e^-$

At cathode: $PbO_2 + SO_4^{2-} + 4H^+ + 2e^- \rightarrow PbSO_4 + 2H_2O$

On charging the battery, the reaction is reversed and $PbSO_4$ on anode and cathode is converted into Pb and PbO_2, respectively.

Fuel cells: *These are galvanic cells which convert the energy of combustion of fuels like hydrogen, methane, methanol, etc. directly into electrical energy.* **H_2-O_2 fuel cell** is an example for fuel cell. which is used in the Apollo space programme. Here hydrogen and oxygen are bubbled through porous carbon electrodes into concentrated aqueous sodium hydroxide solution. The electrode reactions are:

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

Anode: $2H_2 + 4OH^- \rightarrow 4H_2O + 4e^-$

Overall reaction is: $2H_2 + O_2 \rightarrow 2\,H_2O$

Advantages of Fuel cells:

1. The cell *works continuously* as long as the reactants are supplied.

2. It has *higher efficiency* as compared to other conventional cells.

3. It is *eco-friendly* (i.e. pollution free) since water is the only product formed.

Corrosion: *It is the process of formation of oxide or other compounds of a metal on its surface.* Example: The rusting of iron.

Rusting of iron. It occurs in presence of water and air. It is a redox reaction. At a particular spot of the metal, oxidation takes place and that spot behaves as anode. Here Fe is oxidized to Fe^{2+}.

At anode $2Fe \rightarrow 2\,Fe^{2+} + 4e^-$

Electrons released at anodic spot move through the metal and go to another spot on the metal and reduce oxygen in presence of H^+. This spot behaves as cathode.

At cathode $O_2 + 4H^+ + 4\,e^- \rightarrow 2\,H_2O$

The overall reaction is: $2Fe + O_2 + 4H^+ \rightarrow 2Fe^{2+} + 2\,H_2O$

The Fe^{2+} are further oxidised and hydrated to ferric oxide ($Fe_2O_3.\,xH_2O$), which is called **rust**.

Methods to prevent corrosion:

1. By *barrier protection* through coating the metal surface with paint or varnish or electroplating etc.
2. By coating the metal *surface with another electropositive metal* like zinc, magnesium etc. The coating of metal with zinc is called *galvanisation* and the resulting iron is called galvanized iron.
3. By coating with *anti-rust* solution (bis phenol).
4. By *cathodic protection* in which a metal is protected from corrosion by connecting it to another metal that is more easily oxidised.An electrochemical method is to provide a sacrificial electrode of another metal (like Mg, Zn, etc.) which corrodes itself but saves the object.

Model questions:

1) Write Nernst equation for Daniel Cell. (Hint: $E_{cell} = E^0_{cell} + 2.303RT/n \log [M^{n+}]/[M]$)

2) Define Kohlrausch's law. (Hint: C*onductivity is the sum of the conductances*)

3) What are primary cells? Give examples. (Hint: *Non-rechargeable cells, Dry cell*)

4) What are fuel cells? Explain with an example. (Hint: *Energy of combustion to electrical energy.* H_2-O_2 *fuel cell*)

5) Describe corrosion using iron as an example. How to prevent corrosion of iron? (Hint: *Formation of oxide*)

4. CHEMICAL KINETICS

Factors affecting rate of a reaction

The important factors which affect the rate of a chemical reaction are:

1. Concentration of the reactants
2. Temperature
3. Presence of catalyst

Dependence of rate of reaction on concentration

The representation of rate of reaction in terms of molar concentration of reactants as experimentally determined is called rate law or rate equation or rate law expression

For the reaction $aA + bB \text{--------}> cC + dD$

Rate expression is Rate α $[A]^x [B]^y$

x and y may not be equal to a and b . x and y determined experimentally

Rate = $k [A]^x [B]^y$. K is called rate constant or velocity constant or specific reaction rate

x = order of reaction with respect to reactant A.

y = order of reaction with respect to reactant B

overall order of reaction = x + y

Order of reaction: ***It is the sum of powers of the concentration of the reactants in the rate law expression.***

Unit of K

Reaction order	Unit of rate constant (k)
n	$concentration\,)^{1-n}\,time^{-1}$
0	$(mol\,L^{-1})^{1-0}s^{-1} = mol\,L^{-1}S^{-1}$
1	$(mol\,L^{-1})^{1-1}s^{-1} = S^{-1}$
2	$(mol\,L^{-1})^{1-2}s^{-1} = mol^{-1}L\,S^{-1}$

Molecularity of a reaction :

It is the number of reacting species (molecules, atoms or ions) which must collide simultaneously in order to bring about a chemical reaction.

Examples :		
	Unimolecular reaction	$NH_4NO_2 \longrightarrow N_2 + 2\,H_2O$
	Bimolecular reaction	$2\,HI\,(g) \longrightarrow H_2(g) + I_2\,(g)$
	Trimolecular reaction	$2\,NO\,(g) + O_2(g) \longrightarrow 2\,NO_{2\,(g)}$

Difference between Molecularity and order

	Molecularity of reaction	**Order of reaction**
1.	It is the number of species taking part in a chemical reaction.	It is sum of the powers of the concentration terms in rate law.
2.	It is a theoretical concept.	It is an experimental quantity.
3.	It can be neither be zero nor fractional. It is always a whole number.	It may be zero, fractional or an integer.

Pseudo First order reaction :

Reactions which are not truly first order ,but become first order under special conditions are called pseudo unimolecular or pseudo first order reaction

For example,

i) inversion of cane sugar $C_{12}\,H_{22}\,O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$

$R = k\,[C_{12}\,H_{22}O_{11}]$

This reaction is Pseudo first order reaction.

ii) Acid catalysed hydrolysis ethylacetate in excess of water

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$$

Rate = k $[CH_3COOC_2H_5]$

This reaction is Pseudo first order reaction.

Integrated rate equation

	First order reaction R --------> P
Differential rate equation	$-\frac{d[R]}{dt} = k\ [R]$
Integrated rate equation	$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$
Half life period	$t_{1/2} = \frac{0.693}{k}$
Unit of K	S^{-1}
Straight line plot	graph of log [R] against t gives a straight line with slope $-\frac{k}{2.303}$

Examples for first order reaction

- * All natural and artificial radioactive decay of unstable nuclei take place by first order kinetics
- * Hydrogenation of ethene is an example of first order reaction.

$C_2H_4(g) + H_2\ (g) \rightarrow C_2H_6(g)$ Rate = $k\ [C_2H_4]$

Half life of a reaction ($t_{½}$)

It is the time required for half of the reactant converted in to prouduct

First Order reaction

$$k = \frac{2.303}{t}\log\frac{[R]_0}{[R]} \qquad t = \frac{2.303}{k}\log\frac{[R]_0}{[R]}$$

When $t = t_{1/2}$, $[R] = 1/2\ [R]_0$

Thus $t_{1/2} = \frac{2.303}{k}\log\frac{[R]_0}{[R]_0/2} \quad = \frac{2.303}{k}\log 2 \quad = \frac{2.303}{k} \times 0.3010$

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

ie. **$t_{1/2}$ of first order reaction is independent of initial concentration of reactants.**

Effect of Temperature :

As temperature increases rate of reaction increases

For every 10^0C rise in temperature, the rate of reaction becomes almost double.

Threshold energy: The minimum energy that the reacting molecules must posses in order to undergo effective collisions to form product is called **threshold energy**

Activation energy (E_a) = Threshold energy – Actual energy possessed by reacting molecules

Arrhenius Equation:

This is an equation which relates velocity constant with temperature

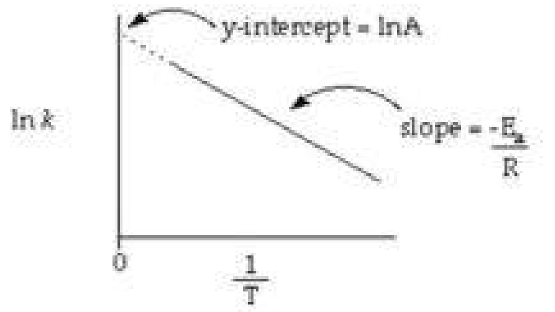
Where A is Arrhenius factor or frequency factor , E_a is the energy of activation

$$k = A e^{-E_a/RT}$$

As temperature increases k increases ,thus rate of reaction increases

Determination of E_a

1. ***A plot of log k vs. 1/T is a straight line whose slope is*** $-\frac{E_a}{2.303\,R}$ ***and intersection is log A.***



2. By using the equation $\log\frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$

   k_1 and k_2 are the values of rate constants at temperature T_1 and T_2

Model questions

1. Write two factors influencing rate of a reaction
2. For a reaction A + B-----→ C + D, the rate equation is $r = K[A]^{3/2}[B]^{1/2}$. Give the overall order and molecularity of the reaction

   [order = 3/2 + ½ =4/2 =2 ,molecularity =2]
3. For the reaction, $2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$, the rate law is given as, Rate = $k[NO]^2[O_2]$. The order of the reaction with respect to O_2 is ……

   [ans; 1]
4. Identify the order of reaction if the unit of rate constant is mol L^{-1} s^{-1}

   [ans ; zero]
5. Find the unit of k for a first order reaction.

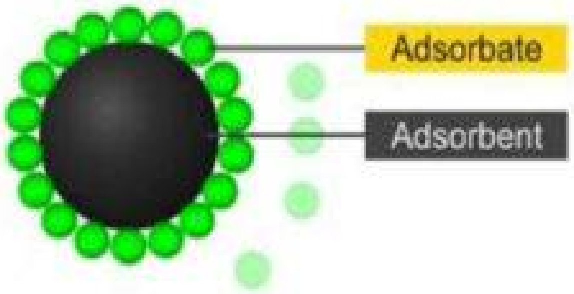
6. Values of 'k' of two reactions are given below. Find the order of each reaction.

   i) $k = 3 \times 10^{-2}$ mol L^{-1} S^{-1} ii) $k = 5 \times 10^{-3}$ mol^{-1} L S^{-1}
7. "Reactions with zero order are possible, but zero molecularity is not". Justify the statement

   [Zero order reaction means the rate of the reaction is independent of the concentration of the reactants. So it is possible. But zero molecularity means there is no reactants. This is not possible]
8. Differentiate molecularity and order of a reaction
9. Write integrated rate equation for a first order reaction.
10. Write the relation between half life ($t_{½}$) and rate constant (k) of a first order reaction
11. Rate constant of a reaction is 5×10^{-2} S^{-1} . Find the half life (t½) of the reaction.
12. Derive an expression for half life period of first order reaction.
13. A first order reaction has a rate constant 1.15×10^{-3} s^{-1} . How long will 5 g of the reactant take to reduce 3g?
14. Write the Arrhenius equation and identify the terms in it
15. The rate of a chemical reaction doubles for an increase of 10K in absolute temperature from 300K. Calculate the activation energy (Ea)? [R = 8.314 J/K/mol and log 2 = 0.3010]
16. The rate constant of a reaction at 293K is 1.7×10^{5} s^{-1} . When the temperature is increased by 20 K, the rate constant is increased to 2.57×10^{6} s^{-1} . Calculate Ea of the reaction.

5.SURFACE CHEMISTRY

Adsorption



It is the accumulation of a substance on the surface of solid or liquid substance.

Adsorption is a surface phenomenon.

Some examples of adsorption are:

1. Powdered charcoal adsorbs gases like H_2 , O_2 , CO_2 , Cl_2 , NH_3 , SO_2 etc.

2. Silica gel adsorbs moisture

Desorption: The process of removal of an adsorbed substance from the surface of adsorbent is called desorption.

Sorption: If adsorption and absorption occur simultaneously, the process is called sorption.

Distinction between adsorption and absorption

Adsorption is a **surface** phenomenon while absorption is a **bulk** phenomenon.

Eg. Coal **adsorb** gas. Sponge **absorbs** water.

Thermodynamic aspects of adsorption

During adsorption Δ**H** = -ve (Highly exothermic) , ΔS = -ve, ΔG = -ve

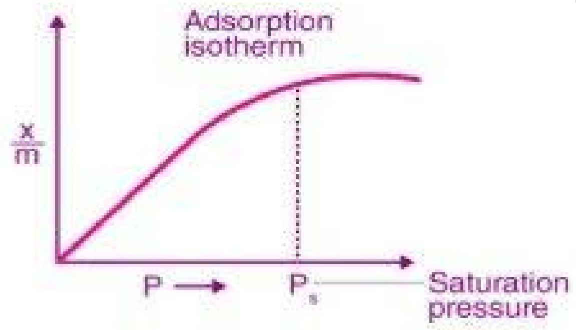
Types of adsorption

it is of two types:- physical adsorption & chemical adsorption.

Physical adsorption (physisorption)	**Chemical adsorption (chemisorption)**
The force of attraction between adsorbent	Here it is **chemical bond**.
Enthalpy of adsorption is low	Enthalpy of adsorption is high.
Not specific.	Highly specific.
Reversible.	Reversible.
Form multi layer of adsorbate	Form single layer of adsorbate
No need of activation energy	Need of activation energy

Freundlich adsorption isotherm

The extent of adsorption (x/m) with pressure (p)



is expressed by the equation **x/m = KP $^{1/n}$** is called Freundlich adsorption isotherm. K and n are constants.

x/m = K.P $^{1/n}$ (where n > 1)

Applications of adsorption

1. Production of high vacuum (by charcoal)
2. Gas masks (by activated charcoal)
3. Control of humidity (Silica and alumina gels)
4. Purification of cane sugar solution.
5. In heterogeneous catalysis (solid catalyst)

Catalysis

A catalyst is a substance that changes the rate of a chemical reaction without undergoing any permanent chemical change by itself.

Chemical reaction involving catalyst is known as **Catalysis.** It is of **two** types

Homogeneous catalysis	**Heterogeneous catalysis**
Reactants and catalyst are in same phase.	Reactant and catalyst are in different phases.
Eg. $2\ SO_{2\ (g)} + O_{2\ (g)} \longrightarrow 2\ SO_{3\ (g)}$ (Nitric oxide catalyst is used which is gas)	eg :$2\ SO_{2\ (g)} + O_{2(g)} \longrightarrow 2\ SO_{3\ (g)}$ (V_2O_5 catalyst is used which is solid) [Contact Process]
Ester hydrolysis	E.g.: $N_2\ (g) + 3H_2\ (g) \xrightarrow{Fe(s)} 2NH_3$ [Haber Process]

Nature of solid catalysts

Activity	**selectivity**
Ability to speed up a chemical reaction E.g.: $N_2\ (g) + 3H_2\ (g) \xrightarrow{Fe(s)} 2NH_3$ [Haber Process]	Ability to direct a reaction to yield a particular product. $CO + H_2 \longrightarrow CH_4 + H_2O$ (Ni catalyst) ; $CO + H_2 \longrightarrow HCHO$ (Cu catalyst)

Shape selective catalyst :

The catalytic which determine size of product molecule formed is called shape selective catalys. eg. Zeolite (**aluminosilicates**). (Reason:They have microporous cavities).

Promoters and poisons

Promoters are substances that enhance the activity of a catalyst while poisons decrease the activity of a catalyst.For example, **molybdenum (Mo) acts as a promoter**and **CO act as poison**in Haber's process for the manufacture of ammonia.

Enzyme (biological catalyst)

catalysis in presence of enzyme is enzyme catalysis. Eg. invertase, maltase, pepsin etc.

The enzyme **invertase** converts cane sugar into glucose and fructose.

Characteristics of enzyme catalysis

1. Highly specific.
2. Highly efficient.
3. Occurs at optimum temperature (298k – 310k).
4. Occurs at optimum pH.(5-7)

Lock and key mechanism of enzymatic action:

Enzyme + substrate → enzyme substrate complex → enzyme product complex → product + enzyme

COLLOIDS

Colloid is a heterogenous mixture of dispersed phase and dispersion medium where particle diameter is in between 1nm and 1000nm.

Classification colloids

1.Based on the nature of particles,colloids are of three types

A. **Multimolecular colloids:** Atoms or small molecules having dimension<1nm bind together by weak vander Wall's force to form particles of colloidal dimension.e.g. Gold sol,sulphur sol

B . **Macromolecular colloids**: size of the particle is in the colloidal range. Example:solutions of starch ,cellulose, protien,etc.

C. Associated colloids (micelles): These are substances which behave as normal electrolytes at low concentrations, but as colloids at higher concentrations.

It is formed only above a particular temperature called Kraft temperature (T_k) and above a particular concentration called critical micelle concentration (CMC). Eg: Soap detergent

Cleansing action of soaps

The cleansing action of soap is due to **micelle formation.**

2. Based on the physical state of dispersed phase and dispersion medium- 2 types

Properties	**Lyophilic colloids**	**Lyophobic colloids**
Force of attraction	Strong.	Weak
Preparation	Easy to prepare	Difficult to prepare
Reversibility	Reversible(ie. they can be easily separated and remixed)	Irreversible.
Stability	Stable	Unstable.

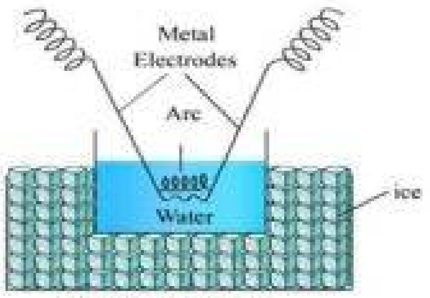
Preparation of colloids

a) Chemical methods:

Colloidal solutions can be prepared by chemical reactions like oxidation, reduction, double decomposition, hydrolysis,etc.

b) Electrical disintegration (Bredig's arc method):

It is used for the preparation of **metal sols** like Ag, Au, Pt etc.



Bredig's arc method

c) Peptization:

The process of conversion of precipitate into a colloidal sol using suitable dispersion medium and electrolyte is called peptization.

The electrolyte added is called peptizing agent.

Purification of colloids

1. Dialysis: It is the process of removing dissolved substances from a colloidal solution by means of **diffusion through a semi-permeable membrane**.The speed of dialysis can be increased by electric field. Then the process is known as **electrodialysis**.

2. Ultrafiltration: It is the process of separating the colloidal particles from the impurities by using ultra filter paper is called ultrafiltration.

Properties of colloids :

i)Tyndall effect : Scattering of light by colloidal particles is called Tyndall effect. Then we can see the path of the light beam.

Application - in the construction of ultra microscope, blue colour of sky etc.

ii) Brownian movement : the zig zag movement of colloidal particles in colloid.

iii) Electrophoresis: The movement of colloidal particles towards cathode or anode under the influence of an electric field.

iv) Coagulation (Precipitation): The process of settling of colloidal particles is called coagulation . It can be done by different ways like electrophoresis, continuous dialysis, addition of electrolyte.

Hardy – Schulze rule and Coagulation

The greater the valency of the active ion, the greater will be the coagulating power. This is known as Hardy – Schulze rule.

Eg. In the coagulation of –ve sol like As_2S_3 , the **coagulating** power is $Al^{3+} > Ba^{2+} > Na^{+}$.

In the coagulation of +ve sol like ferric hydroxide the **coagulating** power is $PO_4^{3-} > SO_4^{2-} > Cl^-$.

Protective colloid

it is a lyophilic sol which is used to stabilise a lyophobic sol. Eg. Gelatin,gum,egg albumin

Emulsion :

liquid in liquid colloidal system is called emulsiom. Eg milk. They divided into **two**.

Water in oil type emulsion	**Oil in water type emulsion**
Dispersed phase is water &Dispersion medium is oil	Dispersed phase is oil & Dispersion medium is water
Eg. Butter, cod liver oil	Eg. milk

The substance which is used to stabilize emulsion is called **emulsifying agent.**Eg. proteins, gums, natural and synthetic soaps, etc.

Applications of Colloids or colloids in daily life

1. Formation of Delta. 2. Electrical precipitation of smoke (Cottrell precipitation).

3. Purification of drinking water. 4. Tanning. (in leather industry)

5. Medicines.(Example, argyrol is a silver sol used as an eye lotion.)

6. **Blood**:-Blood is a colloidal solution of an albuminoid substance. When alum or ferric chloride ($FeCl_3$) solution are added to blood, coagulation of particles take place resulting blood clotting.

7. Blue colour of sky 8. Artificial raining 9. Making rubber sheetsfrom rubber latex

Model questions:

Q1. Gelatine is mostly used in making ice cream. Why ? **(Hint. Gelatine is a protective colloid)**

Q2. Alum purify muddy water by......... **(Answer. Coagulation)**

Q3. What is observed when: (a) A beam of light is passed through a colloidal sol?

(b) NaCl is added to hydrated ferric oxide sol?

(c) electric current is passed through a colloidal sol?

(Hint: a- tyndal effect, b-coagulation, c-electrophoresis)

Q4. Which of the following is true about adsorption? **Or** Thermodynamic principle of adsorption

(a) $\Delta G < 0, \Delta S > 0, \Delta H < 0$ (b) $\Delta G < 0, \Delta S > 0, \Delta H > 0$

(c) $\Delta G < 0, \Delta S < 0, \Delta H < 0$ (d) $\Delta G > 0, \Delta S > 0, \Delta H < 0$ **(Answer. C)**

Q5. What are the differences in each of the following citing examples

(a) Multimolecular colloid and Associated colloid

(b) Coagulation and Peptisation

(c) Homogeneous catalysis and Heterogeneous catalysis

(d) Lyophilic sols and Lyophobic sols. **(Hint:. Refer above notes)**

Q6. The temperature above which the formation of micelle takes place is called ....

(Answer. Kraft temperature)

Q7. What is an adsorption isotherm? Describe Freundlich adsorption isotherm ? **(Hint:Refer notes).**

Q8. Write any four applications of colloids ? . **(Hint:. Refer notes)**

Q9. The accumulation of molecular species at the surface rather than in the bulk of a solid or liquid is termed adsorption. a) What is adsorption isotherm?

b) Write the mathematical expression of Freundlich adsorption isotherm?

c) Enzymes are known as biochemical catalysts. Write any two important characteristics of enzyme catalysis ?. **(Hint:. Refer above notes).**

Q10. Colloids exhibit some special properties. a) Name the property of colloid involved in the construction of ultra microscope? b) Explain the above property c) What are the conditions to be satisfied to exhibit Tyndall effect? **(Hint: a & b Refer above notes, c-there are two conditions (i)The diameter of the dispersed particles is much larger than the wavelength of the light used**

(ii) The refractive indices of the dispersed phase and the dispersion medium differ greatly in magnitude).

Q11. Ferric hydroxide sol can be prepared from freshly prepared ferric hydroxide precipitate. It can also be prepared by adding ferric chloride solution to boiling water. In both cases the sol particles are positively charged.

a) Name the above two methods for the preparation of ferric hydroxide sol?

b) What happens when an electric potential is applied across two electrodes dipped in this sol?

(Answer. A-peptisation & hydrolysis-chemical methods, b- electrophoresis/ particles move to negatively charged electrode).

Q12. In homogenous catalysis, reactants and catalyst are in the same phase. In heterogeneous catalysis, reactants and catalyst are in different phases a) Define catalysis

b) Give one example each for homogenous and heterogeneous catalysis? **(Hint:. Refer notes).**

Q13. As 2 S 3 sol particles are negatively charged. a) What happens when Barium chloride solution is added to the above sol? b) How do you account for the above process?

c) What is the effect of adding Aluminium Chloride instead of Barium chloride? Justify ?

(Hint: a- coagulation take place, b-Ba2+ ion neutralise the charge of colloidal particles and leads to aggregation of them., c- coagulating power increases- Refer Hardy schultz rule)

6. GENERAL PRINCIPLES AND PROCESS OF ISOLATION OF ELEMENTS

Minerals: The *metallic compounds present in the earth crust* are called minerals.

Ore: A mineral from which a *metal can be extracted conveniently* and profitably is called ore.

Metallurgy: The process of *extraction of a metal* from its ore is called metallurgy. Various steps are;

I) Concentration of the ore: The *removal of impurities from the ore is called concentration of the ore.* The impurities present in the ore are called **gangue**. Depending on the nature of the impurities, any one of the following methods can be used.

a) **Hydraulic washing**: This method is used when *the gangue is lighter than the ore*. The powdered ore is washed in a stream of water. The lighter gangue particles are washed away leaving behind the ore particles.

b) **Magnetic separation**: It is based on difference in *the magnetic properties of the ore components*. For this method either the ore or the gangue is magnetic.

c) **Froth floatation**: This method is used for the *concentration of the sulphide ores. Principle of this method is that sulphide ores are preferentially wetted by oils and gangue is wetted by water.* In this process, a suspension of the powdered ore is made with water, *collectors* (e.g. pine oil) and *froth stabilizers* (e.g. cresols) are added. On Agitating the mixture by passing air, froth is formed which carries the mineral particles. The froth is skimmed off and dried to get the ore particles.

d) **Leaching**: it is often used if the *ore is soluble in some suitable solvent.*

Here the powdered ore is treated with a suitable solvent in which ore particles alone dissolve.

e.g. Purification of *Bauxite*: The powdered ore is treated with a concentrated solution of NaOH. Alumina (Al_2O_3) dissolves in NaOH to form sodium aluminate leaving behind the impurities. The aluminate in solution is neutralised by passing CO_2 gas and hydrated Al_2O_3 is precipitated. The sodium silicate remains in the solution and hydrated alumina is filtered, dried and heated to give back pure alumina (Al_2O_3).

II) Extraction of crude metal from concentrated ore:

It involves the following steps: **1) Conversion to oxide:** Since oxide ores can easily reduced, the sulphides and carbonate ores are first converted to corresponding oxides. It can be done by calcination and roasting.

i) Calcination: Here the oxide is *heated in the absence of air or in limited supply of air*. It is used for the conversion of hydroxide and carbonate ores to oxide ore.

$$Fe_2O_3.xH_2O \rightarrow Fe_2O_3 + xH_2O\uparrow$$

$$CaCO_3.MgCO_3 \rightarrow CaO + MgO + 2CO_2\uparrow$$

ii) Roasting: Here the *ore is heated in a regular supply of air* below the melting point of the metal. This method is used for the conversion of sulphide ores to oxide ore.

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

2) Reduction of the oxide to metal: It involves h*eating the metal oxide with suitable reducing agents* like C, CO or another metal. The reducing agent combines with the oxygen of the metal oxide.

$$M_xO_y + yC \rightarrow xM + y\,CO$$

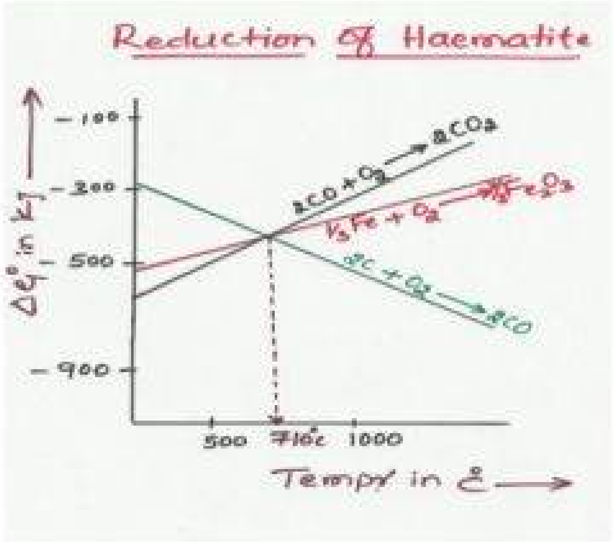
Ellingham diagram: An *Ellingham diagram shows the relation between temperature and the stability of a compound*. It is basically a graphical representation of Gibbs Energy Flow. An Ellingham diagram normally consists of plots of change in the Gibbs energy with temperature for the formation of oxides.

An Ellingham diagram for oxides has several important features.

I) We will plot the temperature on the Y axis and the ΔG on the X axis

(ii) The graphs for most metal to metal oxide reactions show a positive slope.

(iii) The Gibbs energy changes follow a straight line, unless the materials melt (or) vaporise.



(iv) When the temperature is raised, a point will be reached where the graph crosses the line "ΔG is zero." Below this temperature, the free energy of formation of the oxide is negative, so the oxide is stable. Above this temperature, the free energy of formation of the oxide is positive the oxide becomes unstable and will decompose into the metal and dioxygen.

(v) *Any metal will reduce an oxide of another metal that lies above it in an Ellingham diagram.*

Limitations:

1) **It does not consider the kinetics of the reactions.** It does not explain about the rate of the reaction.

2) The reactants and products are in **equilibrium, which is not often true**.

Extraction of Iron

Extraction of iron from its oxide is done in a blast furnace. Here the ore mixes with coke and limestone in the furnace.

At temperatures of 500-800 K $Fe_2O_3 + CO \rightarrow 2FeO + CO_2$

$CaO + SiO_2 \rightarrow CaSiO_3$

Gangue + Flux → Slag

At temperatures of 900-1500 K $C + CO_2 \rightarrow 2CO$

$FeO + CO \rightarrow Fe + CO_2$

iii) Refining of the metal:

Refining is a method of removing impurities in order to obtain metals of high purity.

i) **Distillation**: Here the impure *metal is evaporated to obtain the pure metal.* eg. metals having low boiling point like Zn, mercury (Hg)

ii) **Liquation**: It is used for metals with low melting point like tin (Sn). Here the impure *metal is melted on a sloping surface of a furnace.*

iv) **Zone refining**: This method is based on the principle that *the impurities are more soluble in the melt than in the solid state of the metal.* Eg. germanium, silicon, boron, gallium and indium which are used as semiconductors.

v) **Vapour phase refining**: In this method, t*he metal is converted into its volatile compound and collected at another place*. It is then decomposed to give pure metal.

a) **Mond's process for Refining Nickel**: In this process, nickel is heated in a stream of carbon monoxide forming a volatile complex, nickel tetracarbonyl. It is then decomposed to Ni and CO by heating at very high temperature.

b) **van Arkel Method for Refining Zirconium or Titanium**: Here the *crude metal is heated in an evacuated vessel with iodine. The metal forms it volatile iodide. The metal iodide is decomposed electrically by using a tungsten filament*, electrically heated to about 1800K. The pure metal is thus deposited on the filament.

Model questions:

1) What types of ores can be seperated by magnetic seperation? (Hint: *Ores shows magnetic properties like, Heamatite, Magnetite, Iron pyrites*)
2) What do you mean by leaching? (Hint: *If the ore is soluble in some suitable solvent, eg. Bauxite is concentrated by dissolving hot concentrated NaOH*)
3) Which method can be recommended for purification of titanium and nickel? (Hint: *Titanium by van-Arkel, Nickel by Mond's process*)
4) What is the principle behind the froth flotation process? (Hint: *Principle of this method is that sulphide ores are preferentially wetted by oils and gangue is wetted by water*)
5) What is the role of lime stone in the extraction of iron? (Hint: *Gangue + Flux → Slag*)

7. P-BLOCK ELEMENTS

Dinitrogen (N_2)

- Inert at room temperature
    - Reason – High bond enthalpy of N≡ N bond

Ammonia (NH_3)

- On large scale, obtained by ***Haber's process***

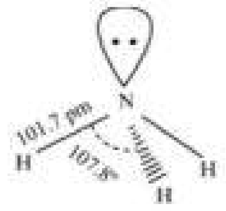
    $N_2 + 3H_2 \rightleftarrows 2NH_3$

    - High pressure favours the formation of NH_3.
    - Optimum condition : Pressure = 200×10^5 Pa (about 200 atm), Temperature ~ 700 K

  - Catalysts used – Iron oxide with small amounts of K_2O and Al_2O_3 to increase the rate of attainment of equilibrium

- *Ammonia act as Lewis base due to presence of lone pair of electron*

Structure



- Trigonal pyramidal

Uses

- In the production of various nitrogen fertilisers
- In the manufacture of HNO_3

Nitric acid (HNO_3)

- On large scale – By ***Ostwald's process***

  Steps involved:

- Catalytic oxidation of NH_3

$$4NH_{3(g)} + \underset{\text{(from air)}}{5O_{2(g)}} \xrightarrow[\text{500K, 9bar}]{\text{Pt/Rh gauge catalyst}} 4NO_{(g)} + 6H_2O_{(g)}$$

- $2NO_{(g)} + O_{2(g)} \longleftrightarrow 2NO_{2(g)}$
- $3NO_{2(g)} + H_2O_{(l)} \longrightarrow 2HNO_{3(aq)} + NO_{(g)}$

HNO_3 act as strong acid strong oxidising agent

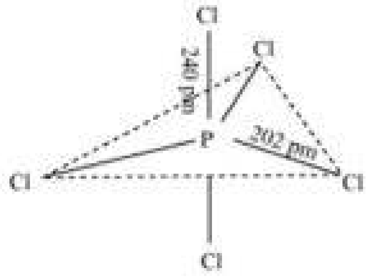
Phosphorus Halides

- PCl₃ hydrolyses in the presence of moisture giving fumes of HCl

$$PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl$$

$$PCl_5 \xrightarrow{\text{Heat}} PCl_3 + Cl_2$$

Trigonal bipyramidal shape in gaseous and liquid phase



Three equatorial bonds are equivalent while the two axial bonds are longer than equatorial bonds. Reason – More repulsion is suffered by axial bonds as compared to equatorial bonds.

Sulphuric Acid

Manufacture (Contact Process)

- Burning of sulphur or sulphide ores in air to produce SO_2

  $S + O_2 \rightarrow SO_2$

- Conversion of SO_2 to SO_3 by the reaction with O_2 in presence of V_2O_5 (catalyst)

  $2SO_{2(g)} + O_{2(g)} \xrightarrow{V_2O_5} 2SO_{3(g)}$; $\Delta_r H^\ominus = -196.6$ kJ mol^{-1}

- Absorption of SO_3 in H_2SO_4 to produce $H_2S_2O_7$ (oleum)
- $SO_3 + H_2SO_4 \rightarrow H_2S_2O_7$

Oleum

- Dilution of oleum ($H_2S_2O_7$) with water gives sulphuric acid (H_2SO_4) of desired concentration.

Uses

- Important industrial chemical
- In the manufacture of fertilisers
- As a laboratory reagent
- In storage batteries

Interhalogen Compounds

- Two different halogens react with each other to form interhalogen compounds.
- General composition – XX', XX'_3, XX'_5, and XX'_7
  - X = Halogen of larger size
  - X' = Halogen of smaller size
  - X is more electropositive than X'.
- XX'_3 (eg;- ClF_3, BrF_3) - Bent T-shaped
- XX'_5 (eg;- IF_5) Square pyramidal

XX'_7 (eg;- IF_7) Pentagonal bipyramidal

In general, interhalogen compounds are more reactive than halogens (except fluorine).

This is because X–X′ bond in interhalogens is weaker than X–X bond in halogens

Group 18 Elements

- Helium (He), Neon (Ne), Argon (Ar), Krypton (Kr), Xenon (Xe), and Radon (Rn)
- All are gases.
- Chemically uncreative – Hence, they are termed as noble gases.

Occurrence

- Occur in atmosphere (except Rn)

Atomic Properties

- General outer electronic configuration is $ns^2\ np^6$.

  Exception – He ($1s^2$)
- High ionisation enthalpy
  - Reason – Stable electronic configuration
  - However, ionisation enthalpy decreases down the group (that is, with the increase in atomic size).
- Large positive values of electron gain enthalpy

  Reason – Stable electronic configurations

Chemical Properties

- Less reactive

  Reason:
  - Completely filled $ns^2\ 2p^6$ valence shell electronic configuration (Except He – $1s^2$)
  - High ionisation enthalpy and more positive electron gain enthalpy
- First noble gas compound – $Xe^+PtF_6^-$
  - Obtained by mixing PtF_6 and Xe

Xenon-Fluorine Compounds

- XeF_2, XeF_4, and XeF_6

$$Xe_{(g)} + F_{2(g)} \xrightarrow{673\text{ K, 1bar}} XeF_{2(s)}$$

(Xe in excess)

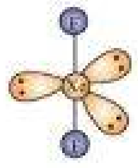
$$Xe_{(g)} + 2F_{2(g)} \xrightarrow{873\text{ K, 7bar}} XeF_{4(s)}$$

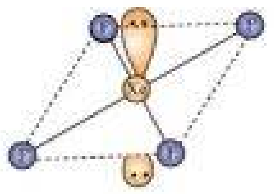
(1:5 ratio)

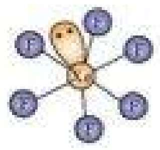
$$Xe_{(g)} + 3F_{2(g)} \xrightarrow{573\text{ K, 6–70bar}} XeF_{6(s)}$$

(1:20 ratio)

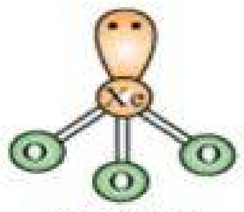
- $XeF_2 \longrightarrow$ Linear
- $XeF_4 \longrightarrow$ Square planar
- $XeF_6 \longrightarrow$ Distorted octahedral


Linear

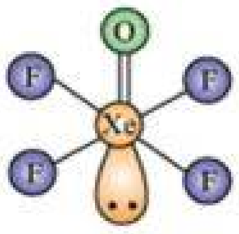

Square planar


Distorted octahedral

- XeO_3 has a pyramidal molecular structure.


Pyramidal

- $XeOF_4$ has a square pyramidal molecular structure.


Square pyramidal

Uses of Noble Gases

- **Helium**
  - In filling balloons for meteorological observations as it is a non-inflammable and light gas
  - In gas-cooled nuclear reactors
- **Liquid Helium**
  - As a cryogenic agent
  - As a diluent for oxygen in modern diving apparatus

Reason– Very low solubility in blood

- **Neon**
  - In discharge tubes and fluorescent bulbs
  - Neon bulbs – Used in botanical gardens and in green houses
- **Argon**
  - To provide an inert atmosphere in high temperature metallurgical processes
  - For filling electric bulbs

- **Xenon and Krypton**
  - In light bulbs designed for special purposes

Model questions:

1. Why does NH_3 act as a Lewis base ?
2. Explain the manufacture of ammonia
3. Mention the conditions required to maximise the yield of ammonia
4. Explain how nitric acid is manufactured by Ostwald's process?
5. Why does PCl_3 fume in moisture ?
6. Briefly explain the manufacture of sulphuric acid by contact process.
7. Write two uses of a) ammonia b) nitric acid c) sulphuric acid
8. What are interhalogen compounds? Write any two examples.
9. Write the formula of any two interhalogen compounds and explain their shapes
10. Why is ICl more reactive than I_2

    [Interhalogen compounds are more reactive than halogens due to weaker $X–X^1$ bonding than X–X bond. Thus, ICl is more reactive than I_2.]
11. Noble gases have very low boiling points. Why?

    [Noble gases being monoatomic and they have only weak dispersion forces between them . Hence, they have low boiling points]
12. Suggest any two fluorides of Xenon
13. Draw the structures of XeO_3 and XeF_6.
14. Why is helium used in diving apparatus? [due its very low solubility in blood]
15. Write uses of noble gases

8. THE d and f BLOCK ELEMENTS

A transition element is defined as the one which has partially filled *d* orbitals in its ground state or in any one of its oxidation states.

Zn, Cd and Hg are not considered as transition elements

Zn, Cd and Hg - general electronic configurations $(n-1)d^{10}ns^2$. The orbitals in these elements are completely filled (d^{10})in the ground state as well as in their common oxidation states. Therefore, they are not considered as transition elements general the electronic configuration d block elements is **(n-1)** $d^{1-10}ns^{1-2}$.

Properties of transition elements

Property	**Reason**
Paramagnetism	Due to presence of unpaired electron
form a large number of complex compounds	Comparatively smaller size of metal ions, high ionic charges and availability of *d*-orbitals for bond formation
Form Interstitial compounds	small atoms like H, C, N are trapped inside the crystal lattices of metals
Form alloys	Because of similar size
Form coloured compound	due to the presence of unpaired d-electrons, d-d transition
catalytic activity	ability to show variable oxidation state

*Atomic size of transition elements decreases with increase in atomic number till middle of the series.

Reason: With increase in atomic number, an extra electron is being added to inner d-orbital Shielding effect of a *d* electron is not much effective .Thus attraction increases and hence size decreases.

*Size of 5d series elements is almost same as 4d elements.

Reason: Lanthanoid contraction

Magnetic properties

- Paramagnetism arises due to the presence of unpaired electrons.
- Magnetic moment can be calculated by using 'spin-only' formula, i.e.,

$$\mu = \sqrt{n(n+2)}$$

Where, n = Number of unpaired electrons μ = Magnetic moment in Bohr magneton (BM)

- Magnetic moment increases with the increase in the number of unpaired electrons.

Potassium Dichromate ($K_2Cr_2O_7$)

- Prepared from chromite ore($FeCr_2O_4$) in the following steps:

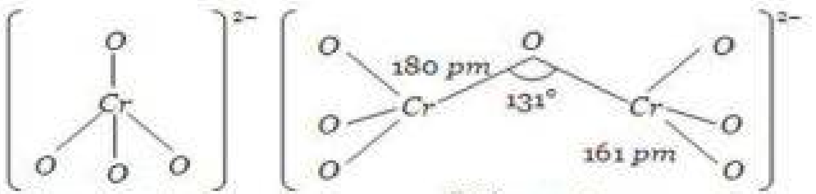
1. Chromite ore is first fused with sodium carbonate in presence of air to form sodium

chromate. $4\ FeCr_2O_4 + 8\ Na_2CO_3 + 7\ O_2 \rightarrow 8\ Na_2CrO_4 + 2\ Fe_2O_3 + 8\ CO_2$

2. The yellow solution of sodium chromate is filtered and acidified with sulphuric acid to orange sodiumdichromate. $2Na_2CrO_4 + 2\ H^+ \rightarrow Na_2Cr_2O_7 + 2\ Na^+ + H_2O$

3. The solution of sodium dichromate is treated with potassium chloride so that orange crystals of potassium dichromate crystallise out.

$$Na_2Cr_2O_7 + 2\ KCl \rightarrow K_2Cr_2O_7 + 2\ NaCl$$



Chromate ion Dichromate

The structure of chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$) ions

- Potassium dichromate is good oxidizing agent in ***acid medium***
- Examples:

1. Oxidises iron (II) solution to iron (III) solution i.e., ferrous ions to ferric ions $Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$

2. It can oxidize iodide to iodine

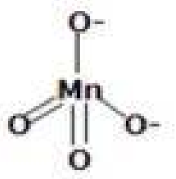
Potassium permanganate(KMnO4*):*

It is prepared from **pyrolusite**(MnO_2).

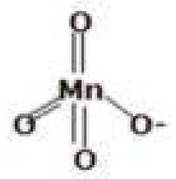
1) Pyrolusite is fused with KOH in the presence of air when potassium manganate is obtained.

$2MnO_2 + 4\ KOH \rightarrow 2K_2MnO_4 + 2H_2O$

2) potassium manganate, with Cl_2 , O_3 , on electrolytic oxidation or disproportionation gives potassium permanganate. $K_2MnO_4 + Cl_2 \rightarrow 2KMnO_4 + 2KCl$



Manganate ion
(Paramagnetic, green)



Permanganate ion
(Diamagnetic, purple)

1) **On heating** it decomposes to manganate and MnO_2

$2KMnO_4 \text{ --------}\rightarrow K_2MnO_4 + MnO_2 + O_2$

2) Oxidising property*:* -Potassium permanganate acts as a powerful oxidizing agent in ***acid, alkaline and neutal medium***.

- Acidified $KMnO_4$ solution oxidises Fe (II) ions to Fe (III) ions i.e., ferrous ions to ferric ions.

$$MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

f-block elements

General the electronic configuration f block elements is **$(n-2)f^{1-14}(n-1)d^{0-1}ns^2$**.

In lanthanoids, the most common oxidation state is +3.

Cerium shows the oxidation state +4 due to its noble gas configuration

Lanthanide Contraction

In lanthanides, the atomic and ionic radii decrease regularly from lanthanum to lutetium. It is called *lanthanide contraction*.

Reason: In lanthanides, as the atomic number increases, the nuclear charge increases one by one and the electrons are added to the anti-penultimate f subshell. Due to its diffused shape, f orbitals have poor shielding effect. So the nucleus can attract the outer most electrons strongly and as a result the radii decreases.

Consequences:

1) Due to Lanthanide Contraction the 2nd and 3rd row transition series elements have similar radii.E.g. Zr – 160pm and Hf -159pm

2) Lanthanides have similar physical properties and they occur together in nature. So their isolation is difficult.

3) The basic character of their hydroxides decreases from lanthanum to lutetium. i.e, $La(OH)_3$ is more basic than $Lu(OH)_3$

Uses of Lanthanides

An important alloy is *mischmetall* which consists of a lanthanoid metal (~ 95%) and iron (~ 5%) and traces of S, C, Ca and Al. A great deal of mischmetall is used in Magnesium based alloy to produce bullets, shell and lighter flint.

Model questions:

1 . What are transition and inner transition elements ?

- Hint – Transition elements – d block elements

-General configuration – $ns^2(n-1)d^{1-10}$

-Inner transition elements – f block elements

-Lanthanoids and Actinoids

-General configuration – $ns^2(n-1)d^{0-1}(n-2)f^{1-14}$

2 . Zn , Cd , Hg are not transition elements . Why ?

- Hint – Transition elements should have partially filled d orbital . Zn , Cd , Hg have completely filled d orbitals

3. Account for magnetic behaviour of transition metals [Why transition elements are Paramagnetic ?

- Hint – They have unpaired electrons – Magnetic behaviour is calculated using spin only formula

4 . Transition elements form coloured compounds . Why ?

- Hint – Due to d-d transition – They have partially filled d orbital

5 . Why transition elements can form a number of complexes ?

- Hint – Their size is small – d orbitals are available for bond formation .

6 . Transition elements are good catalysts . Why ?

- Hint – They can show variable oxidation states – They can bind easily to reactant molecules .

7 . How is $K_2Cr_2O_7$ prepared ?

- Hint – From chromite ore

-Chromite ore is fused with sodium carbonate . Sodium chromate is formed .

- Sodium chromate is acidified . Sodium dichromate is obtained .

- Sodium dichromate is treated with Potassium chloride . We get $K_2Cr_2O_7$

8 . Draw the structure of chromate ion and dichromate ion .

Hint: Refer the note given above

9 . How is potassium permanganate prepared ?

- Hint – From pyrolusite ore

- MnO_2 is fused with KOH . Green potassium chromate is obtained

- K_2MnO_4 is electrolysed . $KMnO_4$ is formed .

10 . Draw the structure of manganate and permanganate ions

Hint: Refer the note given above

11 . What is lanthanide contraction ? What is the reason for it ?

- Hint – The atomic and ionic radii of lanthanides decrease from La to Lu

- Reason : Electrons are added to antipenultimate f orbital . The f orbitals are diffuse . So shielding effect is poor .

12 . What are the consequences of Lanthanide contraction ?

- Hint – 4d and 5d series of transition elements have similar properties

- Lanthanides occur together in nature . Their isolation is difficult .

- Basic character of hydroxides from $La(OH)_3$ to $Lu(OH)_3$ decreases .

13 . What are the uses of d and f block elements ?

-Hint – In alloys – misch metal – steel , brass , bronze etc

- Coinage metals – Cu , Ag , Au

- As catalysts V_2O_5 , Fe etc

- For building purposes

9. CO-ORDINATION COMPOUNDS

These are compounds in which a metal atom/ion is surrounded by a group of anions or neutral molecules. The metal atom/ion is called central atom/ion and the neutral molecules or anions are called ligands. The central atom/ion should contain vacant orbitals and the ligand should contain one or more lone pairs of electrons. The central metal atom or ion and ligands form a co-ordination entity.

A ligand that binds to the central atom/ ion through a single donor atom is said to be unidentate ligand. Eg.: Cl^-, Br^-, I^-, OH^-, H_2O, NH_3, CN_-, NC^-, SCN^- etc.

A ligand that binds to the central atom through two donor atoms is called a bidentate ligand. Eg: Ethane-1, 2-diamine or ethylenediamine ($H_2NCH_2CH_2NH_2$) notated as 'en' and oxalate ion ($C_2O_4^{2-}$). A ligand that binds to the central atom through more than two donor atoms is called polydentate ligand. E.g.: Ethylenediamine tetraacetate ion ($EDTA^{4-}$) is an important hexadentate ligand. The total number of ligand donor atoms to which the metal is directly bonded is called the co-ordination number of the metal atom/ion.

IUPAC Nomenclature of Co-ordination Compounds

The following rules are used while naming co-ordination compounds: (i) The cation is named first in both positively and negatively charged co-ordination entities. (ii) The ligands are named in alphabetical order before the name of the central atom/ion. (iii) Names of the anionic ligands end in –o, those of neutral and cationic ligands are the same except 'aqua' for H_2O, 'ammine' for NH_3, 'carbonyl' for CO and 'nitrosyl' for NO.(iv) Prefixes mono, di, tri, etc., are used to indicate the number of individual ligands in the co-ordination entity. When the names of the ligands include a numerical prefix, then the terms bis (for 2 such ligands), tris (for 3), tetrakis (for 4) are used. Here the name of the ligand is placed in simple bracket. (v) Oxidation state of the metal is indicated by Roman numeral in simple bracket.(vi) If the complex ion is a cation, the central atom is named same as the

element. If the complex ion is an anion, the name of the metal ends with the suffix –ate. For example ferrate for iron, cobaltate for cobalt, zincate for Zn. (vii) The neutral complex molecule is named similar to that of the cationic complex.

Isomerism in Co-ordination Compounds

Compounds having the same molecular formula but different structural formula or spatial arrangement of atoms are called isomers and the phenomenon is called isomerism. The isomerism shown by coordination compounds are broadly divided into two – structural isomerism and stereo isomerism.

I) Structural Isomerism

These are isomers which differ in the structural arrangement of ligands around the central atom. They are of four types:

1) **Ionisation Isomerism**: It arises due to the inter change of ions between the inside and outside of co ordination sphere. They give different types of ions in aqueous solution

An example is $[Co(NH_3)_5SO_4]Br$ and $[Co(NH_3)_5Br]SO_4$.

2) **Linkage isomerism**: It arises in a co-ordination compound containing ambidentate ligand, which can bind to the central atom through more than one donor atoms. Eg. in the complex $[Co(NH_3)_5(ONO)]Cl_2$, the nitrite ligand is bound through oxygen (–ONO), and in $[Co(NH_3)_5(NO_2)]Cl_2$ the nitrite ligand is bound through nitrogen ($-NO_2$) atom.

3) **Co-ordination Isomerism**: If both anionic and cationic parts are complexes, the isomerism arises due to the interchange of ligands between cationic and anionic entities. This type of isomerism is called co ordination isomerism. An example is $[Co(NH_3)_6][Cr(CN)_6]$ and $[Cr(NH_3)_6][Co(CN)_6]$.

4) **Solvate isomerism**: It arises due to the difference in the no. of solvent molecules which are directly bonded to the metal ion as ligand. It is also known as '***hydrate isomerism***' if water is the solvent. An example is $[Cr(H_2O)_6]Cl_3$ and $[Cr(H_2O)_5Cl]Cl_2.H_2O$.

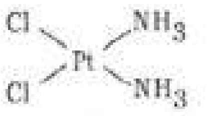
II) Stereoisomerism

These are isomers which differ only in the spatial arrangement of ligands around the central atom. They have same atom to atom bond. These are of two types:

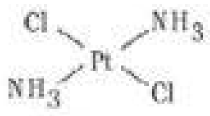
(i) Geometrical isomerism (ii) Optical isomerism

i) Geometrical Isomerism: This type of isomerism arises due to the difference in the arrangements of the ligands around the central atom. It is mainly found in co-ordination complexes with co-ordination numbers 4 (square planar complexes) and 6 (octahedral complexes).

Geometrical isomer in which the same ligands are on the same side of the central metal atom is called *cis isomer* and the isomer in which the same ligands are on the opposite side is called *trans isomer.* Square planar complexes with formula $[MX_2L_2]$ (X and L are unidentate ligands) can show this isomerism.This type of isomerism also arises when bidentate ligands (L – L) are present in complexes with formula $[MX_2(L-L)_2]$ e.g.: $[Co(en)_2Cl_2]+$

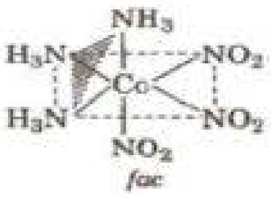


cis



trans

Fac-mer isomerism: It is a type of geometrical isomerism occurs in octahedral co-ordination entities of the type $[Ma_3b_3]$. If similar ligands occupy three adjacent positions of an octahedral face, it is called **facial (fac) isomer**. When the positions are around the meridian of the octahedron, it is called **meridional (mer) isomer**. Eg. $[Co(NH_3)_3(NO_2)_3]$.



fac

mer

ii) **Optical Isomerism:** Optical isomers are mirror images that cannot be superimposed on one another. These are also called *enantiomers*.

There are two forms of optical isomers - *dextro (d)* and *laevo (l)*.

In a co-ordination entity of the type $[PtCl_2(en)_2]^+$, **only the *cis*-isomer shows optical activity**. *The trans- isomer has a plane of symmetry and is optically inactive.*

Magnetic Properties of Co-ordination Compounds

By knowing the magnetic moment, we can predict the geometry of complexes. For eg. $[Mn(CN)_6]^{3-}$ has magnetic moment of two unpaired electrons while $[MnCl_6]^{3-}$has a paramagnetic moment of four unpaired electrons. $[Fe(CN)_6]^{3-}$ has magnetic moment of a single unpaired electron while $[FeF_6]^{3-}$ has a paramagnetic moment of five unpaired electrons. $[CoF_6]^{3-}$ is paramagnetic with four unpaired electrons while $[Co(C_2O_4)_3]^{3-}$ is diamagnetic. This is because $[Mn(CN)_6]^{3-}$, $[Fe(CN)_6]^{3-}$ and $[Co(C_2O_4)_3]^{3-}$ are inner orbital complexes involving d^2sp^3 hybridisation. While $[MnCl_6]^{3-}$, $[FeF_6]^{3-}$ and $[CoF_6]^{3-}$ are outer orbital complexes involving sp^3d^2 hybridisation and are paramagnetic.

Application of Co-ordination Complexes

1. In Qualitative & Quantitative Analysis: Ni^{2+} is detected and estimated by the formation of a complex with Dimethyl Glyoxime (DMG). The brown ring test for the detection of nitrate ion is due to the formation of the brown complex $[Fe(H_2O)_5NO]^{2+}$. **2. In water treatment**: The Hardness of water is estimated by simple titration with Na_2EDTA (sodium salt of EDTA). The hardness of water can be removed by the formation of a complex with calgon. **3. In Metallurgy** for the extraction of

some metals like Ag & Au and for refining of metal like Ni. **4. Biological Applications**: *Chlorophyll*, is a co-ordination compound of **magnesium**, *Haemoglobin* is a co-ordination compound of ***iron*** and *Vitamin* B_{12} is a co-ordination compound of **cobalt. 5. In Catalysis**: Co-ordination compounds are used as catalysts for many industrial processes. **6. In electroplating 7. In Photography 8. In medicine**: Cis-platin is used for the treatment of cancer. EDTA is used in the treatment of lead poisoning.

Model Questions

- Write the IUPAC name of the following (i) $[Ni(CO)_4]$ (ii) $K_4[Fe(CN)_6]$

  Hint : Tetracarbonylnickel(0), Potassiumhexacyanoferrate(II)

- Draw the geometrical isomers of $[PtCl_2(en)_2]^{2+}$. Which among the isomer is optically active? Hint: Cis isomer

- Identify the co-ordination compound which can exhibit linkage isomerism, among the following:

- $[Pt(NH_3)_2Cl_2]$ (b) $[Co(NH_3)_5(SO_4)]Br$ (c) $[Co(NH_3)_5(NO_2)]Cl_2$ (d) $[Cr(NH_3)_6][CoF_6]$ Hint: c

- Write the IUPAC names of the following compounds: (a) $[Ni(CO)_4]$ (b) $K_3[Fe(C_2O_4)_3]$

- Draw the structures of geometrical isomers of $[Fe(NH_3)_2(CN)_4]$

- $[Co(NH_3)_5SO_4]Cl$ and $[Co(NH_3)_5Cl]SO_4$ are co-ordination compounds.

- Identify the isomerism shown by the above compounds.

- Write the IUPAC names of the above compounds.

Hint: (a) Ionisation isomerism

- $[Cr(NH_3)_5CO_3]Cl$ is a co-ordination compound.

    - What is the IUPAC name of above compound ?
    - What is the ionisation isomer of the above mentioned co-ordination compound?

•Consider the co-ordination compound $[Co(NH_3)_5SO_4]Br$. Write the IUPAC name of the co-ordination compound and name the isomerism shown by it.

•Explain three important applications of co.ordination compunds ?

•Which co-ordination compound is used for the treatment of cancer?

Hint: Cisplatin

10.HALOALKANES AND HALOARENES

- **Methods of Preparation**

From Alcohols

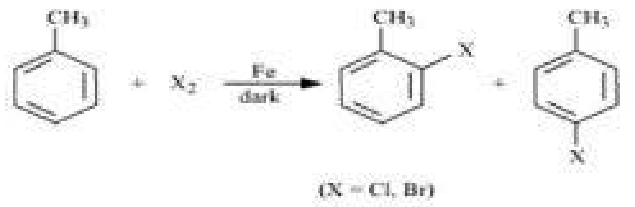
Preparation: 1) from alcohols;

CH_3-OH + (PCl_3 or PCl_5 or $SOCl_2$) --------→ CH_3-Cl

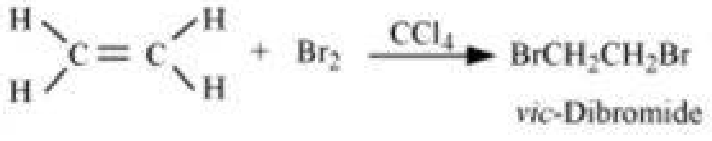
The reaction with $SOCl_2$ is better because the by products are gases (SO_2 and HCl)

From Hydrocarbons

- **Electrophilic Substitution**



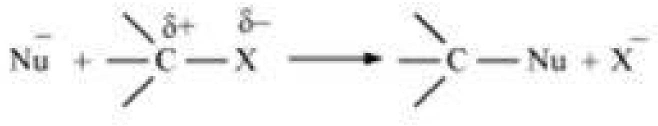
- **From Alkenes**
  - By adding halogens



  - This method is used to detect double bond in a molecule as reddish brown colour of bromine is discharged during the reaction.

Reactions of Haloalkanes

- **Nucleophilic Substitution Reactions**



Mechanism

a) **S_N2 mechanism**:

It occurs in one step.

The reactivity alkyl halides is in the order $1^0 > 2^0 > 3^0$.

It may results in inversion of configuration(if it is asymmetric)

b) **S_N1 mechanism:**

It occurs in Two steps.

In the first step it forms a carbocation

In the second step the nucleophile is able to attack from both sides of the carbon atom.

The reactivity alkyl halides is in the order $3^0 > 2^0 > 1^0$.

It may results in inversion and retension of configuration(if it is asymmetric)

- For both S_N1 and S_N2 reaction, the order of reactivity of halides is

$R{-}F << R{-}Cl < R{-}Br < R{-}I$

Example $CH_3\text{-}Cl + KCN \text{-----}\rightarrow CH_3\text{-}CN$

$CH_3\text{-}Cl + AgCN \text{-------}\rightarrow CH_3\text{-}NC$

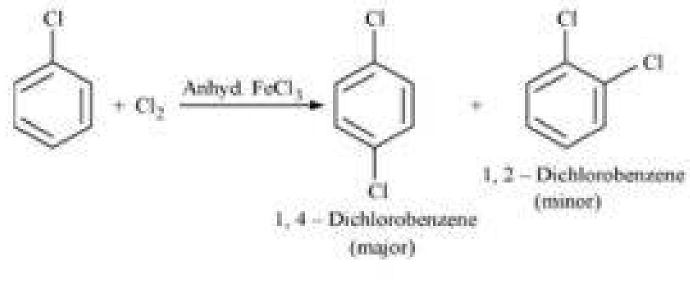
$CH_3\text{-}Cl + aq.NaOH\text{---}\rightarrow CH_3\text{-}OH$

Reactions of Halo arenes

- **Electrophilic Substitution**

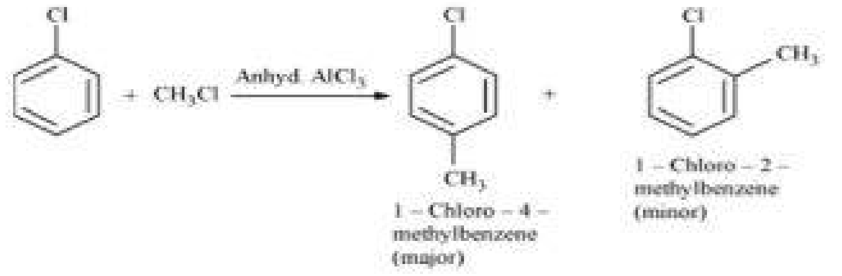
Substitution occurs at *o*- and *p*-direction due to availability of electrons at these positions because of resonance.

- Halogenation



- Nitration

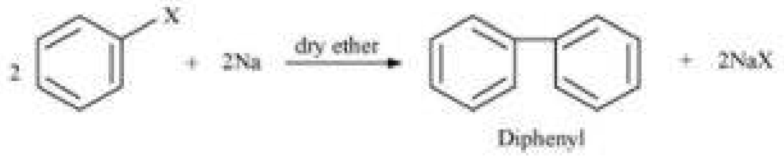
- Friedel–Crafts Alkylation



Reaction with Metals

- Wurtz–Fittig Reaction

- Fittig reaction



Polyhalogen Compounds

- **Trichloromethane or Chloroform ($CHCl_3$)**
  - $CHCl_3$ is oxidised to an extremely poisonous gas phosgene ($COCl_2$) in the presence of light.

$$2CHCl_3 + O_2 \xrightarrow{Light} 2COCl_2 + 2HCl$$

That is why chloroform is stored in closed dark-coloured bottles completely filled so that no air is left inside the bottles.

Model questions:

1. Write a method for the preparation of alkyl halides.
2. Write a method for the preparation of aryl halides
3. Write the differences between S_N1 and S_N2 reaction
4. What is S_N1 reaction?
5. Complete the reaction
   CH_3-Cl + KCN -----→ …………
   CH_3-Cl + AgCN -------→ ………………
   CH_3-Cl + aq.NaOH---→ ………………………..
6. Write any 2 examples of electrophilic substitution reaction of chlorobenzene
7. Write equations showing Wurtz-Fittig reaction and Fittig reaction
8. Chloroform is stored in closed, dark coloured bottles completely filled up to the neck. Give reason.

9. Write the reaction of ethyl bromide with the following reagents : (a) aq. KOH (b) KCN (c) AgCN
10. Write two examples for ambident nucleophiles [ans;- cyanide ion and nitrite ion]

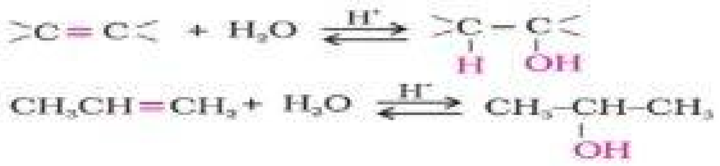
11. ALCOHOLS, PHENOLS AND ETHERS

These are compounds containing C – O single bond. The functional group present in alcohols and phenols is –OH (hydroxyl) group and that present in ethers is –O – group (oxy group).

Preparation of Alcohols

1. From alkenes:

i) By acid catalysed hydration: Alkenes react with water in the presence of acid as catalyst to form alcohols. In the case of unsymmetrical alkenes, the addition reaction takes place in accordance with Markovnikov's rule.



$$>C=C< + H_2O \overset{H^+}{\rightleftharpoons} >\underset{H}{C}-\underset{OH}{C}<$$

$$CH_3CH=CH_2 + H_2O \overset{H^+}{\rightleftharpoons} CH_3-\underset{OH}{CH}-CH_3$$

ii) By hydroboration–oxidation reaction: Addition of **diborane** followed by **oxidation** using hydrogen peroxide in presence of alkali is called Hydroboration-oxidation reaction. Alkenes add diborane to give trialkyl boranes which on oxidation by H_2O_2 in the presence of aqueous sodium hydroxide to form alcohols. The net reaction is the addition of a water molecule to the alkene in a way opposite to the Markovnikov's rule.

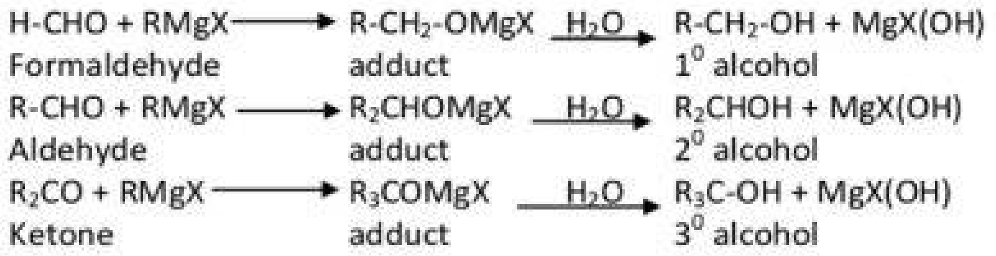
2. From carbonyl compounds

i) Reduction: Carbonyl compounds (aldehydes and ketones) when reduced using lithium aluminium hydride ($LiAlH_4$) or sodium borohydride ($NaBH_4$) or on catalytic hydrogenation (using finely divided metal such as platinum, palladium or nickel), we get alcohols. **Aldehydes give primary alcohols and ketones give secondary alcohols.**

ii) By reduction of carboxylic acids and esters: Carboxylic acids are reduced to primary alcohols by treating with $LiAlH_4$.

3. From Grignard reagents:

Aldehydes and ketones add Grignard reagent followed by hydrolysis, we get alcohols. **Formaldehyde (methanal) gives primary alcohols, aldehydes other than formaldehyde gives secondary alcohols and ketones give tertiary alcohols.**



$$\underset{\text{Formaldehyde}}{H\text{-}CHO + RMgX} \longrightarrow \underset{\text{adduct}}{R\text{-}CH_2\text{-}OMgX} \xrightarrow{H_2O} \underset{1^0\ \text{alcohol}}{R\text{-}CH_2\text{-}OH + MgX(OH)}$$

$$\underset{\text{Aldehyde}}{R\text{-}CHO + RMgX} \longrightarrow \underset{\text{adduct}}{R_2CHOMgX} \xrightarrow{H_2O} \underset{2^0\ \text{alcohol}}{R_2CHOH + MgX(OH)}$$

$$\underset{\text{Ketone}}{R_2CO + RMgX} \longrightarrow \underset{\text{adduct}}{R_3COMgX} \xrightarrow{H_2O} \underset{3^0\ \text{alcohol}}{R_3C\text{-}OH + MgX(OH)}$$

Preparation of phenol

1. Dow's process:-Chlorobenzene is heated with NaoH at 623 K temperature and 300 atm pressure, forms sodium phenoxide which on acidification gives phenol.

2. Benzene diazonium chloride warm with water to form phenol

Chemical Reactions of Alcohols

1. **Reaction with hydrogen halides**: Alcohols react with hydrogen halides in presence of anhydrouszinc chloride ($ZnCl\ 2$) to form alkyl halides.

The order of reactivity of alcohols with HCl is 3^0 alcohols > 2^0 alcohols > 1^0 alcohols.

Lucas Test- distinction between primary, secondary and Tertiary alcohols.

Lucas Reagent is a mixture of **concentrated hydrochloric Acid and anhudrous Zinc chloride.**

Primary alcohols + Lucas Reagent ⟶ No Reaction

Secondary alcohols Lucas reagent ⟶ Turbidity appears within 5 seconds

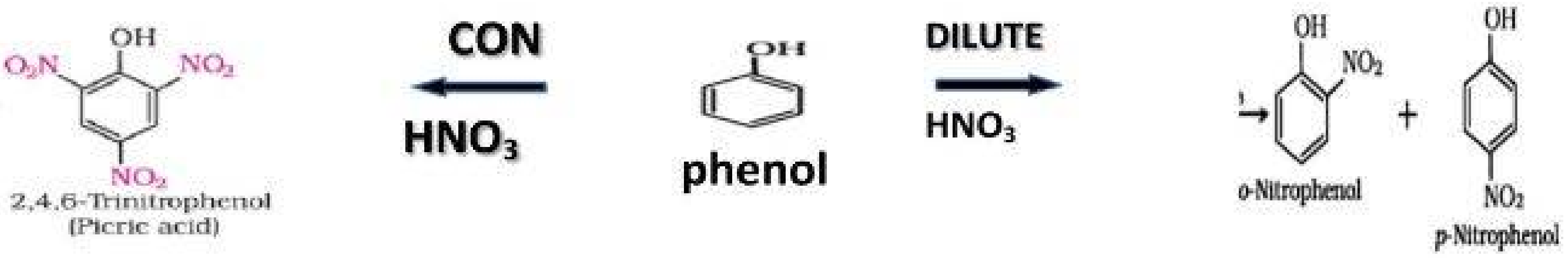
Tertiary alcohols Lucas Reagent ⟶ Turbidity appears immediately.

2. Dehydration: On heating with Conc. H_2SO_4 or H_3PO_4, alcohols undergo dehydration (removal of a molecule of water) to form **alkenes.**

3. Reimer-Tiemann reaction:

Phenol +chloroform +NaOH+ acidification ⟶ salycylaldehyde

4. Nitration of Phenol



Ethanol

Ethanol is manufactured by the **fermentation** of molasses (contain 20% sucrose)

STEP 1. $\text{SUCROSE} + \text{WATER} \xrightarrow{\text{Invertase}} \text{GLUCOSE} + \text{FRUCTOSE}$

STEP 2. $\text{GLUCOSE} \xrightarrow{\text{Zymase}} \text{ETHANOL} + \text{CARBONDIOXIDE}$

Rectified spirit- 95% ethyl alcohol

Denatured spirit /Methylated spirit- Rectified spirit made poisonous by adding methyl alcohol to become unfit to drink

Absolute alcohol- 100% ethyl alcohol

Preparation of Ethers

1. Williamson synthesis:

Alkyl halide + sodium alkoxide $\longrightarrow$ Ether.

Eg1. Sodium phenoxide when treated with methyl bromide in presence of NaOH, we get **Anisole** (C_6H_5-O-CH_3).

2. For the preparation of **tert-butyl methyl ether**, methyl bromide should be treated with sodium tert-butoxide.

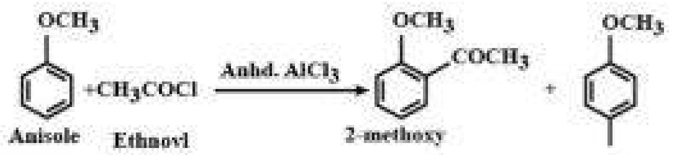
NOTE:If we use **tert-butyl bromide** and **sodium methoxide**, dehydrohalogenation occurs and the product formed is **alkene.**

Chemical Reactions of Ethers or Anisole

Friedel-Crafts reaction:

i) Alkylation: Anisole react with **alkyl halide** chloride in presence of anhydrous aluminium chloride (a Lewis acid) as catalyst, we get 4-methoxy toluene as the major product.

(ii) Acylation: Anisole react with **acetyl halide** we get a mixture of ortho and para methoxyacetophenone.



Model questions:

Q 1. Write the preparation of propan-2-ol from a Grignard reagent.

(Hint: Ethanal + methyl magnetium chloride to form addition product which on hydrolysis to form propan-2-ol).

Q 2. Write the chemical equation representing Reimer-Tiemann reaction. **(refer above notes).**

Q 3. Phenol when treated with Conc. HNO 3 gives .... **(Answer: 2,4,6-Trinitrophenol).**

Q 4. Write a test to distinguish between phenol and alcohol.

Answer : Alcohol Neutral give no reaction neutral ferric chloride

Phenol give Violet Colour with neutral ferric chloride

Q 5. Explain a method for the manufacture of ethanol **(refer above notes).**

Q 6. How will you prepare the following compounds using a Grignard reagent?

i) Primary alcohol ii) Secondary alcohol **(refer above notes).**

Q 7. Primary, secondary and tertiary alcohols can be distinguished by Lucas test.

i) What is Lucas reagent?

ii) Write the observations, for primary, secondary and tertiary alcohols in Lucas test **(refer notes)**

Q 8. Mixture of Conc. HCl and anhydrous ZnCl 2 is an important reagent which helps to distinguish between 1^0 ,2^0 and 3^0 alcohols.

a) Give the name of the above reagent.

b) Give one example each for 1^0 ,2^0 and 3^0 alcohols.

c) Explain how the above reagent helps to distinguish above three types of alcohols. **(refer notes).**

Q 9. Phenols are more acidic than alcohols.

a) Name the product obtained when phenol is treated with chloroform in the presence of NaOH.

b) Name the above reaction.

c) What is the product obtained when phenol is treated with Conc. HNO 3 ?

d) Write the structure and IUPAC name of the above product.

(Hint. A-salicylaldehyde , b-Reimer-salicylaldehyde ,c- picric acid , d- 2,4,6-trinitrophenol).

Q 10. Williamson's synthesis is an important method of ether synthesis.

a)To synthesis tertiary butyl ether, which of the following reagent sets are better? Justify.

i) $(CH_3)_3$ C-Br + CH_3ONa

ii)$(CH_3)_3$ C-ONa + CH_3 Br. **(Answer: ii, otherwise product become alkenerefer above note)**

b) Alcohols undergo dehydration. How is ethanol converted to ethene? **(refer above notes).**

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12. ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

Preparation of Aldehydes and Ketones

1. **By oxidation of alcohols**: *Primary alcohols* on oxidation with mild oxidising agents like CrO_3 to give aldehydes while *secondary alcohols* give ketones. $R\text{-}CH_2OH \xrightarrow{[O]} R\text{-}CHO$

2. **By dehydrogenation of alcohols**: Alcohols when heated with Cu catalyst at 573K, Primary alcohols give aldehydes, secondary alcohols give ketones. $R\text{-}CH_2OH \xrightarrow{Cu/573\ K} R\text{-}CHO$

Preparation of Aldehydes from acyl chloride:

Rosenmund's Reduction: *Acid chlorides react with hydrogen in presence of Pd supported on $BaSO_4$, we get aldehydes.* $R\text{-}COCl + H_2 \xrightarrow{Pd/BaSO4} R\text{-}CHO + HCl$

Preparation of Aromatic aldehydes:

1. By oxidation of methylbenzene: Methyl benzenes when oxidised using mild oxidising agents like chromyl chloride (CrO_2Cl_2) or chromic oxide (CrO_3) in acetic anhydride, we get benzaldehyde.

Etard reaction: *Chromyl chloride oxidises methyl group to a chromium complex, which on hydrolysis gives corresponding benzaldehyde.*

2. By Gatterman – Koch reaction: *When benzene is treated with carbon monoxide and hydrogen chloride in the presence of anhydrous aluminium chloride or cuprous chloride, we get benzaldehyde.*

Preparation of Ketones:

Friedel-Crafts acylation reaction: *When benzene or substituted benzene is treated with acid chloride (R-COCl) in the presence of anhydrous aluminium chloride, we get a ketone.*

Chemical reactions. Reduction reactions:

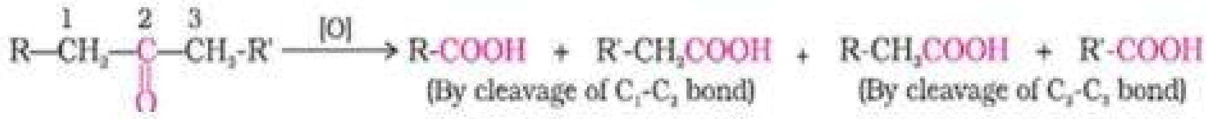
i) Reduction to alcohols: When reduced using sodium borohydride ($NaBH_4$) or lithium aluminium hydride ($LiAlH_4$) or H_2 in presence of Ni, Pd or Pt catalyst (Catalytic hydrogenation), aldehydes give primary alcohols, while ketones give secondary alcohols.

ii) Reduction to Hydrocarbons: a) Clemmensen reduction: *Aldehydes and ketones can be reduced to alkanes on treatment with zinc amalgam and concentrated hydrochloric acid.* During this reaction, the carbonyl group is reduced to $-CH_2-$ (methylene) group.

b)Wolff-Kishner reduction: *Carbonyl group can be reduced to methylene group, by treating with hydrazine followed by heating with sodium or potassium hydroxide in high boiling solvent like ethylene glycol.*

Oxidation: ***Aldehydes*** are easily *oxidised to carboxylic acids* on treatment with oxidising agents like nitric acid. *Mild oxidising* agents like CrO_3, Tollens' reagent and Fehlings' reagent can also oxidise aldehydes. $CH_3\text{-}CHO \xrightarrow{[O]} CH_3\text{-}COOH$

Ketones when oxidised using *strong oxidising* agents and at high temperatures, we get a mixture of carboxylic acids having lesser number of carbon atoms.



$$\overset{1}{R\text{—}CH_2}\text{—}\underset{\|\atop O}{\overset{2}{C}}\text{—}\overset{3}{CH_2}\text{-}R' \xrightarrow{[O]} \underbrace{R\text{-}COOH + R'\text{-}CH_2COOH}_{\text{(By cleavage of } C_1\text{-}C_2 \text{ bond)}} + \underbrace{R\text{-}CH_2COOH + R'\text{-}COOH}_{\text{(By cleavage of } C_2\text{-}C_3 \text{ bond)}}$$

Tollens' test: Tollen's reagent is *freshly prepared ammoniacal Silver nitrate.* Tollens' reagent, give a silver mirror with aldehydes.

Fehling's test: Fehling reagent is a *mixture of Fehling solution A and Fehling solution B.* Fehling solution A is aqueous copper sulphate and Fehling solution B is alkaline sodium potassium tartarate (Rochelle salt). On heating with Fehling's reagent, aldehyde gives a reddish brown precipitate of cuprous oxide (Cu_2O). *Aromatic aldehydes do not give this test.*

Aldol condensation Reaction: *Aldehydes and ketones having at least one α-hydrogen atom when treated with dilute alkali, we get β-hydroxy aldehydes (aldol) or β-hydroxy ketones (ketol) respectively. This is known as Aldol reaction.*

Cannizzaro Reaction: *Aldehydes having no α-hydrogen atom (e.g. HCHO, C_6H_5-CHO, CCl_3-CHO etc), when treated with Conc. Alkali (NaOH or KOH) undergo self oxidation and reduction (disproportionation) to form one molecule of the alcohol and one molecule of carboxylic acid salt. This reaction is called Cannizzaro reaction.* $2\ HCHO \xrightarrow{\text{Conc. KOH}} CH_3\text{-}OH + H\text{-}COOK$

CARBOXYLIC ACIDS

Preparation of Carboxylic acids: 1. From aldehydes: Aldehydes on oxidation with mild oxidising agents like CrO_3 or Tollen's reagent to give carboxylic acids. $CH_3\text{-}CHO \xrightarrow{[O]} CH_3\text{-}COOH$

2. From alkylbenzenes: Aromatic carboxylic acids can be prepared by vigorous oxidation of alkyl benzenes with chromic acid. The entire side chain is oxidised to the carboxyl group.

Chemical Reactions:

A) Reactions Involving Cleavage of O–H Bond:

1. **Acidity**: Carboxylic acids react with metals and liberate hydrogen gas.

$$2\ \text{R-COOH} + 2\ \text{Na} \longrightarrow 2\ \text{R-COONa} + H_2$$

Carboxylic acids react with sodium carbonates and *bicarbonates* and give brisk effervescence of carbon dioxide. $\text{R-COOH} + \text{NaHCO}_3 \longrightarrow \text{R-COONa} + H_2O + CO_2$

Due to the formation of *hydronium ion in water, carboxylic acids are acidic in nature.*

The acidity of a substance is expressed in terms of pKa value, greater the value of Ka, smaller will be pKa and stronger will be the acid.

Comparison of acidic character: *Carboxylic acids are weaker than mineral acids, but they are stronger acids than other organic compounds like alcohols and many simple phenols.*

The carboxylate ion formed is stabilised by equivalent *resonance structures*. Therefore carboxylate ion is more stable than phenoxide ion so it is more acidic.

Effect of substituents on the acidity of carboxylic acids: *Electron withdrawing groups increase the acidity. But electron donating groups decrease the acidity.*

B) Reactions Involving Cleavage of C–OH Bond

Reaction with ammonia: Carboxylic acids react with ammonia to give *ammonium salts* which on further heating at high temperature give *amides*.

Kolbe's electrolysis: An aqueous solution of potassium salt of carboxylic acid is electrolysed, we get *alkanes having twice the number of carbon atoms* that present in the alkyl group of the acid. This reaction is known as *Kolbe electrolysis.*

$$2\ CH_3\text{-COOH} + 2H_2O \xrightarrow{\text{electrolysis}} CH_3\text{-}CH_3 + 2KOH + H_2 + 2CO_2$$

C) Substitution Reactions in the Hydrocarbon Part:

1. Halogenation [HVZ Reaction]: Carboxylic acids having *α-hydrogen atom*, when treated with *halogen* in the presence of red phosphorus, we get α-halocarboxylic acids. This reaction is known as *Hell-Volhard-Zelinsky (HVZ)* reaction.

2. Electrophilic substitution reactions: The –COOH group is a *deactivating group and meta-directing*. So on electrophilic substitution reactions, we get *metaderivatives*.

- **Nitration:** Benzoic acids in presence of conc. Nitric acid/Conc. Sulphuric acid gives *m-Nitrobenzoic acids acid.*
- **Bromination:** Benzoic acids in presence of $Br_2/FeBr_3$ gives *m-Bromobenzoic acid.*
- *Carboxylic acids do not undergo Friedel-Crafts reactions because the carboxyl group is deactivating and the catalyst aluminium chloride (Lewis acid) gets bonded to the carboxyl group to form salts.*

Model questions:

1) Explain the following reactions: a) Rosenmund reduction b) Gatterman – Koch c) Clemmensen reduction d) Aldol condensation. (Hint: a) *Acid chlorides with H_2, b) benzene treat with CO, c) aldehydes and ketones with Zn/Hg and HCl, d) aldehydes and ketones having α-hydrogen atom with dilute alkali*)

2) Explain the acidity of carboxylic acids. (Hint: *carboxylic acids are acidic*)

3) What is Friedel-Crafts acylation reaction? (Hint: *benzene with acid chloride/anhydrous aluminium chloride*)

4) What are the products on the oxidation of primary alcohols and secondary alcohols? (Hint: *Primary gives aldehydes, secondary gives ketones*)

5) How carboxylic acids obtained from aldehydes? (Hint: *Aldehydes on oxidation*)

13. AMINES

Preparation of Amines:

1. **Reduction of nitro compounds**: Nitro compounds when reduced by passing hydrogen gas in the presence of finely divided nickel, palladium or platinum or by reduction with metals in acidic medium, we get amines.

2. Reduction of Nitriles: Nitriles on reduction with lithium aluminium hydride ($LiAlH_4$) or catalytic hydrogenation produce primary amines.

$$R\text{-}CN \xrightarrow{LiAlH4\ /\ ii)\ H2O} R\text{-}CH_2\text{-}NH_2$$

3. Reduction of amides: The amides on reduction with lithium aluminium hydride give amines.

$$R\text{-}CO\text{-}NH_2 \xrightarrow{i)\ LiAlH4\ /\ ii)\ H2O} R\text{-}CH_2\text{-}NH_2$$

4. Hoffmann bromamide degradation reaction: In this method, an amide is treated with Bromine and ethanolic solution of NaOH to give an amine.

$$CH_3\text{-}CO\text{-}NH_2 + Br_2 + 4\ NaOH \rightarrow CH_3\text{-}NH_2 + Na_2CO_3 + 2\ NaBr + 2\ H_2O$$

Chemical Reactions:

1. **Carbylamine reaction (isocyanide test):** Aliphatic and aromatic primary amines on heating with chloroform and alcoholic potassium hydroxide form foul smelling isocyanides or carbylamines. This reaction is known as **carbylamines reaction or isocyanide test** and is used as **a test for primary amines**. Secondary and tertiary amines do not give this reaction.

$$CH_3\text{-}NH_2 + CHCl_3 + 3\ KOH \rightarrow CH_3\text{-}NC + 3\ KCl + 3\ H_2O$$

2. Reaction with benzene sulphonyl chloride [Hinsberg's Test]: This test is used for the distinction of primary, secondary and tertiary amines and also for the separation of a mixture of amines. Benzenesulphonyl chloride ($C_6H_5SO_2Cl$) is known as Hinsberg's reagent.

a) Primary amines react with benzenesulphonyl chloride to form N-alkyl benzenesulphonamide, which is soluble in alkail.

b) Secondary amines react with benzene sulphonyl chloride to give N,N-dialkylbenzene sulphonamide, which is insoluble in alkali.

c) Tertiary amines do not react with benzenesulphonyl chloride. Nowadays, Benzenesulphonyl chloride is replaced by p-toluenesulphonyl chloride.

3. Electrophilic substitution Reactions: Bromination: Aniline reacts with bromine water at room temperature to give a white precipitate of 2,4,6- tribromoaniline.

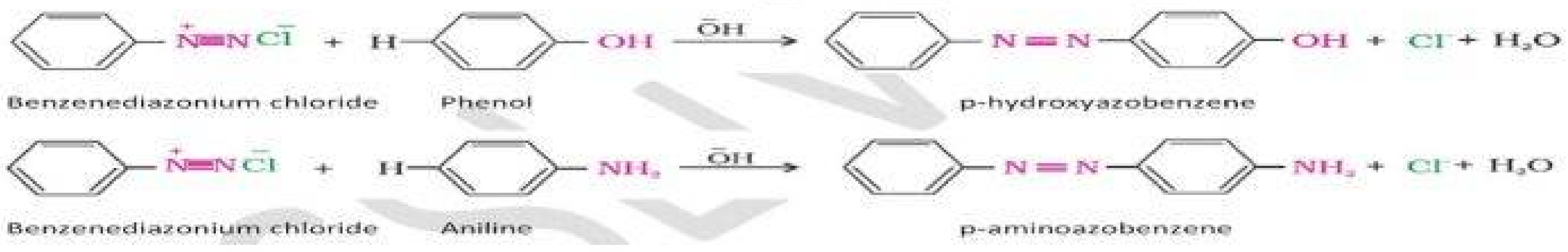
AROMATIC DIAZONIUM SALTS

Chemical reactions:

1. When a diazonium salt is treated with hydrogen halide in presence of cuprous halide, we get halobenzene. This reaction is called **Sandmeyer's reaction**. For the preparation of cyanobenzene, benzenediazonium salt is treated with KCN in presence of cuprous cyanide.

If cuprous halide is replaced by copper powder, the reaction is called **Gattemann's reaction**.

2. Reactions involving retention of diazo group: Coupling reactions: When benzene diazonium chloride is treated with phenol or aniline, the para position of is coupled with the diazonium salt to form p-hydroxyazobenzene or p-aminoazobenzene. This type of reaction is known as **coupling reaction**. This is an example of electrophilic substitution reaction.

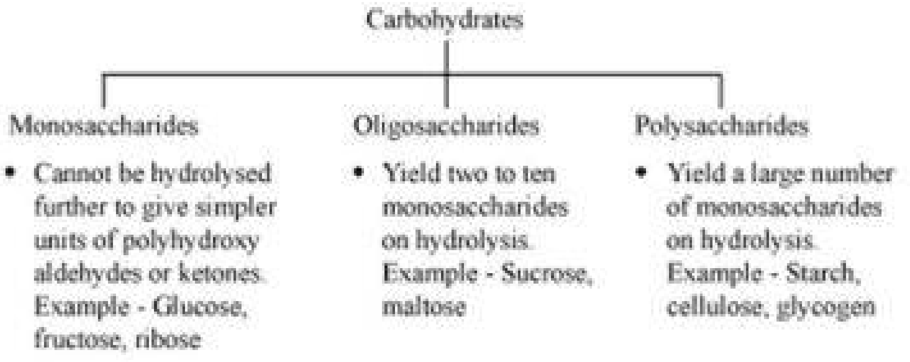


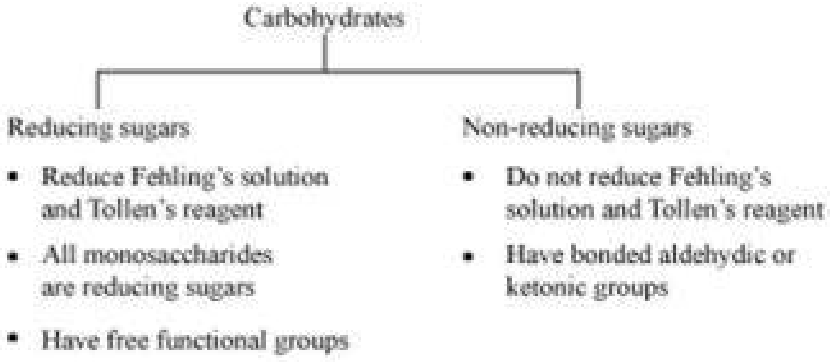
Model questions:

1. Explain the reaction of primary, secondary and tertiary amines with Hinsberg's reagent. (Hint*: Benzenesulphonylchloride*)
2. The reaction in which an amide is converted into a primary amine by the action of Br_2 and alcoholic NaOH is known as ……………..
3. What is Sandmeyer's reaction? (Hint: *Benzenediazonium chloride with hydrogen halide in presence of cuprous halide*)
4. Describe a chemical reaction given only by primary amines. (Hint: *Carbylamine test*)
5. What is coupling reaction? (Hint: *The para position of benzene ring is coupled with the diazonium salt*)

14. BIOMOLECULES

Classification of Carbohydrates Classification





Glucose

- **Preparation of glucose**
  - By boiling sucrose with dilute HCl or H_2SO_4 in alcoholic solution

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

  - By boiling starch with dilute H_2SO_4, at 393 K, under pressure

$$\underset{\text{Starch or cellulose}}{(C_6H_{10}O_5)_n} + nH_2O \xrightarrow[393K,\,2-3\text{atoms}]{H^+} \underset{\text{Glucose}}{nC_6H_{12}O_6}$$

Disaccharides

Glycosidic linkage − Linkage between two monosaccharide units through oxygen atom

- **Sucrose**
  - Hydrolysis of sucrose:

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

  - The product formed on the hydrolysis of sucrose is called *invert sugar* as the sign of rotation changes from dextro (+) of sucrose to laevo (−) of the product.
  - Non-reducing sugar

Polysaccharides

They mainly act as food storage or structural materials.

- **Starch**
  - Main storage-polysaccharide of plants
  - *Polymer of α-glucose*; consists of two components − amylose and amylopectin
- **Cellulose**
  - Predominant constituent of the cell wall of plant cells.
  - Straight-chain polysaccharide, *polymer of β-D-Glucose*
- **Glycogen**
  - Storage-polysaccharide in animal body
  - Also known as animal starch because its structure is similar to amylopectin.

Proteins

Proteins are polymers of α – amino acids joined through peptide linkage (-CONH- bond)

Denaturation of Proteins: When a protein in its native form, is subjected to physical change like change in temperature or chemical change like change in pH, the hydrogen bonds are disturbed. Due to this, protein loses its biological activity. This is called *denaturation of protein.*

- During denaturation 2° and 3° structures are destroyed but 1° structure remains intact

  Example – Coagulation of egg white on boiling, curdling of milk

Nucleic Acids

- Two types:
  - Deoxyribonucleic acid (DNA)
  - Ribonucleic acid (RNA)
- Chemical composition of nucleic acids:
  - Nucleic acid contains a pentose sugar, phosphoric acid and a base (heterocyclic compound containing nitrogen).
  - In DNA, sugar is β-D-2-deoxyribose; in RNA, sugar is β-D-ribose
  - Bases in DNA: Adenine (A), guanine (G), cytosine (C) and thymine (T)
  - Bases in RNA: Adenine (A), guanine (G), cytosine (C) and uracil (U)

The pentose sugar combines with the base to form nucleoside, which combines with the phosphoric acid group to form nucleotide. The nucleotide units combine to form nucleic acid.

Nucleotides are joined together by phosphodiester linkage

Model questions:

1. Which of the following is a polysaccharide?
   i) Maltose ii) sucrose iii) fructose iv) cellulose
2. Write a method to prepare Glucose from Starch. Write the chemical equation of the reaction.
3. Write one example each of monosaccharide and oligosaccharide.

4. Write any two methods of preparation of glucose
5. What is invert sugar ?
6. What is the basic structural difference between Starch and Cellulose?

7. What are polysaccharides? Give two examples of polysaccharides?
8. What is a peptide linkage?
9. What is denaturation of proteins?
10. Write any three differences of RNA and DNA
11. Differentiate between nucleoside and nucleotide
12. Write the names of linkages and monomeric units in the following class of biomolecules.

    i) Starch ii) Protein iii) Nucleic acid

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15. POLYMERS

Classification of Polymers:

I) **Classification Based on Source**:

i) **Natural polymers**: These polymers are found in nature. Examples are proteins, cellulose, starch, natural fibres and natural rubber.

ii) **Semi-synthetic polymers**: Cellulose derivatives such as cellulose acetate (rayon) and cellulose nitrate are examples.

iii) **Synthetic polymers**: These are man-made polymers. E.g. plastics like polythene, poly styrene, PVC etc. Synthetic fibres like nylon 6,6 and synthetic rubbers like Buna – S.

II) **Classification Based on Structure of Polymers**:

i) **Linear polymers**: They contain long and straight chains of polymers. E.g. high density polythene, polyvinyl chloride, etc

ii) **Branched chain polymers**: These polymers contain linear chains having some branches. E.g. low density polythene (LDPE).

iii) **Cross linked or Network polymers**: These are usually formed from bi-functional and tri-functional monomers and contain strong covalent bonds between various linear polymer chains. E.g. bakelite, melamine, etc.

III) **Classification Based on Mode of Polymerisation**:

i) **Addition polymers**: *Polymers formed by addition polymerisation reaction.* Here the monomer molecules should possess double or triple bonds. Addition polymers are now known as chain growth polymers. E.g. polythene, polypropene, polystyrene, polyvinyl chloride etc.

ii) **Condensation polymers**: *These are polymers formed by condensation polymerisation reaction, where elimination of small molecules such as water, alcohol, hydrogen chloride, etc take place.* Here the monomers should be bifunctional or polyfunctional. Condensation polymers are now known as step growth polymers. E.g. Nylon- 6,6, Nylon- 6, terylene, glyptal etc.

IV) **Classification based on the type of monomers**:

i) **Homopolymers**: These are polymers containing *only one type of monomer unit*. E.g.: polythene, polystyrene. polypropene etc.

ii) **Copolymers**: These are polymers containing *different types of monomer units*. E.g.: Polyesters like glyptal, terylene etc. poly amides like Nylon-6, Nylon-6,6 etc.

V) **Classification based on the Molecular Forces**: i) **Elastomers**: *These are rubber like solids with elastic properties.* Here the polymer chains held together by the weakest intermolecular forces (van der Waal's force). E.g. buna-S, buna-N, neoprene, etc.

ii) **Fibres**: *Fibres are the thread forming solids which possess high tensile strength and high modulus.* Here the polymer chains are held together by strong intermolecular force they have close packed structure and are crystalline in nature.

iii) **Thermoplastic polymers**: *These are the linear or slightly branched long chain molecules repeatedly softening on heating and hardening on cooling*. Eg. polythene, polystyrene, polyvinyls, etc.

iv) **Thermosetting polymers**: *These polymers are cross linked they undergo extensive cross link chemical change on heating*. Eg. Terylene.

Addition Polymerisation or Chain Growth Polymerisation:

1.Teflon: It is manufactured by heating *tetrafluoroethene* with a free radical or persulphate catalyst at high pressures. It is chemically inert and resistant to attack by corrosive reagents.

2. Polythene: Polymerisation of ethene.

a) **Low density polythene (LDPE).** Addition polymerisation of of ethane under high pressure, temperature and catalyst.

b) **High density polythene (HDPE)**. Addition polymerisation of ethene in presence of tertraethylaluminium and titaniumtetrachloride.

Condensation Polymerisation or Step Growth polymerization:

1. **Polyamides**: a) **Nylon 6,6** is prepared by the condensation polymerisation of *hexamethylenediamine with adipic acid* under high pressure and at high temperature. It is used in making sheets, bristles for brushes and in textile industry.

b) **Nylon 6** is obtained by *heating caprolactum* with water at a high temperature. It is used for the manufacture of tyre cords, fabrics and ropes.

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

Vulcanisation of rubber: *To improve the physical properties of natural rubber, it is heated with sulphur and an appropriate additive at a temperature of 373 to 415 K.* This process is called vulcanisation. On vulcanisation, sulphur forms cross links between the different poly isoprene units and thus the rubber gets stiffened.

Biodegradable Polymers: Polymers which *undergo degradation by microorganisms.*

1. **Poly β-hydroxybutyrate – co-β-hydroxy valerate (PHBV):** It is obtained by the copolymerisation of 3- hydroxybutanoic acid (β-hydroxy butyric acid) and 3 - hydroxypentanoic acid (β-hydroxy valeric acid). Used in packaging orthopaedic devices.
2. **Nylon 2-nylon 6:** A biodegradable polyamide of gycine and aminocaproic acid.

Model Questions:

1) Classify the polymers based on addition and condensation polymerization, Terylene, PVC, bakelite, polythene. (Hint: *Addition – PVC, polythene. Condensation - Terylene, bakelite*)
2) What is vulcanization? (Hint: *Heating with sulphur*)
3) What are biodegradable polymers? (Hint: *Degradation by microorganisms*)
4) Give the name of monomers of i) Nylon 6,6 ii) Dacron
5) What is the difference between addition polymerization and condensation polymerization?(Hint: *Addition polymerization- monomer molecules should possess double or triple bonds. Condensation polymerization - monomers should be bifunctional or polyfunctional*)

16. CHEMISTRY IN EVERYDAY LIFE

Antacid: The chemicals used to reduce the acidity in stomach are called antacids.

Eg. $NaHCO_3$, metal hydroxides, ranitidine etc.

Neurologically Active Drugs:

Tranquilizers and analgesics are neurologically active drugs.

Tranquilizers are a class of chemical compounds used for the treatment of stress and several mental diseases by inducing a sense of well-being. They are essential component of **sleeping pills**

Eg. Iproniazid, phenelzine (nardil), chlordiazepoxide, meprobamate, Equanil, derivatives of barbituric acid like veronal, amytal, nembutal, luminal and seconal.

Iproniazid, phenelzineare used as anti-depressant drugs.

Analgesics : They reduce pain &They are classified into **TWO**:

(i) Non-Narcotic Analgesics	**(ii) Narcotic Analgesics**
They give immediate relief from pain and fever and prevent platelet coagulation	They help to relieve the feeling of pain. These are sleep inducing analgesics
They remove the cause of pain.	They do not remove the cause of pain.
Eg. aspirin, paracetamol, novalgin etc	E.g. morphine, heroin, codeine etc.

Anti microbials: Eg. **Antiseptics and disinfectants**

Antiseptics	**Disinfectants**
Chemicals which either kill or prevent the growth of **harmful** microorganisms	These are chemicals which kill the microorganisms and are **harmful to the living tissues**
It can be applied to the living tissues such as wounds, cuts, ulcers and diseased skin surfaces	It can be applied to floors, drainage system, instruments,
Eg. 0.2% phenol, tincture of iodine, dettol etc.	Eg. 1% phenol , Cl_2 , SO_2 etc.

Note: Some substance can act both as an antiseptic and disinfectant at different concentrations. For example 0.2% solution of phenol is an antiseptic, while its one percent solution is disinfectant.

Model questions:

Q 1. Give an example for a Non-narcotic analgesic.(**Hint: refer above notes for the answer)**

Q 2. Differentiate between antiseptics and antibiotics. **(Hint: refer above notes for the answer)**

Q 3. Tranquilizers and analgesics are neurologically active drugs.

a) What are tranquilizers? Give one example. **(Hint: refer above notes for the answer)**

b) What are analgesics? Give one example. **(Hint: refer above notes for the answer)**

Q 4. Antiseptics, disinfectants and antibiotics are antimicrobial drugs.

a) Write one similarity between antiseptics and disinfectants?

b) Write one difference between antiseptics and disinfectants?

(Hint: a- Both are chemicals which either kill or prevent the growth of microorganisms).