CLASS XII CHEMISTRY

INDEX

CLASS XII (2023-24) (THEORY)

Time: 3 Hours **70 Marks**

S.No.	Title	No. of Periods	Marks
1.	Solutions	10	7
2.	Electrochemistry	12	9
3.	Chemical Kinetics	10	7
4.	d -and f -Block Elements	12	7
5.	Coordination Compounds	12	7
6.	Haloalkanes and Haloarenes	10	6
7.	Alcohols, Phenols and Ethers	10	6
8.	Aldehydes, Ketones and Carboxylic Acids	10	8
9.	Amines	10	6
10.	Biomolecules	12	7
	Total		**70**

SYLLABUS

Unit I: Solutions (10 Periods)

Types of solutions, expression of concentration of solutions of solids in liquids, solubility of gases in liquids, solid solutions, Raoult's law, colligative properties - relative lowering of vapour pressure, elevation of boiling point, depression of freezing point, osmotic pressure, determination of molecular masses using colligative properties, abnormal molecular mass, Van't Hoff factor.

Unit II: Electrochemistry (12 Periods)

Redox reactions, EMF of a cell, standard electrode potential, Nernst equation and its application to chemical cells, Relation between Gibbs energy change and EMF of a cell, conductance in electrolytic solutions, specific and molar conductivity, variations of conductivity with concentration, Kohlrausch's Law, electrolysis and law of electrolysis (elementary idea), dry cell-electrolytic cells and Galvanic cells, lead accumulator, fuel cells, corrosion.

Unit III: Chemical Kinetics (10 Periods)

Rate of a reaction (Average and instantaneous), factors affecting rate of reaction: concentration, temperature, catalyst; order and molecularity of a reaction, rate law and specific rate constant, integrated rate equations and half-life (only for zero and first order reactions), concept of collision theory (elementary idea, no mathematical treatment), activation energy, Arrhenius equation.

Unit IV: d and f Block Elements (12 Periods)

General introduction, electronic configuration, occurrence and characteristics of transition metals, general trends in properties of the first-row transition metals – metallic character, ionization enthalpy, oxidation states, ionic radii, colour, catalytic property, magnetic properties, interstitial compounds, alloy formation, preparation and properties of $K_2Cr_2O_7$ and $KMnO_4$. Lanthanoids - Electronic configuration, oxidation states, chemical reactivity and lanthanoid contraction and its consequences. Actinoids - Electronic configuration, oxidation states and comparison with lanthanoids.

Unit V: Coordination Compounds (12 Periods)

Coordination compounds - Introduction, ligands, coordination number, colour, magnetic properties and shapes, IUPAC nomenclature of mononuclear coordination compounds. Bonding, Werner's theory, VBT, and CFT; structure and stereoisomerism, importance of coordination compounds (in qualitative analysis, extraction of metals and biological system).

Unit VI: Haloalkanes and Haloarenes. (10 Periods)

Haloalkanes: Nomenclature, nature of C–X bond, physical and chemical properties, optical rotation mechanism of substitution reactions. Haloarenes: Nature of C–X bond, substitution reactions (Directive influence of halogen in monosubstituted compounds only). Uses and environmental effects of - dichloromethane, trichloromethane, tetrachloromethane, iodoform, freons, DDT.

Unit VII: Alcohols, Phenols and Ethers (10 Periods)

Alcohols: Nomenclature, methods of preparation, physical and chemical properties (of primary alcohols only), identification of primary, secondary and tertiary alcohols, mechanism of dehydration, uses with special reference to methanol and ethanol. Phenols: Nomenclature, methods of preparation, physical and chemical properties, acidic nature of phenol, electrophillic substitution reactions, uses of phenols. Ethers: Nomenclature, methods of preparation, physical and chemical properties, uses.

Unit VIII: Aldehydes, Ketones and Carboxylic Acids (10 Periods)

Aldehydes and Ketones: Nomenclature, nature of carbonyl group, methods of preparation, physical and chemical properties, mechanism of nucleophilic addition, reactivity of alpha hydrogen in aldehydes, uses. Carboxylic Acids: Nomenclature, acidic nature, methods of preparation, physical and chemical properties; uses.

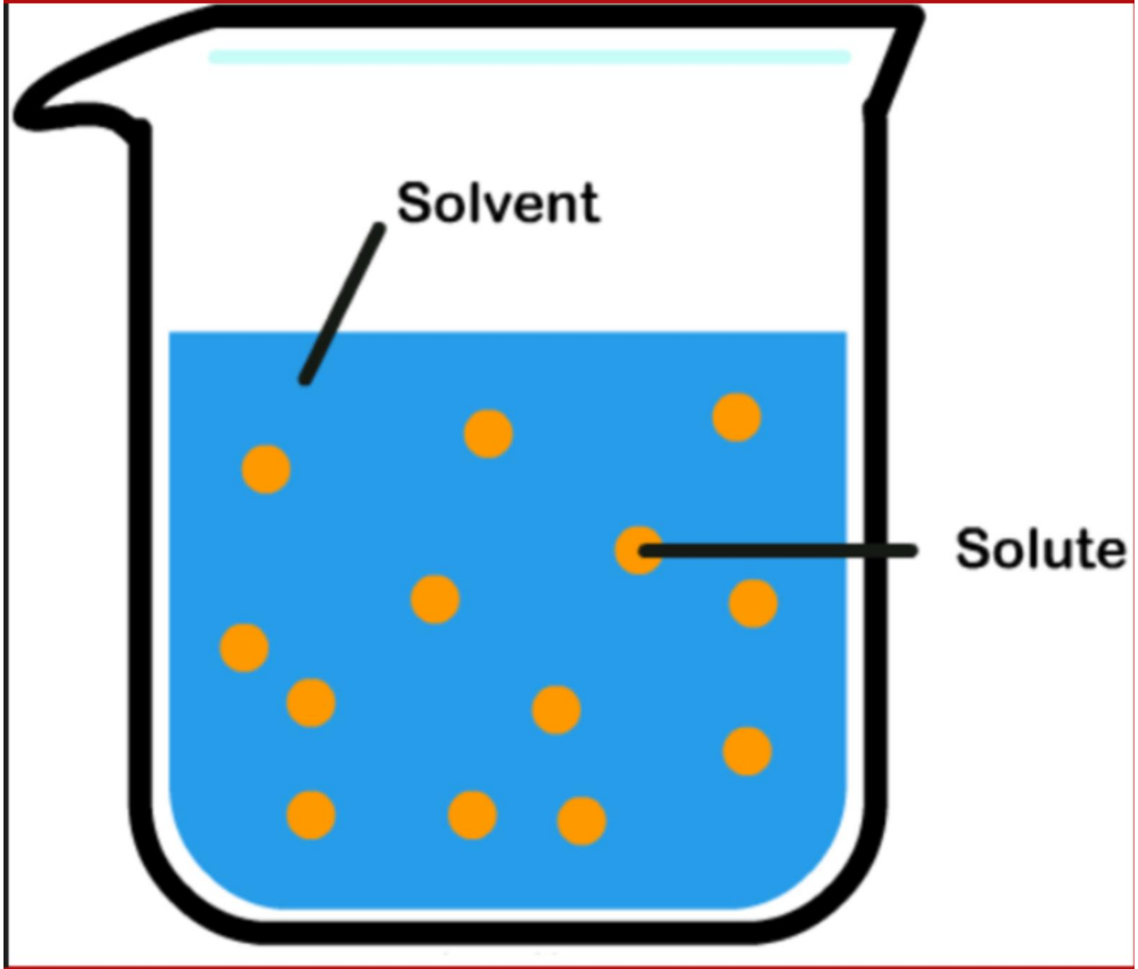
Unit IX: Amines (10 Periods)

Amines: Nomenclature, classification, structure, methods of preparation, physical and chemical properties, uses, identification of primary, secondary and tertiary amines. Diazonium salts: Preparation, chemical reactions and importance in synthetic organic chemistry.

Unit X: Biomolecules (12 Periods)

Carbohydrates - Classification (aldoses and ketoses), monosaccharides (glucose and fructose), D-L configuration oligosaccharides (sucrose, lactose, maltose), polysaccharides (starch, cellulose, glycogen); Importance of carbohydrates. Proteins -Elementary idea of - amino acids, peptide bond, polypeptides, proteins, structure of proteins - primary, secondary, tertiary structure and quaternary structures (qualitative idea only), denaturation of proteins; enzymes. Hormones - Elementary idea excluding structure. Vitamins - Classification and functions. Nucleic Acids: DNA and RNA.

UNIT I: SOLUTIONS



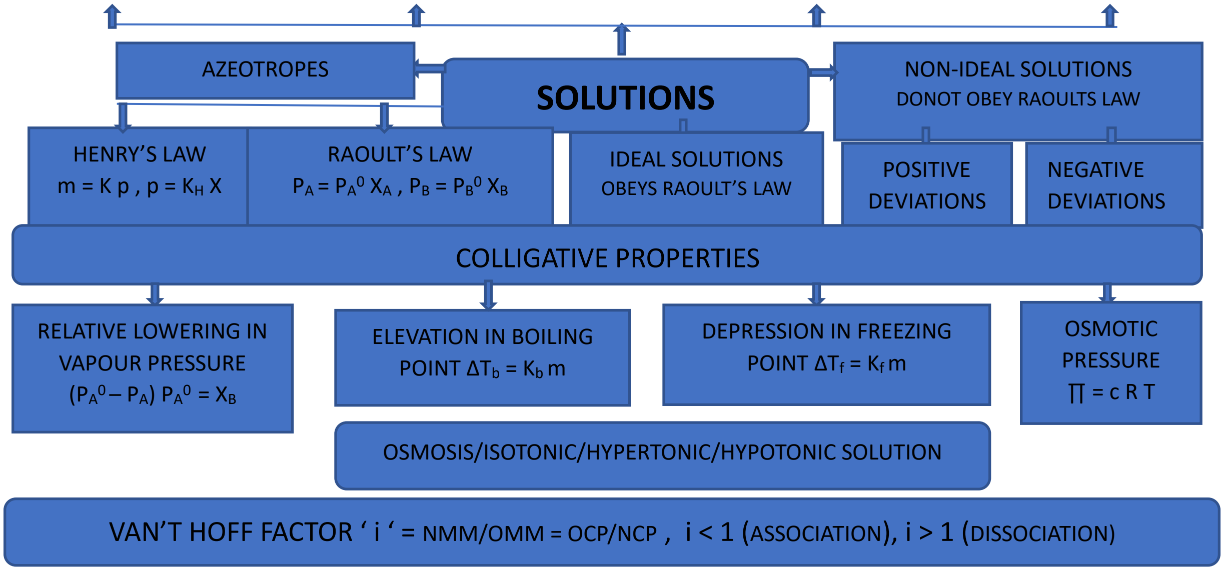
SOLUTE + SOLVENT = SOLUTION

MOLARITY (M) = n_B x 1000/V(ml)

MOLALITY (m) = n_B x 1000/w(g)

MOLE FRACTION (x) $x_B = n_B / n_A + n_B$

NORMALITY (N) = Ngeqv x 1000/V(ml)



A **solution** is a homogeneous mixture of two or more chemically non-reacting substances. Solutions are the homogeneous mixtures of two or more than two components. A solution having two components is called a **binary solution.** It includes **solute and solvent**.

A solution may be classified as **solid, liquid or a gaseous solution**. **Types of Solutions:**

Type of solution	**Solute**	**Solvent**	**Common examples**
Solid solutions	Solid	Solid	Copper dissolved in gold
	Liquid	Solid	Amalgam of mercury with sodium
	Gas	Solid	Solution of hydrogen in palladium
Liquid Solutions	Solid	Liquid	Glucose dissolved in water
	Liquid	Liquid	Ethanol dissolved in water
	Gas	Liquid	Oxygen dissolved in water

Gaseous Solution	Solid	Gas	Camphor in nitrogen gas
	Liquid	Gas	Chloroform mixed with nitrogen gas
	Gas	Gas	Mixture of oxygen and nitrogen gases

Concentration: It is the amount of solute in given amount of solution.

Mass by volume percentage (w/v): Mass of the solute dissolved in 100 mL of solution.

$$\text{Mass \% of component} = \frac{\text{Mass of the component in the solution}}{\text{Total mass of the solution}} \times 100$$

Molality (m): It is the number of moles of solute present in 1kg of solvent.

$$\text{Molality (m)} = \frac{\text{Mass of solute (w)}}{\text{Molar mass of solute} \times \text{Mass of solvent (g)}} \times 1000$$

Molarity (M): It is the number of moles of solute present in 1L of solution.

$$\text{Molarity (M)} = \frac{\text{Mass of solute (w)}}{\text{Molar mass of solute} \times \text{Volume of solution (ml)}} \times 1000$$

Normality: It is the number of gram equivalent of solute dissolved per litre of solution.

$$\text{Normality (N)} = \frac{\text{No. of gm. equiv. of solute}}{\text{Volume of solution (ml)}} \times 1000$$

Saturated solution: It is a solution in which no more solute can be dissolved at the same temperature and pressure. If dissolution process is an endothermic process, solubility increases with increase in temperature.
If dissolution process is an exothermic process, solubility decreases with increase in temperature.

Solubility is defined as the amount of solute in a saturated solution per 100g of a solvent. The **solubility of a gas in a liquid** depends upon:
(a) the nature of the gas and the nature of the liquid,
(b) the temperature of the system, and
(c) the pressure of the gas.

The **effect of pressure on the solubility of a gas in a liquid** is governed by **Henry's Law**: It states that the solubility of a gas in a liquid at a given temperature in directly proportional to the partial pressure of the gas

$$p = K_H x$$

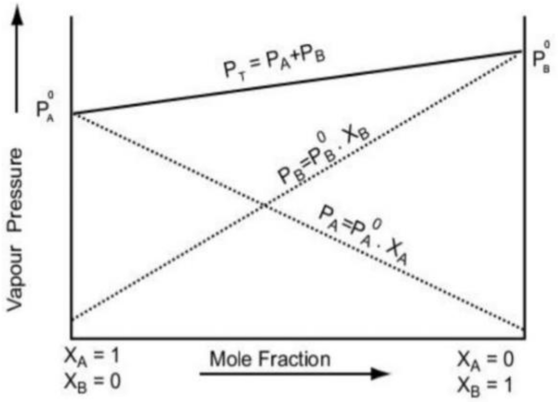
Where p is the partial pressure of the gas; and x is the mole fraction of the gas in the solution and K_H is Henry's Law constant.

The **vapour pressure of a liquid** is the pressure exerted by its vapour when it is in dynamic equilibrium with its liquid, in a closed container.

Raoult's Law, the vapour pressure of a solution containing a non-volatile solute is directly proportional to the mole fraction of the solvent (X_A). The proportionality constant being the vapour pressure of the pure solvent,

$P_A \alpha X_A$

$P_A = P_A^\circ X_A$



$P_A = P_A^\circ X_A$

$P_B = P_B^\circ X_B$

$P_A + P_B = P_A^0 X_A + P_B^0 X_B$

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

$= P_A^0 - P_A^0 X_B + P_B^0 X_B$

$P_{total} = P_A^0 + (P_B^0 - P_A^0) X_B$

The binary liquid in liquid solutions can be classified into two types; ideal and non-ideal solutions.

Ideal Solution: An ideal solution is a solution where the intermolecular interactions between solute-solute (A-A) and solvent-solvent (B-B) are similar to the interaction between solute-solvent (A-B). An ideal solution fulfils the following criteria:

- It obeys Raoult's law for all the concentration and temperature ranges. This states that the partial vapour pressure of each component is proportional to the mole fraction of the component in a solution at a given temperature.
- The enthalpy of mixing is zero, i.e., $\Delta H_{mix} = 0$. It means that no heat is absorbed or released.
- The volume of mixing is zero, $\Delta V_{mix} = 0$. It means that the volume of the solution is equal to the sum of the volume of components.

The ideal solution is possible with components of the same size and polarity. There is no association, dissociation or reaction taking place between components. A perfect ideal solution is rare but some solutions are near to the ideal solution. Examples are Benzene and toluene, hexane and heptane, Bromoethane and Chloroethane, Chlorobenzene and bromobenzene, etc.

Non-ideal Solution:

1. (i) When a solution does not obey Raoult's law for all the concentration and temperature ranges it is known as a non-ideal solution. A non-ideal solution may show positive or negative deviation from Raoult's law.
2. (ii) $\Delta H_{mix} \neq 0$
3. (iii) $\Delta V_{mix} \neq 0$

(a) Non-ideal solution showing positive deviation

Here the total vapour pressure is higher than that calculated from Raoult's equation. The interaction between solute-solvent (A-B) is weaker than those of pure components (A-A or B-B). The ΔH_{mix} and ΔV_{mix} are positive. E.g., ethanol and acetone, carbon disulphide and acetone, acetone and benzene, etc.

(b) Non-ideal solution showing negative deviation

Here the total vapour pressure is lower than that calculated from Raoult's equation. The interaction between solute-solvent (A-B) is stronger than those of pure components (A-A or B-B). The ΔH_{mix} and ΔV_{mix} are negative. E.g., phenol and aniline, chloroform and acetone, etc.

Difference between Ideal and Non-ideal Solution

S.No.	**Ideal Solution**	**Non-ideal Solution**
1	They obey Raoult's law	They do not obey Raoult's law
2	Intermolecular interaction between solute and solvent is the same as that of pure components	Intermolecular interaction between solute and solvent is weaker or stronger than that of between pure components
3	The total vapour pressure is the same as predicted from Raoult's law	The total vapour pressure increases or decreases from the predicted value according to Raoult's law
4	No heat is released or absorbed so the enthalpy of mixing is zero, $\Delta H_{mix} = 0$	Heat is either absorbed or released so the enthalpy of mixing is either positive or negative, $\Delta H_{mix} \neq 0$
5	The total volume is equal to the sum of the volume of components (solute and solvent) so the volume of mixing is zero, $\Delta V_{mix} = 0$	The volume of mixing is not zero, $\Delta V_{mix} \neq 0$. There is either expansion or contraction.
6	Components can be separated by fractional distillation	Components can't be separated in the pure form by fractional distillation
7	Does not form an azeotrope	Forms azeotrope mixture

8	Examples: Benzene and toluene, hexane and heptane, etc. All the dilute solutions nearly behave as an ideal solution	Examples: Ethanol and acetone, carbon disulphide and acetone, phenol and aniline, chloroform and acetone, etc.

Colligative properties of solutions are those properties which depend only upon the number of solute particles in the solution and not on their nature.

Such properties are:

(a) Relative lowering in vapour pressure,

(b) Elevation of boiling point,

(c) Depression of freezing point and

(d) Osmotic pressure.

(a)Relative lowering in vapour pressure: According to Raoult's Law, the relative lowering of vapour pressure of a solution is equal to the mole fraction of the solute.

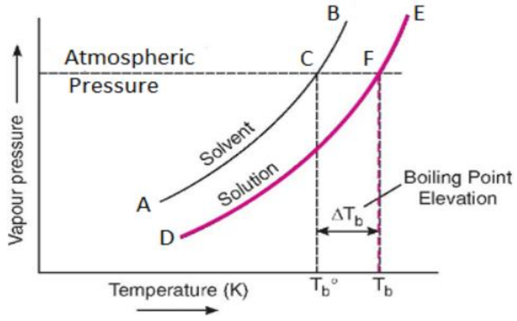
$(P_A^0 - P_A)/P_A^0 = X_B = n_B / (n_A + n_B)$

$(P_A^0 - P_A)/P_A^0 = (w_B/M_B)/W_A/MA$

$$M_B = \frac{w_B M_A}{w_A (P_A^0 - P_A)/P_A^0)}$$

(b) Elevation of boiling point: Boiling point of a liquid is the temperature at which its vapour pressure becomes equal to the atmospheric pressure. The boiling point of the pure solvent is T_b^0 while that of the solution is T_b. Since, T_b is greater than T_b^0, there is an elevation or increase in boiling temperature of the solution as compared to that of solvent. The elevation in boiling point, ΔT_b may be expressed as:

$\Delta T_b = T_b - T_b^0$



The **elevation in boiling point** is found to be proportional to the molality of the solution.

$\Delta T_b \alpha m$

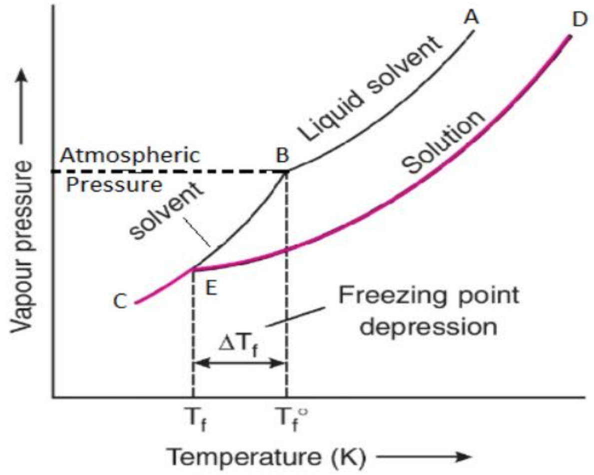
$\Delta T_b = K_b m$, where ΔT_b is the elevation in boiling point, 'm' is the molality and K_b is the Molal elevation constant

$\Delta T_b = K_b m = (K_b x w_B x 1000)/M_B x w_A$

$$M_B = \frac{(K_b \text{ x } w_B \text{ x } 1000)}{\Delta T_b \text{ x } w_A}$$

(c) Depression of freezing point: Freezing point is the temperature at which the solid and the liquid states of the substance have the same vapour pressure. Freezing point temperature of puree solvent is T_f^0 and freezing point temperature of the solution is T_f. The T_f is less than T_f^0. This shows that the freezing temperature of the solution is less than that of pure solvent and the depression in freezing temperature

(ΔT_f) is given as: $\Delta T_f = T_f^0 - T_f$



The **depression in freezing point** (ΔT_f) is proportional to the molality of the solution.

$\Delta T_f \ \alpha \ m$

$\Delta T_f = K_f m$ Where K_f is molal depression constant (freezing point depression constant).

$\Delta T_f = K_f m = (K_f \text{ x } w_B \text{ x } 1000)/M_B \text{ x } w_A$

$$M_B = \frac{(K_f \text{ x } w_B \text{ x } 1000)}{\Delta T_f \text{ x } w_A}$$

Osmosis: The spontaneous flow of solvent molecules from a dilute solution into a concentrated solution when the two are separated by a perfect semipermeable membrane.

(d) Osmotic pressure (π) is the pressure which must be applied to the solution side (more concentrated solution) to just prevent the passage of pure solvent into it through a semipermeable membrane. According to Van't Hoff equation,

$\pi = cRT = (n_B/V)\ RT = (w_B/M_B V)\ RT$

$$M_B = \frac{w_B\ RT}{\pi\ V}$$

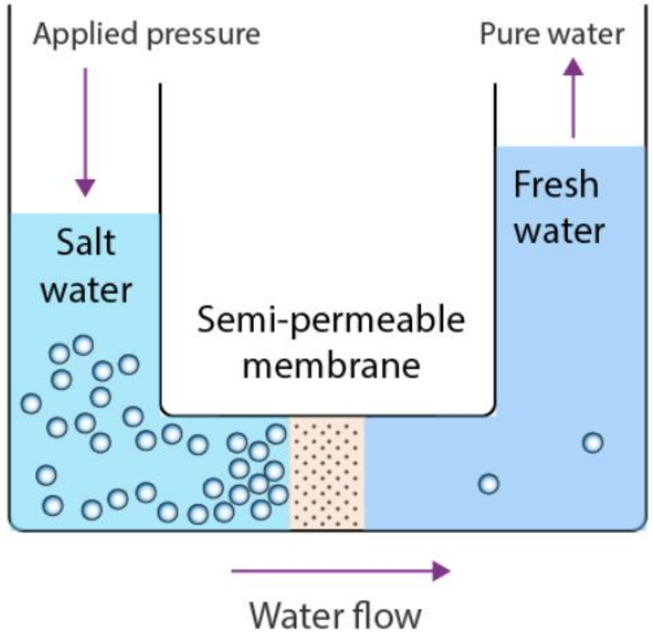
where n is the osmotic pressure of the solution,

C is the concentration of solution, n_B is the number of moles of solute, M_B is the molar mass of the solute, V is the volume of the solution in liters,

R is the gas constant, and T is the temperature on the Kelvin scale.

Reverse Osmosis:

The direction of osmosis can be reversed if a pressure larger than the osmotic pressure is applied to the solution side. That is, now the pure solvent flows out of the solution through the semi permeable membrane. This phenomenon is called reverse osmosis



Isotonic solutions are those solutions which have the same osmotic pressure. Also, they have same molar concentration.
For isotonic solutions, $\pi_1 = \pi_2$ Also, $C_1 = C_2$
Hypertonic solutions if a solution has more osmotic pressure than some other solutions.
Hypotonic solutions if a solution has less osmotic pressure than some other solutions.

Abnormal molecular mass: A molar mass that is either lower or higher than the expected or normal value is called as abnormal molar mass.

Van't Hoff factor: In 1880 Van't Hoff introduced a factor *i*, known as the Van't Hoff factor, to account for the extent of dissociation or association. This factor *i* is defined as:

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

$$= \text{Observed colligative property} / \text{Calculated colligative property}$$

$$i = \frac{\text{Total number of moles of particles after association/dissociation}}{\text{Number of moles of particles before association/dissociation}}$$

Here abnormal molar mass is the experimentally determined molar mass and calculated colligative properties are obtained by assuming that the non-volatile solute is neither associated nor dissociated.
In case of association, value of *i* is less than unity while for dissociation it is greater than unity. For example, the value of *i* for aqueous KCl solution is close to 2, while the value for ethanoic acid in benzene is nearly 0.5.
Inclusion of Van't Hoff factor modifies the equations for colligative properties as follows:

Relative lowering of vapour pressure of solvent,
$(P_A^0 - P_A)/P_A^0 = iX_B$
Elevation of Boiling point, $\Delta T_b = i\, K_b$ m
Depression of Freezing point, $\Delta T_f = i\, K_f$ m
Osmotic pressure of solution, $\pi = i\, n_B R\, T / V$

Values of *i* for KCl, NaCl, $MgSO_4$ and K_2SO_4

Salt	Van't Hoff Factor *i* for complete dissociation of solute
KCl	2
NaCl	2
$MgSO_4$	2
K_2SO_4	3

Assignment:
1. The atmospheric pollution is generally measured in the units of
(a) mass percentage
(b) volume percentage
(c) volume fraction
(d) ppm

Ans. (d) ppm

2. Temperature dependent term among the following is –
(a) Molality
(b) Molarity
(c) Mole fraction
(d) Weight percentage

Ans. (b) Molarity

3. The law which indicates the relationship between solubility of a gas in liquid and pressure is
(a) Raoult's law
(b) Henry's law
(c) Lowering of vapour pressure
(d) Van't Hoff law

Ans. (b) Henry's law

4. Partial pressure of a solution component is directly proportional to its mole fraction. This is known as

(a) Henry’s law
(b) Raoult’s law
(c) Distribution law
(d) Ostwald’s dilution law

Ans. (b) Raoult’s law

5. Which of the following solutions shows positive deviation from Raoult’s law?
(a) Acetone + Aniline
(b) Acetone + Ethanol
(c) Water + Nitric acid
(d) Chloroform + Benzene
Ans. (b) Acetone + Ethanol

6. The system that forms maximum boiling azeotrope is
(a) Acetone-chloroform
(b) ethanol-acetone
(c) n-hexane-n-heptane
(d) carbon disulphide-acetone

Ans. (a) Acetone-chloroform

7. A plant cell shrinks when it is kept in a
(a) hypotonic solution
(b) hypertonic solution
(c) isotonic solution
(d) pure water

Ans. (b) hypertonic solution

8. The osmotic pressure of a solution can be increased by
(a) increasing the volume
(b) increasing the number of solute molecules
(c) decreasing the temperature
(d) removing semipermeable membrane

Ans. (b) increasing the number of solute molecules

9. Sprinkling of salt helps in clearing the snow-covered roads in hills. The phenomenon involved in the process is
(a) lowering in vapour pressure of snow
(b) depression in freezing point of snow
(c) melting of ice due to increase in temperature by putting salt
(d) increase in freezing point of snow

Ans. (b) depression in freezing point of snow

10. The Van’t Hoff factor [i] for a dilute aqueous solution of the strong electrolyte barium hydroxide is?
(a) 0
(b) 1
(c) 2
(d) 3

Ans. (d) 3

Q11. If 1.202 g mL^{-1} is the density of 20% aqueous KI, determine the following:
(a) Molality of KI
(b) Molarity of KI
(c) Mole fraction of KI
Ans. 20% solution of KI means 20g of KI are present in 100g of solution or 80g of water.
(a) Molar mass of KI = 166
Moles of KI = 20/166 = 0.120
Molality = 0.120 x 1000 /80 = 1.5 m
(b) Volume of solution = 100/1.202 = 83.19 ml
Molarity = 0.120 x 1000 / 83.19 = 1.44 M
(c) Moles of KI = 20/166 = 0.120
Moles of water = 80/18 = 4.44
Mole fraction of KI 0.120/(4.44+0.120) = 0.0263

Q12. Calculate Henry’s law constant when the solubility of H_2S (a toxic gas with rotten egg like smell) in water at STP is 0.195 m
Ans. Moles of H_2S = 0.195
Moles of water = 1000/18 = 55.55
Mole fraction of H_2S = 0.195 / (55.55+0.195) = 0.0035
$p = K_H x_2$
$K_H = p / x_2$ = 0.987 bar / 0.0035 = 282 bar.

Q13. 18g of glucose, $C_6H_{12}O_6$, is dissolved in 1 kg of water in a sauce pan. At what temperature will the water boil. K_b for water is 0.52 K kg $mol^{-1}$and boiling point of water is 373.15 K.
Ans. $\Delta T_b = K_b m = (K_b \times w_B \times 1000)/M_B \times w_A$
(0.52 x 18 x 1000) / (180 x 1000) = 0.052
boiling point of the solution = 373.15 + 0.052 = 373.202 K

Q14. 2 g of benzoic acid (C_6H_5COOH) dissolved in 25 g of benzene shows a depression in freezing point equal to 1.62 K. Molal depression constant for benzene is 4.9 K kg mol^{-1}. What is the percentage association of acid if it forms dimer in solution?
Ans. $\Delta T_f = K_f m = (K_f \times w_B \times 1000)/M_B \times w_A$
M_B = (4.9 x 2 x 1000) / (1.62 x 25) = 241.98 $gmol^{-1}$

Molar mass of C_6H_5COOH = 122 $gmol^{-1}$

$2C_6H_5COOH \rightleftharpoons C_6H_5COOH)_2$

Initial moles 1 0

Moles after association (1- α) α/2

Total moles after association = 1- α + α/2 = 1- α/2

i = Normal molar mass/ Observed molar mass = 122 / 241.98 = 0.504

i = (1- α/2) / 1 = 0.504

α = 0.992

Thus, the degree of association of benzoic acid in benzene = 99.2%

Q15. Determine the osmotic pressure of a solution prepared by dissolving 25 mg of K_2SO_4 in 2 litres of water at 25° C, assuming that it is completely dissociated.

Ans. If K_2SO_4 is completely dissociated, then i = 3

Molar mass of K_2SO_4 = 174

$\pi = i\, cRT = i\, (n_B/V)\, RT = i\, (w_B\, RT/M_B V)$

$= 3 \times 25 \times 10^{-3} \times 0.082 \times 298 / 174 \times 2$

$\pi = 5.27 \times 10^{-3}$ atm.

Q16 A 0.877% aqueous solution of an unknown substance is isotonic with 5% solution of sucrose (molar mass-342g/mol).calculate the molar mass of the unknown substance.

Ans isotonic solution has same osmotic pressure

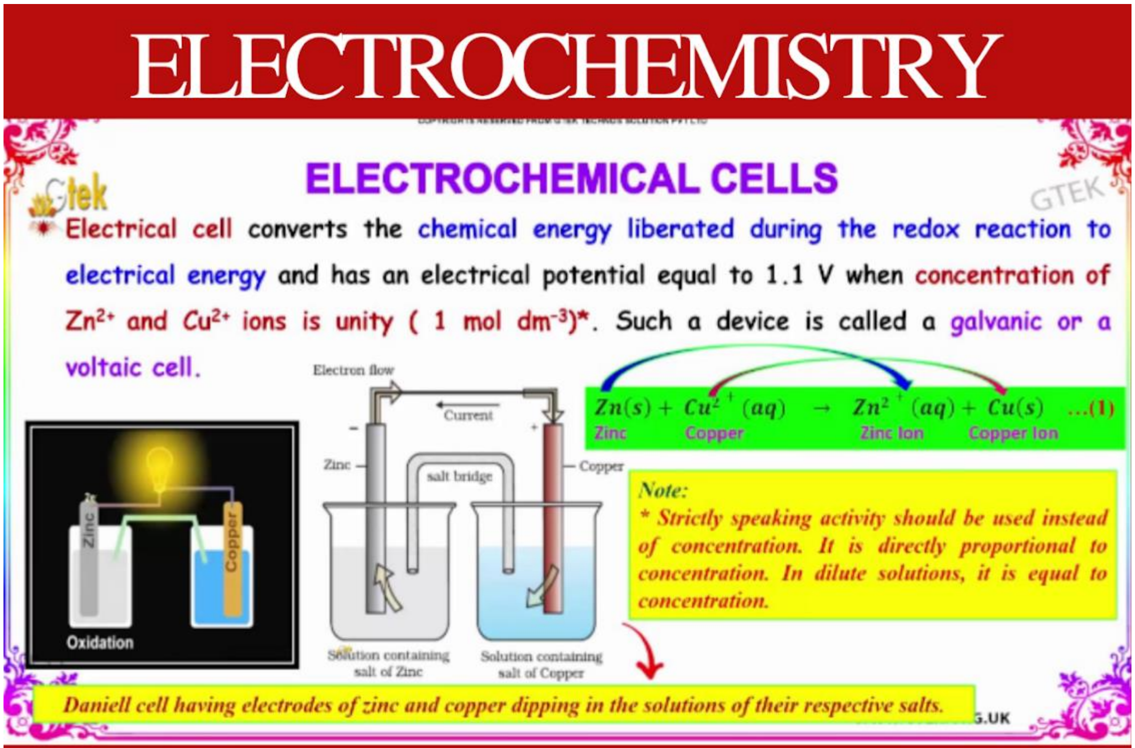
$\Rightarrow \pi_1 = \pi_2$

let Mx be the molar mass of X

then 5/342x1000/100=0.877/Mx X 1000/100

= 60 g/mol

UNIT-2 ELECTROCHEMISTRY



ELECTROCHEMISTRY

ELECTROCHEMICAL CELLS

- Electrical cell converts the chemical energy liberated during the redox reaction to electrical energy and has an electrical potential equal to 1.1 V when concentration of Zn^{2+} and Cu^{2+} ions is unity (1 mol dm^{-3})*. Such a device is called a galvanic or a voltaic cell.

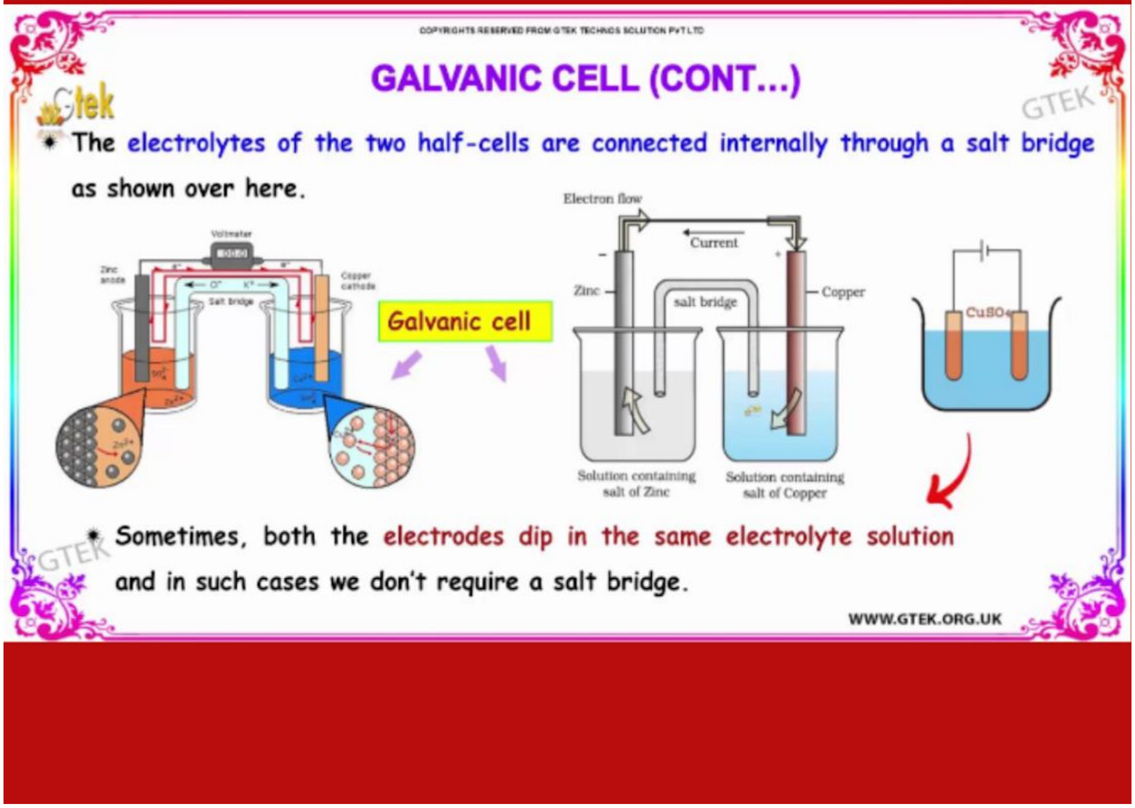
$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s) \quad \ldots(1)$$

Zinc Copper Zinc Ion Copper Ion

Note:

** Strictly speaking activity should be used instead of concentration. It is directly proportional to concentration. In dilute solutions, it is equal to concentration.*

Daniell cell having electrodes of zinc and copper dipping in the solutions of their respective salts.



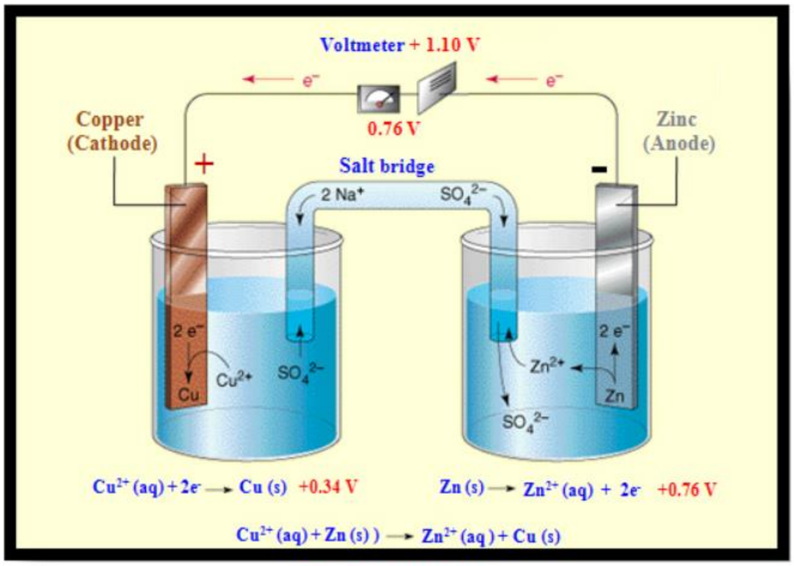
GALVANIC CELL (CONT...)

- The electrolytes of the two half-cells are connected internally through a salt bridge as shown over here.

- Sometimes, both the electrodes dip in the same electrolyte solution and in such cases we don't require a salt bridge.

Electrochemistry is the study of production of electricity from energy released during spontaneous chemical reactions and the use of electrical energy to bring about non-spontaneous chemical transformations.

A galvanic cell is an electrochemical cell that converts the chemical energy of a spontaneous redox reaction into electrical energy. In this device the Gibbs energy of the spontaneous redox reaction is converted into electrical work which may be used for running a motor or other electrical gadget like heater, fan, geyser, etc.
Daniell cell is the one such cell in which the following redox reaction occurs.



The Daniell Cell

Daniell cell having electrodes of zinc and copper dipping in the solutions of their respective salts.

(i) $Cu^{2+} + 2e^- \text{--->} Cu(s)$ (reduction half reaction)

(ii) $Zn(s) \text{--->} Zn^{2+} + 2e^-$ (oxidation half reaction)

$Zn(s) + Cu^{2+}(aq) \text{---->} Zn^{2+}(aq) + Cu(s)$

The reduction half reaction occurs on the copper electrode while the oxidation half reaction occurs on the zinc electrode. These two portions of the cell are also called **half-cells** or **redox couples**. The copper electrode may be called the reduction half-cell reaction and the zinc electrode, the oxidation half-cell reaction.

Electrode potential/Standard electrode potential:
A potential difference develops between the electrode and the electrolyte which is called **electrode potential**. When the concentrations of all the species involved in a half-cell is unity then the electrode potential is known as **standard electrode potential**. According to IUPAC convention, standard reduction potentials are now called standard electrode potentials. In a

galvanic cell, the half-cell in which oxidation takes place is called **anode** and it has a negative potential with respect to the solution. The other half-cell in which reduction takes place is called **cathode** and it has a positive potential with respect to the solution. Thus, there exists a potential difference between the two electrodes and as soon as the switch is in the *on* position the electrons flow from negative electrode to positive electrode. The direction of current flow is opposite to that of electron flow.

The potential difference between the two electrodes of a galvanic cell is called the cell potential and is measured in volts. The cell potential is the difference between the electrode potentials (reduction potentials) of the cathode and anode. It is called the cell electromotive force (e.m.f.) of the cell when no current is drawn through the cell.

EMF of a cell: The e.m.f. of the cell is positive and is given by the potential of the half-cell on the right-hand side minus the potential of the half-cell on the left-hand side i.e.,
$\mathbf{E_{cell} = E_{right} - E_{left}}$

This is illustrated by the following example: Half-cell reactions:
Cathode (reduction): $2Ag^{+}(aq) + 2e^{-} \text{--->} 2Ag(s)$
Anode (oxidation): $Cu(s) \text{--->} Cu^{2+}(aq) + 2e^{-}$
Overall reaction: $Cu(s) + 2Ag^{+}(aq) \text{---->} Cu^{2+}(aq) + 2\,Ag(s)$
Silver electrode acts as a cathode and copper electrode acts as an anode. The cell can be represented as: $Cu(s)|Cu^{2+}(aq)||Ag^{+}(aq)|Ag(s)$
$E_{cell} = E_{right} - E_{left} = E_{Ag^{+}/Ag} - E_{Cu^{2+}/Cu}$
In view of this convention, the half reaction for the Daniell cell in Figure can be written as:
Left electrode: $Zn(s) \rightarrow Zn^{2+}(aq,\ 1\ M) + 2\ e^{-}$
Right electrode: $Cu^{2+}(aq,\ 1\ M) + 2\ e^{-} \rightarrow Cu(s)$
The overall reaction of the cell is the sum of above two reactions and we obtain the equation:
$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$
e.m.f. of the cell = $E^{0}cell = E^{0}_{R} - E^{0}_{L} = 0.34V - (-0.76)\ V = 1.10\ V$

Nernst equation and its application to chemical cells:

For the electrode reaction:
$M^{n+}(aq) + ne^{-} \text{--->} M(s)$
The electrode potential at any concentration measured with respect to standard hydrogen electrode can be represented by:

$$E_{(M^{n+}/M)} = E^{\ominus}_{(M^{n+}/M)} - \frac{RT}{nF}\ln\frac{[M]}{[M^{n+}]}$$

but concentration of solid M is taken as unity and we have

$$E_{(M^{n+}/M)} = E^{\ominus}_{(M^{n+}/M)} - \frac{RT}{nF}\ln\frac{1}{[M^{n+}]}$$

R is gas constant (8.314 JK–1 mol^{-1}), F is Faraday constant (96487 C mol^{-1}), *T* is temperature in kelvin and $[M^{n+}]$ is the concentration of the species, M^{n+}.
In Daniell cell, the electrode potential for any given concentration of Cu^{2+} and Zn^{2+} ions,

For Cathode:

$$E_{(\mathrm{Cu}^{2+}/\mathrm{Cu})} = E^{\ominus}_{(\mathrm{Cu}^{2+}/\mathrm{Cu})} - \frac{RT}{2F} \ln \frac{1}{[\mathrm{Cu}^{2+}(\mathrm{aq})]}$$

For Anode:

$$E_{(\mathrm{Zn}^{2+}/\mathrm{Zn})} = E^{\ominus}_{(\mathrm{Zn}^{2+}/\mathrm{Zn})} - \frac{RT}{2F} \ln \frac{1}{[\mathrm{Zn}^{2+}(\mathrm{aq})]}$$

The cell potential, $E_{(\mathrm{cell})} = E_{(\mathrm{Cu}^{2+}/\mathrm{Cu})} - E_{(\mathrm{Zn}^{2+}/\mathrm{Zn})}$

$E_{cell} = E^0_{cell} – (RT/2F) \ln \{[Zn^{2+}] / [Cu^{2+}]\}$

E (cell) depends on the concentration of both Cu^{2+} and Zn^{2+} ions. It increases with increase in the concentration of Cu^{2+} ions and decrease in the concentration of Zn^{2+} ions.

We know that, $\ln X = 2.303 \log X$, R is gas constant ($8.314\ JK^{-1}\ mol^{-1}$),
F is Faraday constant ($96487\ C\ mol^{-1}$), *T* is temperature in kelvin, 298K. Then

$$E_{cell} = E^0{}_{cell} – \frac{(0.059)}{2} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

For a general electrochemical reaction of the type:

$$\mathrm{a\,A + bB \xrightarrow{ne} cC + dD}$$

Nernst equation can be written as:

$$E_{(\mathrm{cell})} = E^{\ominus}_{(\mathrm{cell})} - \frac{RT}{nF} \ln Q$$

$$= E^{\ominus}_{(\mathrm{cell})} - \frac{RT}{nF} \ln \frac{[\mathrm{C}]^{c}[\mathrm{D}]^{d}}{[\mathrm{A}]^{a}[\mathrm{B}]^{b}}$$

Equilibrium Constant from Nernst Equation:

If the circuit in Daniell cell is closed then we note that the reaction
$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$ takes place and as time passes, the concentration of Zn^{2+} keeps on increasing while the concentration of Cu^{2+} keeps on decreasing.
At the same time voltage of the cell as read on the voltmeter keeps on decreasing. After some time, we shall note that there is no change in the concentration of Cu^{2+} and Zn^{2+} ions and at the same time, voltmeter gives zero reading. This indicates that equilibrium has been attained. In this situation the Nernst equation may be written as:
$E_{cell} = 0 = E^0_{cell} – (RT/2F) \ln\{[Zn^{2+}] / [Cu^{2+}]\}$
$E^0_{cell} = (RT/2F) \ln\{[Zn^{2+}] / [Cu^{2+}]\}$

But at equilibrium,
$[Zn^{2+}] / [Cu^{2+}] = Kc$
$E^0_{cell} = (RT/2F) \ln Kc$
$E^0_{cell} = (0.059/2) \log Kc$

at T = 298K the above equation can be written as
$E^0_{cell} = (0.059/2) \log Kc$
$(E^0_{cell} = 1.10\ V)$

log Kc = [(1.10V x 2)]/0.059 = 37.288
Kc = 2 × 10^{37} at 298K.
In general,
E^0_{cell} = (2.303RT/nF) ln Kc
This gives a relationship between equilibrium constant of the reaction and standard potential of the cell in which that reaction takes place.

Electrochemical Cell and Gibbs Energy of the Reaction:
Electrical work done in one second is equal to electrical potential multiplied by total charge passed. If we want to obtain maximum work from a galvanic cell then charge has to be passed reversibly. The reversible work done by a galvanic cell is equal to decrease in its Gibbs energy and therefore, if the emf of the cell is E and nF is the amount of charge passed and $\Delta_r G$ is the Gibbs energy of the reaction, then $\Delta_r G = -nFE_{cell}$
Ecell is an intensive parameter but $\Delta_r G$ is an extensive thermodynamic property and the value depends on *n*.
Thus, if we write the reaction
$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$
$\Delta rG = -2 F E_{cell}$
If the concentration of all the reacting species is unity, then $E_{cell} = E^0_{cell}$
$\Delta_r G^0 = -n F E^0_{cell}$
We can calculate equilibrium constant by the equation:
$\Delta_r G^0 = -RT \ln K$.

Conductance of Electrolytic Solutions:
The electrical resistance is represented by the symbol *'R'* and it is measured in ohm (**Ω**). The electrical resistance of any object is directly proportional to its length, l, and inversely proportional to its area of cross section, *A*. That is,
$R \propto l/A$ or $R = \rho (l/A)$
The constant of proportionality, ρ (rho), is called **resistivity** (specific resistance). Its SI units are ohm metre (**Ω** m) or ohm centimetre (**Ω** cm).
The resistivity for a substance is its resistance when it is one metre long and its area of cross section is one m^2. It can be seen that:
1 **Ω** m = 100 **Ω** cm or 1 **Ω** cm = 0.01 **Ω** m
The inverse of resistance, R, are called **conductance**, G, and we have the relation:
$G = 1/R = A/\rho l = \kappa (A/l)$ $[\kappa = 1/\rho]$
The SI unit of conductance is Siemens, represented by the symbol 'S' and is equal to ohm^{-1} (also known as mho) or Ω^{-1}.
The inverse of resistivity, called **conductivity** (specific conductance) is represented by the symbol, κ (Greek, kappa). The SI units of conductivity are S m^{-1}. Conductivity of a material in S m^{-1} is its conductance when it is 1 m long and its area of cross section is 1 m^2. It may be noted that 1 S cm^{-1} = 100 S m^{-1}.

Electrical conductance through metals is called metallic or electronic conductance and is due to the movement of electrons. The electronic conductance depends on:

(i) The nature and structure of the metal

(ii) The number of valence electrons per atom

(iii) Temperature (it decreases with increase of temperature).

When electrolytes are dissolved in water its conductivity increases. The conductance of electricity by ions present in the solutions is called electrolytic or ionic conductance. The conductivity of electrolytic (ionic) solutions depends on:

(i) The nature of the electrolyte added

(ii) Size of the ions produced and their solvation

(iii) The nature of the solvent and its viscosity

(iv) Concentration of the electrolyte

(v) Temperature (it increases with the increase of temperature)

Conductivity of Ionic Solutions: In the conductivity cell the solution confined between the electrodes is a column of length l and area of cross section A. The resistance of such a column of solution is given by the equation:

$R = \rho\, l/A = l/\kappa A$

The quantity l/A is called cell constant denoted by the symbol, G^*. It depends on the distance between the electrodes and their area of cross-section.

The cell constant, G^*, is then given by the equation:

$G^* = l/A = R\,\kappa$

$K = \text{cell constant}/R = G^*/R$

Molar conductivity: It is defined as the conducting power of all the ions produced by dissolving one mole of an electrolyte in solution. It is denoted by the symbol Λ_m (Λ = lambda). It is related to the conductivity of the solution by the equation:

Molar conductivity = $\Lambda_m = \kappa/c$

In the above equation, if κ is expressed in $S\ m^{-1}$ and the concentration, c in $mol\ m^{-3}$ then the units of Λ_m is in $S\ m^2\ mol^{-1}$.

$\Lambda_m\ (S\ cm^2\ mol^{-1}) = [\kappa\ (S\ cm^{-1}) \times 1000\ (cm^3/L)]\ /\ \text{Molarity}\ (mol/L)$

$$\Lambda_m = \frac{\kappa \times 1000}{\text{Molarity}}$$

$1\ S\ m^2\ mol^{-1} = 10^4\ S\ cm^2\ mol^{-1}$ or

$1\ S\ cm^2 mol^{-1} = 10^{-4}\ S\ m^2\ mol^{-1}$.

Variation of Conductivity and Molar Conductivity with Concentration:

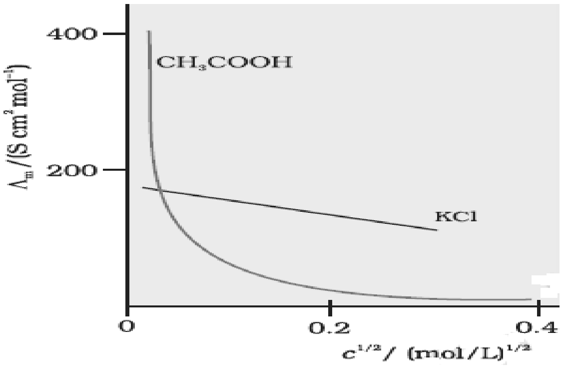
Both conductivity and molar conductivity change with the concentration of the electrolyte. Conductivity always decreases with decrease in concentration both, for weak and strong electrolytes. This can be explained by the fact that the number of ions per unit volume that carry the current in a solution decrease on dilution. The conductivity of a solution at any given concentration is the conductance of one unit volume of solution kept between two platinum electrodes with unit area of cross section and at a distance of unit length.

This is clear from the equation: $G = \kappa\, A/l$ (both *A* and *l* is unity in their units in m or cm)

Molar conductivity of a solution at a given concentration is the conductance of the volume *V* of solution containing one mole of electrolyte kept between two electrodes with area of cross section *A* and distance of unit length. Therefore,
$\Lambda_m = \kappa A/l$
Since $l = 1$ and $A = V$ (volume containing 1 mole of electrolyte)
$\Lambda_m = \kappa V$

Molar conductivity increases with decrease in concentration. This is because the total volume, *V*, of solution containing one mole of electrolyte also increases. At a given concentration, Λ_m can be defined as the conductance of the electrolytic solution kept between the electrodes of a conductivity cell at unit distance but having area of cross section large enough to accommodate sufficient volume of solution that contains one mole of the electrolyte. When concentration approaches zero, the molar conductivity is known as
limiting molar conductivity and is represented by the symbol Λ_m^0. The variation in Λ_m with concentration is different for strong and weak electrolytes.

Molar conductivity Λ_m versus c½ for acetic acid (weak electrolyte) and potassium chloride (strong electrolyte) in aqueous solutions.



Strong Electrolytes

For strong electrolytes, Λ_m increases slowly with dilution and can be represented by the equation:
$\Lambda_m = \Lambda_m^0 - A\, c^{1/2}$
If we plot Λ_m against $c^{1/2}$, we obtain a straight line with intercept equal Λ_m^0 and slope equal to '*A*'. The value of the constant '*A*' for a given solvent and temperature depends on the type of electrolyte i.e., the charges on the cation and anion produced on the dissociation of the electrolyte in the solution. Thus, NaCl, $CaCl_2$, $MgSO_4$ are known as 1-1, 2-1 and 2-2 electrolytes respectively. All electrolytes of a particular type have the same value for '*A*'.

Kohlrausch's law of independent migration of ions. The law states that limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte.
If $\lambda^\circ_{Na^+}$ and $\lambda^\circ_{Cl^-}$ are limiting molar conductivity of the sodium and chloride ions respectively, then the limiting molar conductivity for sodium chloride is given by the equation:
$\Lambda_m^0 = \lambda^\circ_{Na^+} + \lambda^\circ_{Cl^-}\ \nu$
In general, if an electrolyte on dissociation gives ν_+ cations and ν_- anions then its limiting molar conductivity is given by: $\Lambda_m^0 = \nu_+\lambda^\circ_+ + \nu_-\lambda^\circ_-$
$\lambda^\circ_+ + \lambda^\circ_-$ are the limiting molar conductivities of the cation and anion respectively.

Weak Electrolytes

Weak electrolytes like acetic acid have lower degree of dissociation at higher concentrations, for such electrolytes, the change in Λ_m with dilution is due to increase in the degree of dissociation. At any concentration *c*, if α is the degree of dissociation, then

$\alpha = \Lambda_m / \Lambda_m^0$

`**ELECTROLYSIS:** It is a process of decomposition of an electrolyte by the passage of electricity through its aqueous solution or molten (fused) state of electric current.

Quantitative Aspects of Electrolysis

Faraday's Laws of Electrolysis:

(i) **Faraday** first law of electrolysis: The amount of chemical reaction which occurs at any electrode during electrolysis by a current is proportional to the quantity of electricity passed through the electrolyte (solution or melt).

$w \propto Q$ or $w = ZQ$, Where Z is called electrochemical equivalent. If a current of I amperes is passed for t seconds, then $Q = It$ so that, $w = ZIt$

(ii) **Faraday** second law of electrolysis: The amounts of different substances liberated by the same quantity of electricity passing through the electrolytic solution are proportional to their chemical equivalent weights (Atomic Mass of Metal ÷ Number of electrons required to reduce the cation).

For example, when same current is passed through two electrolytic solutions, containing copper sulphate and silver nitrate connected in series, the weight of copper and silver deposited are:

(Weight of Cu deposited) / (Weight of Ag deposited) = (Eq. wt. of Cu) / (Eq. wt. of Ag)

The amount of electricity (or charge) required for oxidation or reduction depends on the stoichiometry of the electrode reaction. For example, in the reaction:

$Ag^+ (aq) + e^- \rightarrow Ag(s)$

One mole of the electron is required for the reduction of one mole of silver ions.

The charge on one electron is equal to 1.6021×10^{-19} C.

Therefore, the charge on one mole of electrons is equal to:

$N_A \times 1.6021 \times 10^{-19}$ C $= 6.02 \times 10^{23}$ mol^{-1} $\times 1.6021 \times 10^{-19}$ C = 96487 C mol^{-1}

This quantity of electricity is called **Faraday** and is represented by the symbol **F**.

For approximate calculations we use 1F ≃ 96500 C mol^{-1}.

$Mg^{2+} + 2e^- \rightarrow Mg$

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

For the above electrode reactions, one mole of Mg^{2+} and Al^{3+} require 2 mol of electrons (2F) and 3 mol of electrons (3F) respectively.

Products of Electrolysis:

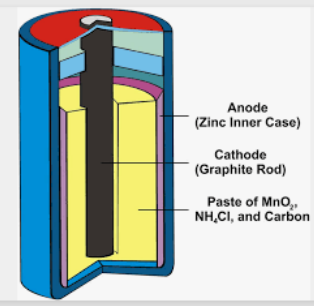
The products of electrolysis depend on the different oxidising and reducing species present in the electrolytic cell and their standard electrode potentials. Moreover, some of the electrochemical processes although feasible, are so slow kinetically that at lower voltages these do not seem to occur. For the occurrence of such reactions some extra potential (called *over potential*) is required.

(i) **Electrolysis of molten sodium chloride**: During the electrolysis of molten NaCl, the products of electrolysis are sodium metal and Cl_2 gas. The reactions may be expressed as:
At cathode: $2Na^+ + 2e– \rightarrow 2Na$ (reduction)
At anode: $2Cl^- \rightarrow Cl_2 + 2e–$ (oxidation)
The overall reaction: 2NaCl ---> $2Na + Cl_2$

(ii) **Electrolysis of aqueous sodium chloride**: During the electrolysis of aqueous sodium chloride solution, the products are NaOH, Cl_2 and H_2.
At the cathode: Na+ (aq) + e– →Na (s) E^0cell = – 2.71 V
H^+ (aq) + e– →½ H_2 (g) E^0cell = 0.00 V
The reaction with higher value of E^0 is preferred and therefore, the reaction at the cathode during electrolysis is:
H+ (aq) + e– →½ H_2(g)
But H+ (aq) is produced by the dissociation of H_2O, i.e., H_2O (*l*) →H^+ (aq) + OH^- (aq)
Therefore, the net reaction at the cathode: H_2O (*l*) + e^- →½H_2(g) + OH^- (aq)
At the anode: Cl– (aq) →½ Cl_2 (g) + e^- E^0cell = +1.36 V
2H2O (*l*) → O_2 (g) + $4H^+$(aq) + $4e^-$ E^0cell = +1.23 V
The reaction at anode with lower value of E^0 is preferred and therefore, water should get oxidised in preference to Cl^- (aq). However, on account of over potential of oxygen, the reaction Cl^- (aq) →½ Cl_2 (g) is preferred. Thus, the net reactions may be summarized as:
NaCl (aq) ^{H2O} Na^+ (aq) + Cl^-(aq)
At cathode: H_2O (*l*) + e^- →½ H_2(g) + OH^- (aq)
At anode: Cl^- (aq) →½Cl_2(g) + e^-
Net reaction: NaCl (aq) + H_2O (*l*) →Na^+(aq) + OH^-(aq) + ½H_2(g) + ½Cl_2(g)
NaCl (aq) + H_2O (*l*) →NaOH(aq) + ½H_2(g) + ½Cl_2(g)

Dry Cell:

A dry cell consists of a zinc container act as anode and the cathode is a carbon (graphite) rod surrounded by powdered manganese dioxide and carbon. The space between the electrodes is filled with moist paste of ammonium chloride and zinc chloride.



Anode: $Zn(s) \rightarrow Zn^{2+} + 2e^-$
Cathode: $\underline{2MnO_2 + 2NH_4^+ + 2e^- \rightarrow 2MnO(OH) + 2NH_3}$

$$\underline{Zn(s) + 2MnO_2 + 2NH_4^+ \rightarrow Zn^{2+} + 2MnO(OH) + 2NH_3}$$

Dry cell is commonly used in transistors and clocks

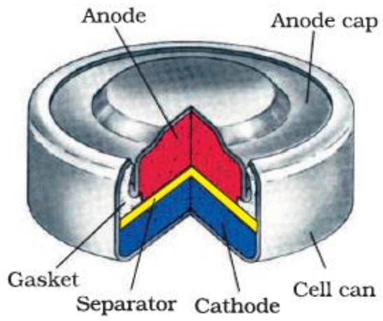
Mercury cell: It consists of zinc – mercury

Amalgam as anode and a paste of HgO and carbon as the cathode. The electrolyte is a paste of KOH and ZnO.
The electrode reactions for the cell are given below:

$$\text{Anode: } Zn(Hg) + 2OH^- \longrightarrow ZnO(s) + H_2O + 2e^-$$

$$\text{Cathode: } HgO + H_2O + 2e^- \longrightarrow Hg(l) + 2OH^-$$

$$Zn(Hg) + HgO(s) \longrightarrow ZnO(s) + Hg(l)$$



The cell potential is approximately 1.35 V and remains constant during its life as the overall reaction does not involve any ion in solution whose concentration can change during its lifetime. It is suitable for low current devices like hearing aids, watches, etc.

A secondary cell (lead storage battery) commonly used in automobiles and invertors. It consists of a lead anode and a grid of lead packed with lead dioxide (PbO_2) as cathode. A 38% solution of Sulphuric acid is used as an electrolyte.
The cell reactions when the battery is in use are given below:

$$\text{Anode: } Pb(s) + SO_4^{2-}(aq) \longrightarrow PbSO_4(s) + 2e^-$$

$$\text{Cathode: } PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O(l)$$

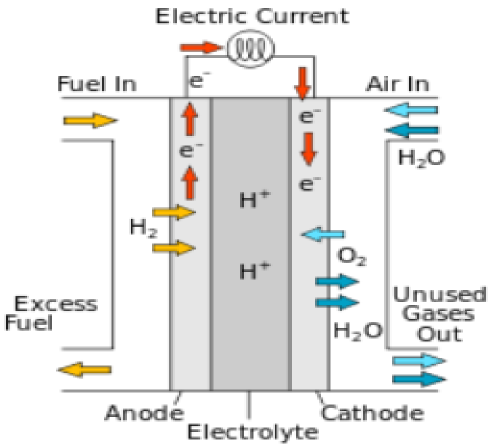
$$Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \longrightarrow 2PbSO_4(s) + 2H_2O(l)$$

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

Another important secondary cell is the **nickel-cadmium cell** which has longer life than the lead storage cell but more expensive to manufacture.
The overall reaction during discharge is:
$Cd(s) + 2Ni(OH)_3(s)$ ----------- $CdO(s) + 2Ni(OH)_2(s) + H_2O(l)$

Fuel cells: To convert the energy of combustion of fuels like hydrogen, methane, methanol, etc. directly into electrical energy are called **fuel cells**.
Fuel cells use the reaction of hydrogen with oxygen to form water. The cell was used for providing electrical power in the Apollo space Programme.

Fuel Cells



Fuel cell using H_2 and O_2 produces electricity. In this cell, hydrogen and oxygen are bubbled through porous carbon electrodes into concentrated NaOH solution. Catalysts like finely divided platinum or palladium metal are incorporated into the electrodes for increasing the rate of electrodes reactions.

The electrode reactions are given below:

Cathode: $O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$

Anode: $2H_2(g) + 4OH^-(aq) \longrightarrow 4H_2O(l) + 4e^-$

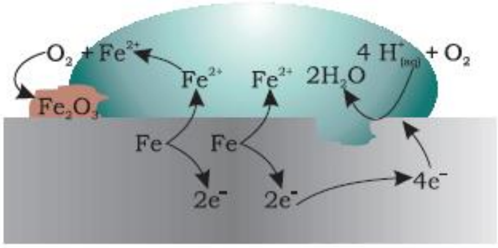
Overall reaction being:

$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$

The cell runs continuously as long as the reactants are supplied. Fuel cells produce electricity with an efficiency of about 70%. Fuel cells are pollution free.

Corrosion:

In corrosion, a metal is oxidised by loss of electrons to oxygen and formation of oxides. Corrosion of iron (commonly known as rusting) occurs in presence of water and air. The chemistry of corrosion is an electrochemical phenomenon.



Corrosion of iron in atmosphere

We can write the reaction

Anode: $2\,Fe(s)$ ----------- $2Fe^{2+} + 4\,e^-$ $E^0_{(Fe2+/Fe)} = -0.44$ V

Cathode: $O_2(g) + 4\,H^+(aq) + 4\,e^- \rightarrow 2\,H_2O(l)$ $E^0_{(H+/O2/H2O)} = 1.23$ V

The overall reaction being:

$2Fe(s) + O_2(g) + 4H^+(aq) \rightarrow 2Fe^{2+}(aq) + 2\,H_2O(l)$ $E^0_{cell} = 1.67$ V

The ferrous ions are oxidised by atmospheric oxygen to ferric ions which come out as rust in the form of hydrated ferric oxide ($Fe_2O_3 . x\ H_2O$) and with further production of hydrogen ions.

Prevention of corrosion can be done by covering the surface with paint or by some chemicals (e.g. bisphenol).
Another method is to cover the surface by other metals (Sn,Zn,etc) that are inert or react to save the object.
An electrochemical method is to provide a sacrificial electrode of another metal (like Mg, Zn, etc.) which corrodes itself but save the object.

ASSIGNMENT:
Q1. The charge required for the reduction of 1 mol of MnO_4^- to MnO_2 is
(a) 1 F
(b) 3 F
(c) 5 F
(d) 6 F
Ans. (b) 3 F

Q2. If limiting molar conductivity of Ca^{2+} and Cl^- are 119.0 and 76.3 S cm^2 mol^{-1}, then the value of limiting molar conductivity of $CaCl_2$ will be
(a) 195.3 S cm^2 mol^{-1}
(b) 271.6 S cm^2 mol^{-1}
(c) 43.3 S cm^2 mol^{-1}
(d) 314.3 S cm^2 mol^{-1}.
Ans. (b) 271.6 S cm^2 mol^{-1}

Q3. The emf of the cell:
Ni / Ni^{2+} (1.0 M) // Au^{3+} (1.0 M) / Au (E° = -0.25 V for Ni^{2+}/Ni; E° = 1.5 V for Au^{3+}/Au) is
(a) 1.25 V
(b) -1.25 V
(c) 1.75 V
(d) 2.0 V
Ans. (c) 1.75 V

Q4. In a dry cell, which of the following is the electrolyte?
(a) Potassium hydroxide
(b) Sulphuric acid
(c) Ammonium chloride
(d) Manganese dioxide
Ans. (c) Ammonium chloride

Q5. Which of the following statements about a lead storage cell (or a lead-acid battery) is false?
(a) It is a primary cell
(b) The cathode is made up of lead (IV) oxide
(c) The anode is made up of lead
(d) The electrolyte used is an aqueous solution of Sulphuric acid

Ans. (a) It is a primary cell

Q6. Λ_m^0 for NaCl, HCl and CH_3COONa are 126.4, 425.9 and 91.0 S cm^2 mol^{-1} respectively. Calculate Λ_m^0 for CH_3COOH.

Solution: Λ_m^0 (HCl) + Λ_m^0 (CH_3COONa) - Λ_m^0 (NaCl)

425.9 + 91.0 - 126.4 = 390.5 S cm^2 mol^{-1}

Q7. Calculate E_{cell} for the reaction given below, if $E^0_{cell} = 3.17V$

Mg (s) + 2Ag^+ (0.0001M) Mg^{2+} (0.130M) + 2Ag (s)

Solution:

$E_{cell} = E^0_{cell} – (0.059/2) \log \{[Mg^{2+}] / [Ag^+]^2\}$

$= 3.17 – 0.0295 \log [(0.130)/ (0.0001)^2]$

= 3.17 V – 0.21V = 2.96 V

Q8. A solution of $CuSO_4$ is electrolysed for 10 minutes with a current of 1.5 amperes. What is the mass of copper deposited at the cathode?

Solution: t = 10 x 60 = 600 s

Q = I X t = 1.5 A × 600 s = 900 C

According to the reaction:

Cu^{2+} (aq) + $2e^-$ = Cu(s)

We require 2F or 2 × 96500 C to deposit 1 mol or 63 g of Cu.

For 900 C, the mass of Cu deposited

= (63 g mol^{-1} × 900 C)/ (2 × 96500 C mol^{-1})

= 567 / 1930 g

= 0.2938 g.

Q9. The electrical resistance of a column of 0.05 mol L^{-1} NaOH solutions of diameter 1 cm and length 50 cm is 5.55×10^3 ohm. Calculate its resistivity, conductivity and molar conductivity.

Solution:

A = π r2 = 3.14 × 0.52 cm^2 = 0.785 cm^2 = 0.785×10^{-4} m^2

l = 50 cm = 0.5 m

R = ρ l/ A

ρ (resistivity) = RA/l = [5.55×10^3 ohm x 0.785 cm^2] / 50 cm = 87.135 ohm cm

Conductivity (κ) = 1/ ρ = [1 / 87.135] S cm^{-1} = 0.01148 S cm^{-1}

Molar conductivity, Λ_m = [κ (S cm^{-1}) x 1000 (cm^3/L)] / Molarity (mol/L)

= [0.01148 ×1000]/ 0.05

= 229.6 S cm^2 mol^{-1}

Q10. Conductivity of 0.00241 M acetic acid is 7.896×10^{-5} S cm^{-1}. Calculate its molar conductivity. If Λ^0_m for acetic acid is 390.5 S cm^2 mol^{-1}. What is the dissociation constant?

Answer: Molar conductivity, Λ_m = 32.76 S cm^2 mol^{-1}

α = 32.76/390.5 = 8.39×10^{-2}

Dissociation constant = 1.86×10^{-5}

Q11. Explain the following:

1. How much charge is required for 1 mol of MnO_4^- to Mn^{2+}
2. How much electricity is required in coulomb for the oxidation of 1 mol of H_2O to O_2
3. How much electricity in terms of Faraday is required to produce 40g of Al from molten Al_2O_3

Ans. 1. Reduction of 1 mol of MnO_4^- requires = 5 x 96500 C
2. Oxidation of 1 mol of H_2O requires = 2 x 96500 C
3. $Al^{3+} + 3e^- \rightarrow Al$
1 mol of Al requires 3 mol of electrons or 3 F
27g of Al requires = 3F
40g of Al requires = (3 x 40) / 27 = 4.44F

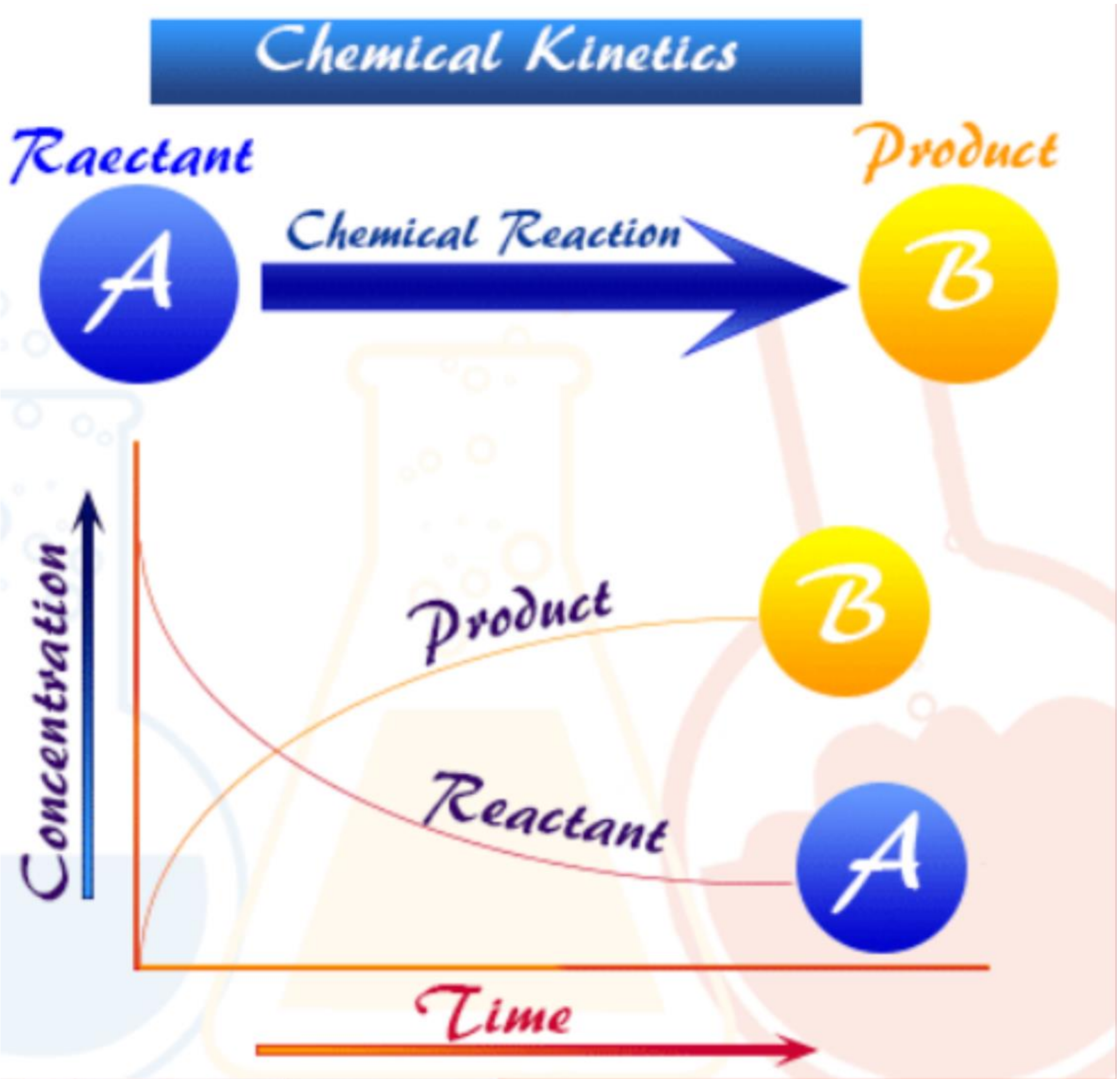
Q12. The standard electrode potential for Daniell cell is 1.1V. Calculate the standard Gibbs energy for the reaction: $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$
Solution: $\Delta_r G^0 = – n F E^0cell$
The value of n in the above equation is 2, F = 96500 C mol–1 and E^0cell = 1.1 V
Therefore, $\Delta rG^0 = – 2 \times 1.1V \times 96500 \text{ C mol}^{-1}$
$= – 212300 \text{ J mol}^{-1}$
$= – 212.3 \text{ kJ mol}^{-1}$

Q13. Calculate the equilibrium constant of the reaction:
$Cu(s) + 2Ag^+(aq)$ $Cu^{2+}(aq) + 2Ag(s)$
$E^0cell = E^0Ag+/Ag - E^0Cu^{2+}/Cu = 0.80 – 0.34 = 0.46$ V
Ans. $log\ Kc = (2 \times 0.46)/0.059 = 15.59$
$Kc = 3.92 \times 10^{15}$

Q14. The standard electrode potential for Daniell cell is 1.1V. Calculate the standard Gibbs energy for the reaction: $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$
Solution: $\Delta_r G^0 = – n F E^0cell$
The value of n in the above equation is 2, F = 96500 C mol–1 and E^0cell = 1.1 V
Therefore, $\Delta rG^0 = – 2 \times 1.1V \times 96500 \text{ C mol}^{-1}$
$\Delta rG^0 = – 212300 \text{ J mol}^{-1}$
$\Delta rG^0 = – 212.3 \text{ kJ mol}^{-1}$

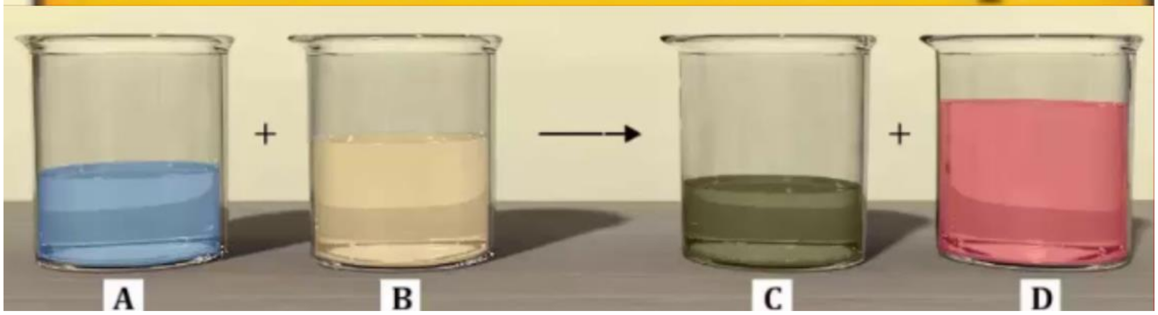
Q15. Write the cell reaction of a lead storage battery when it is discharged. How does the density of the electrolyte change when the battery is discharged?
Ans. $Pb + PbSO_4 + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O$
Density of electrolyte decreases because water is formed and sulphuric acid is consumed as the product during discharge of the battery.

Unit III: Chemical Kinetics




Rate Law

$mA + nB \longrightarrow oC + pD$



ORDER	UNITS OF RATE CONSTANT	INTEGRATED RATE CONSTANT
0	Mol L^{-1} s^{-1}	$K = [R]_0 – [R]/t$
1	s^{-1}	$K = 2.303/t \log[R]_0/[R]$
2	Mol^{-1} L s^{-1}	$K = [1/[R] -1/[R]_0]/t$

FIRST ORDER GAS PHASE REACTION	$K = 2.303/t \log [p_i/(2p_i – p_t)]$

Chemical Kinetics the branch of chemistry, which deals with the study of reaction rates and their mechanisms.

Rate of a Chemical Reaction: the rate of a reaction can be defined as the change in concentration of a reactant or product in unit time. It can be expressed in terms of:
(i) The rate of decrease in concentration of any one of the reactants.
(ii) The rate of increase in concentration of any one of the products.
Consider a hypothetical reaction, R ---> P
One mole of the reactant R produces one mole of the product P. If $[R]_1$ and $[P]_1$ are the concentrations of R and P respectively at time t_1 and $[R]_2$ and $[P]_2$ are their concentrations at time t_2 then, $\Delta t = t_2 – t_1$
$\Delta[R] = [R]_2 – [R]_1$
$\Delta [P] = [P]_2 – [P]_1$
The square brackets in the above expressions are used to express molar concentration.
Rate of disappearance of R = Decrease in concentration of R / Time taken = - R/t (1)
Rate of appearance of P = Increase in concentration of P /Time taken = P/t (2)
Since, $\Delta[R]$ is a negative quantity (as concentration of reactants is decreasing), it is multiplied with –1 to make the rate of the reaction a positive quantity.
Equations (1) and (2) given above represent the average rate of a reaction, r_{av}.
Average rate depends upon the change in concentration of reactants or products and the time taken for that change to occur. (Ref. ncert Fig. 4.1)

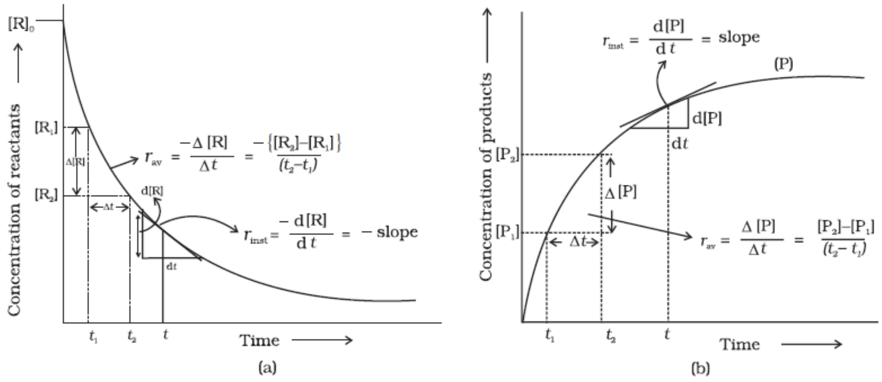


Fig. 4.1: Instantaneous and average rate of a reaction

Units of rate of a reaction: The units will be **mol $L^{-1}s^{-1}$**.
In gaseous reactions, the units of the rate equation will be **atm s^{-1}**.

Factors affecting rate of reaction: The important factors are:

1. Concentration of the reacting species.
2. Temperature of the system.
3. Nature of reactant and products.
4. Presence of a catalyst.
5. Surface area.
6. Exposure to radiation.

Rate Law and Rate Constant:

Consider a general reaction: aA + bB ----> cC + dD
Where a, b, c and d are the stoichiometric coefficients of reactants and products.
The rate expression for this reaction is Rate $\propto [A]^x [B]^y$
Where exponents x and y may or may not be equal to the stoichiometric coefficients (a & b) of the reactants. Above equation can also be written as
Rate = $k [A]^x [B]^y$
$-d[R]/dt = k[A]^x [B]^y$
This form of equation is known as differential rate equation, where k is a proportionality constant called **rate constant**.
The equation, Rate = $k [A]^x [B]^y$ which relates the rate of a reaction to concentration of reactants is called rate law or rate expression.
Rate law is the expression in which reaction rate is given in terms of molar concentration of reactants with each term raised to some power, which may or may not be same as the stoichiometric coefficient of the reacting species in a balanced chemical equation.
For example:

$2NO (g) + O_2 (g) \text{ ----> } 2NO_2 (g)$

Rate = $k [NO]^2 [O_2]$
$-d[R]/dt = k [NO]^2 [O_2]$

Order of reaction:

Rate = k $[A]^x$ $[B]^y$
x and y indicate the rate is to the change in concentration of A and B.
Sum of these exponents, i.e., x + y in above equation gives the overall order of a reaction.
whereas x and y represent the order with respect to the reactants A and B respectively.
Order of reaction is defined as the sum of powers of the concentration of the reactants in the rate law expression is called the order of that chemical reaction.
Order of a reaction can be 0, 1, 2, 3 and even a fraction.
A zero-order reaction means that the rate of reaction is independent of the concentration of reactants.
Units of rate constant:
Zero order rate of reaction: mol L^{-1} s^{-1}
First order rate of reaction: s^{-1}
Second order rate of reaction: L mol^{-1} s^{-1}

Molecularity of a reaction: The number of reacting species (atoms, ions or molecules) taking part in an elementary reaction, which must collide simultaneously in order to bring about a chemical reaction is called molecularity of a reaction.
For examples:

NH_4NO_2 -----> N_2 + $2H_2O$	Unimolecular reaction
2HI (g) ----> H_2 (g) + I_2 (g)	Bimolecular reaction
2NO (g) + O_2 (g) -----> $2NO_2$ (g)	Trimolecular reaction

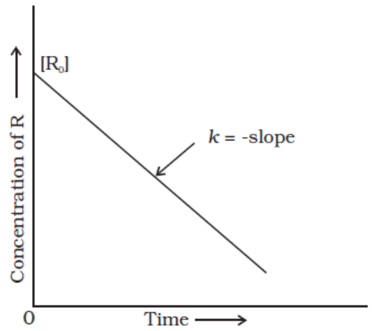
Important points of distinction between order and molecularity

S.No.	**Order**	**Molecularity**
1	**Order** is the sum of powers of the concentration terms in the rate law expression.	**Molecularity** is the number of reacting species undergoing simultaneous collision in the elementary or simple reaction.
2	Order of a reaction is determined experimentally.	Molecularity is a theoretical concept.
3	Order of a reaction can be zero.	Molecularity of a reaction cannot be zero.

Integrated rate equations:

Zero order reaction: Zero order reaction means that the rate of the reaction is proportional to zero power of the concentration of reactants.
Consider the reaction,
R -----> P
Rate = -d[R] /dt = k $[R]^0$
Rate = -d[R] /dt = k x 1
d[R] = -k dt
Integrating both sides
[R] = -k t +I (1)
Where, I is the constant of integration
At t = 0 the concentration of reactant [R] = $[R]_0$
Where $[R]_0$ is the initial concentration of reactant.
$[R]_0$ = -k x 0 + I = I, Substituting the value of I in the equation (1)
[R] = -k t + $[R]_0$
k ={$[R]_0$ - [R]}/t

Variation in the concentration Vs time plot for a zero-order reaction



Example of Zero order reaction is the decomposition of gaseous ammonia.

$2NH_3$ (g) ------> N_2 (g) + 3 H_2 (g)

Rate = $k\,[NH_3]^0 = k$

the rate of the reaction is proportional to the

First Order Reactions: The rate of the reaction is proportional to the first power of the concentration of the reactant R.

For example:

R -----> P

Rate = $-d[R]/dt = k\,[R]$

$d[R]/[R] = -k\,dt$,

Integrating this equation and we get

$\ln [R] = -kt + I$ (1)

At t = 0,

$\ln [R]_0 = -k \times 0 + I$,

$I = \ln [R]_0$, Substituting the value of I in the equation (1)

$\ln [R] = -kt + \ln [R]_0$

$k = \{\ln [R]_0 - \ln [R]\}/t$

Remember that, (log a – log b = log(a/b)

$k = (1/t) \ln \{[R]_0/[R]\}$

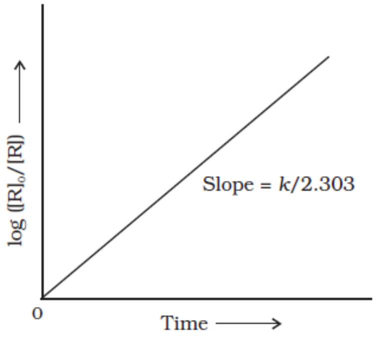
$\ln \{[R]/[R]_0\} = -kt$, taking antilog both sides

$[R] = [R]_0\, e^{-kt}$

We know that, ln a = 2.303 log a

$\boldsymbol{k = (2.303/t) \log \{[R]_0/[R]\}}$

If we plot a graph between log $[R]_0/[R]$ Vs t, the slope is k/2.303 for first order reaction



First order gas phase reaction: A(g) -----> B(g) + C(g)

Total pressure $p_t = p_A + p_B + p_C$
$A(g) \longrightarrow B(g) + C(g)$

	A(g)	B(g)	C(g)
At t = 0	p_i atm	0 atm	0 atm
At time t	$(p_i - x)$	x atm	x atm

$p_t = (p_i - x) + x + x = p_i + x$
$x = (p_t - p_i)$
$p_A = p_i - x = p_i - (p_t - p_i) = 2p_i - p_t$
$k = (2.303/t) \log [p_i / p_A]$
$k = (2.303/t) \log [p_i/(2p_i - p_t)]$

Half-life of a reaction: The half-life of a reaction is the time in which the concentration of a reactant is reduced to one half of its initial concentration. It is represented as $t_{1/2}$.

For a zero-order reaction, rate constant is
$k = \{[R]_0 - [R]\}/t$
At $t = t_{1/2}$, $[R] = [R]_0 /2$

$k = \{[R]_0 - [R]_0 /2\}/t_{1/2} = [R]_0 /2\, t_{1/2}$

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

For a first order reaction, rate constant is

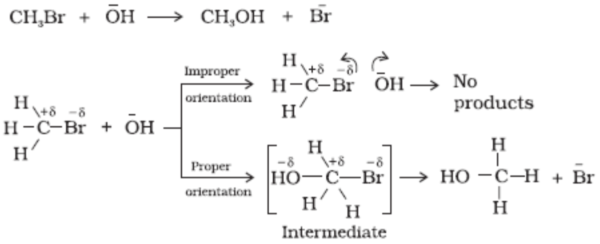
$k = (2.303/t) \log \{[R]_0/[R]\}$
At $t = t_{1/2}$, $[R] = [R]_0 /2$
$k = (2.303/t_{1/2}) \log \{[R]_0/[R]_0 /2\}$
$k = (2.303/t_{1/2}) \log 2$
$k = (2.303/t_{1/2})\ 0.3010$

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

For zero order reaction $t_{1/2} \propto [R]_0$.
For first order reaction $t_{1/2}$ is independent of $[R]_0$.

Collision Theory of Chemical Reactions:
Collision frequency: It is defined as the number of collisions per second per unit volume of the reaction mixture is known as collision frequency (Z).
Effective collision: The collisions in which molecules **collide with proper orientation**, breaking of bonds between reacting species and formation of new bonds to form products are called as **effective collisions.**
Ineffective collision: The collisions in which molecules **collide with improper orientation** no products are formed are called as in**effective collisions.**

For example, formation of methanol from Bromoethane depends upon the orientation of reactant molecules. The proper orientation of reactant molecules lead to bond formation whereas improper orientation makes them simply bounce back and no products are formed. Diagram showing molecules having proper and improper orientation: -



Rate of reaction is proportional to

i. the number of collisions per unit volume per second (collision frequency, Z) between the reacting species.

ii. the fraction of effective collisions (properly oriented and possessing sufficient energy), f:

i.e., Rate = - dx/dt = f x Z

Temperature Dependence of the Rate of a Reaction: For the effect of temperature on reaction rates is that the rate of a reaction or rate constant becomes almost doubled for every 10° rise in temperature. Increase in the rate of reaction with the rise in temperature is mainly due to the increase in number of effective collisions.
The temperature dependence of the rate of a chemical reaction can be accurately explained by Arrhenius equation.

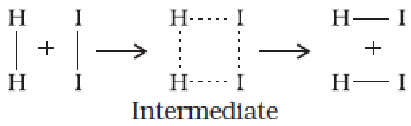
Arrhenius equation and calculation of Activation energy:

$$k = A\ e^{-Ea/RT}$$

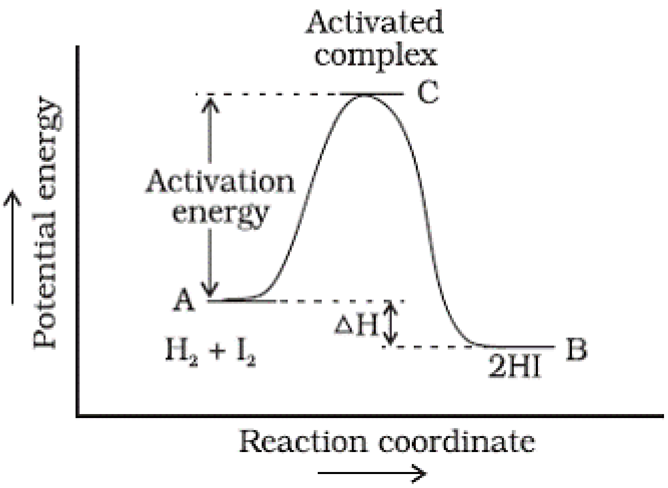
Where A is the Arrhenius factor or the frequency factor. It is also called pre-exponential factor. It is a constant specific to a particular reaction. R is gas constant and Ea is activation energy measured in joules/mole ($J\ mol^{-1}$).

Concept of Activation energy: The excess energy (over and above the average energy of the reactants) which must be supplied to the reactants to undergo chemical reactions is called activation energy.
It is equal to the difference between the threshold energy needed for the reaction and the average kinetic energy of all the reacting molecules. That is,
Activation energy = Threshold energy - Average kinetic energy of the reacting molecules
Ea = Threshold energy – Energy of reactants
Low Activation energy: Fast reactions
High Activation energy: Slow reactions

It can be understood clearly using the following simple reaction:
H_2 (g) + I_2 (g)   2HI (g)



This reaction can take place only when a molecule of hydrogen and a molecule of iodine collide to form an unstable intermediate. The energy required to form this intermediate, called **activated complex**, is known as **activation energy (Ea)**.

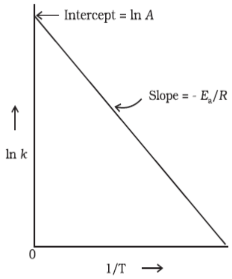


According to Arrhenius equation-

$$k = A\ e^{-Ea\ /RT}$$

Taking logarithm both side

$$\ln k = -\frac{E_a}{RT} + \ln A$$



The plot of ln k Vs 1/T gives a straight line.
Slope = – $Ea\ /R$ and intercept = ln A.
So we can calculate Ea and A using these values.

$$\ln k = -\frac{E_a}{RT} + \ln A$$

Converting to common logarithm lnX = 2.303 log X
2.303log k = 2.303log A – Ea/RT
log k = log A – Ea/2.303 RT
Let k1 and k2 are the rate constants for the reaction at two different temperatures T1 and T2 respectively.
log k_1 = log A – Ea/2.303 RT_1 …(i)

log k_2 = log A – Ea/2.303 RT_2…(ii)
Subtracting eq. (i) from (ii)
log k_2 - log k_1 = Ea/2.303 R [1/T_1 – 1/T_2]

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

Assignments:

Q1. Which of the following observations is incorrect about the order of a reaction?
a. Order of a reaction is always a whole number
b. The stoichiometric coefficient of the reactants doesn’t affect the order
c. Order of reaction is the sum of power to express the rate of reaction to the concentration terms of the reactants.
d. Order can only be assessed experimentally
Ans. (a)
Q2. In the reaction 2A + B → A_2B, order of reaction is two with respect to A and one with respect to B, if the concentration of A is doubled and that of B is halved, then the rate of the reaction will
a. decrease 2 times
b. increase 4 times
c. increase 2 times
d. remain the same
Ans. (c)
Q3. when the rate of the reaction is equal to the rate constant, the order of the reaction is
a. zero order
b. first order
c. second order
d. third order
Ans. (a)
Q4. A substance ‘A’ decomposes by a first-order reaction starting initially with [A] = 2.00M and after 200min, [A] becomes 0.15M. For this reaction $t_{1/2}$ is
a. 53.72 min
b. 50.49 min
c. 48.45 min
d. 46.45 min
Ans. (a)
Q5. A catalyst alters, which of the following in a chemical reaction?
a. Entropy
b. Enthalpy
c. Internal energy
d. Activation energy
Ans. (d)

Q6. Express the rate of the following reaction:
5 Br- (aq) + BrO_3^- (aq) + 6 H^+ (aq) → 3 Br_2 (aq) + 3 H_2O (l)

Ans. Rate = $-\frac{1}{5}\frac{\Delta[Br-]}{\Delta t} = -\frac{\Delta[BrO3-]}{\Delta t} = \frac{1}{6}\frac{\Delta[H+]}{\Delta t} = \frac{1}{3}\frac{\Delta[Br2]}{\Delta t} = \frac{1}{3}\frac{\Delta[H2O]}{\Delta t}$

Q7. For the reaction R P, the concentration of a reactant changes from 0.03M to 0.02M in 25 minutes. Calculate the average rate of reaction using units of time both in minutes and seconds.
Ans. Average rate = 4×10^{-4} mol L^{-1} min^{-1}
Rate = 6.67×10^{-6} mol L^{-1} s^{-1}

Q8. Calculate the overall order of a reaction which has the rate expression:
(a) Rate = $k\,[A]^{1/2}\,[B]^{3/2}$
(b) Rate = $k\,[A]^{3/2}\,[B]^{-1}$
Ans. (a) Second order
(b) half order.

Q9. Identify the reaction order from each of the following rate constants.
(i) $k = 2.3 \times 10^{-5}$ L mol^{-1} s^{-1}
(ii) $k = 3 \times 10^{-4}$ s^{-1}
Ans. (i) Second order reaction
(ii) first order reaction.

Q10. For a reaction, A + B Product; the rate law is given by, $r = k\,[A]^{1/2}\,[B]^{2}$.
What is the order of the reaction?
Ans. Order = 2.5

Q11. The initial concentration of N_2O_5 in the following first order reaction
N_2O_5(g) 2 NO_2 (g) + 1/2O_2 (g) was 1.24×10^{-2} mol L^{-1} at 318 K. The concentration of N_2O_5 after 60 minutes was 0.20×10^{-2} mol L^{-1}.
Calculate the rate constant of the reaction at 318 K.
Answer: $k = 0.0304$ min^{-1}

Q12. Show that in a first order reaction, time required for completion of 99.9% is 10 times of half-life ($t_{1/2}$) of the reaction.
$t = 6.909/k$
For half-life of the reaction
$t_{1/2} = 0.693/k$
$t/t_{1/2} = 10$

Q13. The rate constant for a first order reaction is 60 s^{-1}. How much time will it take to reduce the initial concentration of the reactant to its 1/16th value?
Ans. t = 2.303/k {log$[A]_0$/[A]}
= 2.303/60 {log (a/a/16)}
= 0.038 log16
= 0.038 x 1.204
= 0.046 seconds

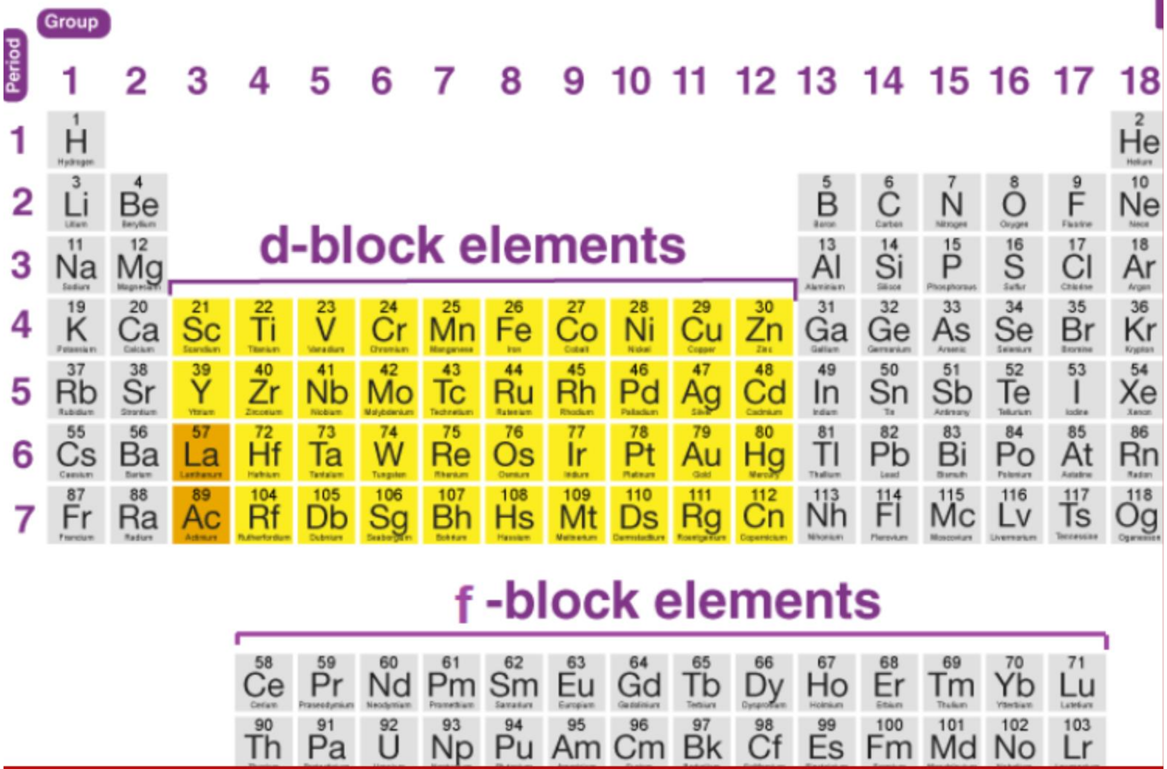
Q14. A first order reaction takes 40 min for 30% decomposition. Calculate $t_{1/2}$.

Ans. $k = 2.303/t \{\log[A]_0/[A]\}$
$= 2.303/40 \{\log (a/0.70a)\}$
$= 2.303/40 \{0.1549\}$
$k = 8.92 \times 10^{-3}\ \text{min}^{-1}$
$t_{1/2} = 0.693/k$
$t_{1/2} = 0.693/8.92 \times 10^{-3}\ \text{min}^{-1}$
$t_{1/2} = 77.7$ min.

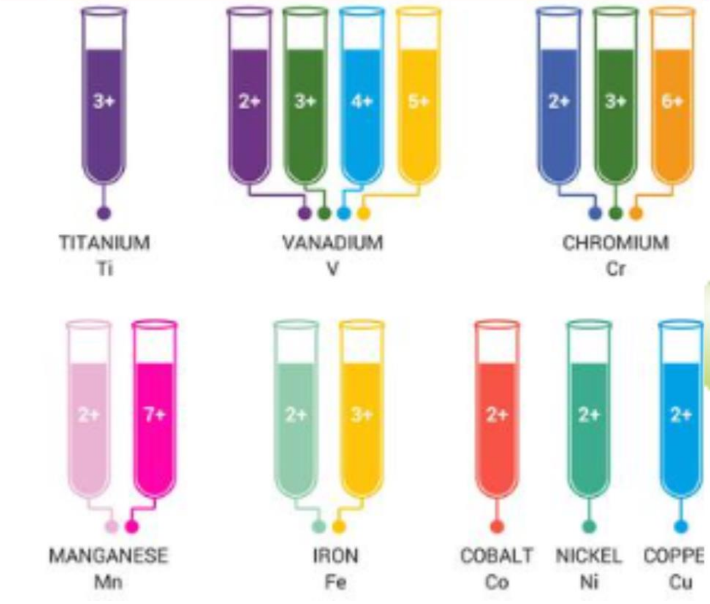
Q15. The rate of the chemical reaction doubles for an increase of 10K in absolute temperature from 298K. Calculate *E*a.
Ans. $\log k_2 - \log k_1 = Ea/2.303\ R\ [1/T_1 – 1/T_2]$
$\log k_2/k_1 = Ea/2.303\ R\ [1/T_1 – 1/T_2]$
$\log 2 = (Ea/2.303 \times 8.314)\ [1/298 – 1/308]$
$Ea = \log 2 \times 2.303 \times 8.314 \times 298 \times 308$
10
Ea = 52.898 kJ

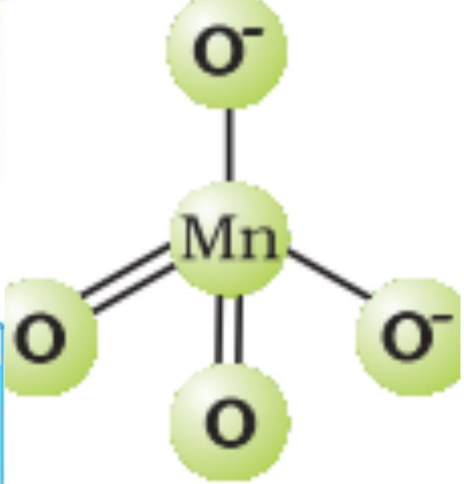
UNIT IV d-AND f-BLOCK ELEMENTS

d- & f- block elements

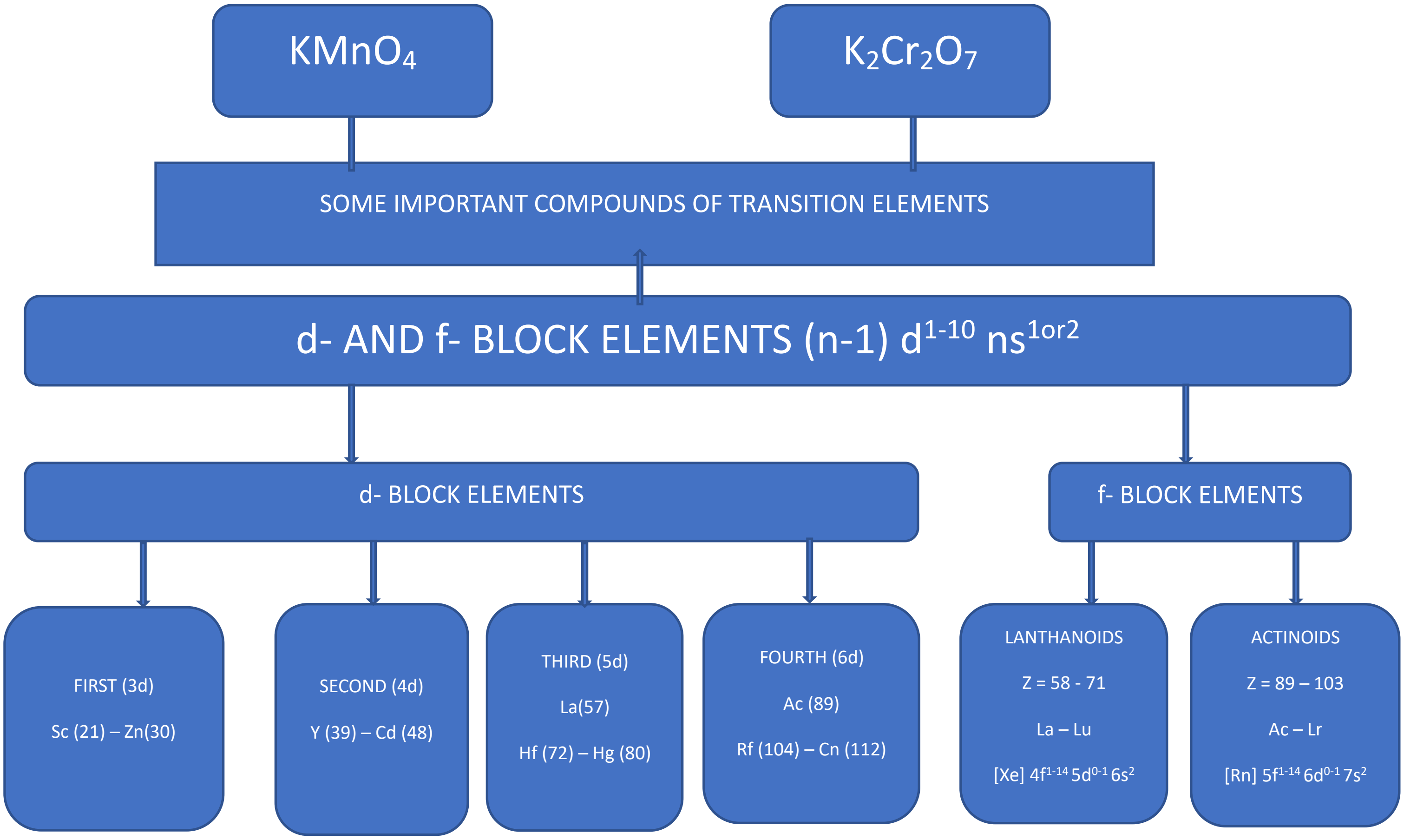


Colours in Transition metal





Tetrahedral



$KMnO_4$

$K_2Cr_2O_7$

SOME IMPORTANT COMPOUNDS OF TRANSITION ELEMENTS

d- AND f- BLOCK ELEMENTS $(n\text{-}1)\ d^{1\text{-}10}\ ns^{1or2}$

d- BLOCK ELEMENTS

f- BLOCK ELMENTS

FIRST (3d)

Sc (21) – Zn(30)

SECOND (4d)

Y (39) – Cd (48)

THIRD (5d)

La(57)

Hf (72) – Hg (80)

FOURTH (6d)

Ac (89)

Rf (104) – Cn (112)

LANTHANOIDS

Z = 58 - 71

La – Lu

[Xe] $4f^{1\text{-}14}\,5d^{0\text{-}1}\,6s^2$

ACTINOIDS

Z = 89 – 103

Ac – Lr

[Rn] $5f^{1\text{-}14}\,6d^{0\text{-}1}\,7s^2$

General introduction: The *d*-block of the periodic table contains the elements of the group's 3-12 in which the *d* orbitals are progressively filled in each of the four long periods.

The *f*-block consists of elements in which 4 *f* and 5 *f* orbitals are progressively filled. They are placed in a separate panel at the bottom of the periodic table.

The names *transition metals* and *inner transition* metals are often used to refer to the elements of *d*-and *f*-blocks respectively.

There are mainly four series of the transition metals, 3*d* series (Sc to Zn), 4*d* series (Y to Cd), 5*d* series (La and Hf to Hg) and 6*d* series which have Ac and elements from Rf to Cn.

The two series of the inner transition metals; 4*f* (Ce to Lu) and 5*f* (Th to Lr) are known as *lanthanoids* and *actinoids* respectively.

Electronic configuration of First Transition Series: The general electronic configuration of d-block elements is (n-1) d^{1-10} ns $^{1-2}$.Scandium (Z = 21) to Zinc (Z = 30)3d-orbitals are gradually filled.

Element	**Symbol**	**At. No.**	**Electronic configuration**
Scandium	Sc	21	[Ar] $3d^1$ $4s^2$
Titanium	Ti	22	[Ar] $3d^2$ $4s^2$
Vanadium	V	23	[Ar] $3d^3$ $4s^2$
Chromium	Cr	24	**[Ar] $3d^5$ $4s^1$**
Manganese	Mn	25	[Ar] $3d^5$ $4s^2$
Iron	Fe	26	[Ar] $3d^6$ $4s^2$
Cobalt	Co	27	[Ar] $3d^7$ $4s^2$
Nickel	Ni	28	[Ar] $3d^8$ $4s^2$
Copper	Cu	29	**[Ar] $3d^{10}$ $4s^1$**
Zinc	Zn	30	[Ar] $3d^{10}$ $4s^2$

General Characteristics of transition elements:

1. Nearly all the transition elements have typical metallic properties such as high tensile strength, ductility, malleability, high thermal and electrical conductivity and metallic lustre.
2. Except mercury which is liquid at room temperature, other transition elements have typical metallic structures.
3. They have high melting and boiling points and have higher heats of vaporization than non-transition elements.
4. The transition elements have very high densities as compared to the metals of groups I and II (s-block).
5. The first ionization energies of d-block elements are higher than those of s-block elements but are lesser than those of p-block elements.
6. They are electropositive in nature.
7. Most of them form-coloured compounds.
8. They have good tendency to form complexes.
9. They exhibit several oxidation state.
10. Their compounds are generally paramagnetic in nature.
11. They form alloys with other metals.
12. They form interstitial compounds with elements such as hydrogen, boron, carbon, nitrogen etc.
13. Most of the transition metals such as Mn, Ni, Co, Cr, V, Pt etc. and their compounds have been used as good catalysts.

General Properties of transition elements(first row transition metals):

1. **Ionic radii:** In general, the ionic radii decrease with increase in oxidation state. For the same oxidation state, the ionic radii generally decrease with increase in nuclear charge.
2. **Metallic character:** All transition elements are metals. The metallic character of transition elements is due to their relatively low ionization enthalpies and number of vacant orbitals in the outermost shell. The hardness of these metals suggests the

presence of strong bonding due to overlap of unpaired electrons between different metal atoms. Therefore, these elements exhibit high enthalpies of atomization. In general, the greater number of unpaired d-electrons, greater is the number of bonds and therefore, greater is strength of these bonds.

3. **Ionization enthalpies:** There is an increase in ionization enthalpy along each series of the transition elements from left to right due to an increase in nuclear charge which accompanies the filling of the inner *d* orbitals.
   Zinc has highest first ionization enthalpy in first transition series because electron has to be removed from 4s orbital of stable ($3d^{10}$ $4s^2$) configuration.
4. **Oxidation states:**The transition metals exhibit a large number of oxidation states in their compounds. Most of these show variable oxidation states. The existence of the transition elements in different oxidation states means that their atoms can lose different number of electrons. This is due to the participation of inner (n-1) d-electrons in addition to outer ns-electrons because the energies of the ns and (n-1) d-subshells are almost equal. The lower oxidation state is generally shown when only ns-electrons participate in bonding and higher oxidation states are exhibited when both ns and (n-1) d-electrons take part in bonding.

DifferentOxidation States of the first row Transition Metals

Element	**Outer electronic configuration**	**Oxidation states**
Sc	$3d^1$ $4s^2$	**+3**
Ti	$3d^2$ $4s^2$	**+2, + 3, +4**
V	$3d^3$ $4s^2$	**+2, + 3, +4, +5**
Cr	$3d^5$ $4s^1$	**+2, + 3, +4, +5, +6**
Mn	$3d^5$ $4s^2$	**+2, + 3, +4, +5, +6, +7**
Fe	$3d^6$ $4s^2$	**+2, + 3, +4, +6**
Co	$3d^7$ $4s^2$	**+2, + 3, +4**
Ni	$3d^8$ $4s^2$	**+2, + 3, +4**
Cu	$3d^{10}$ $4s^1$	**+1, +2**
Zn	$3d^{10}$ $4s^2$	**+2**

1. **Formation of Coloured ions:** The colour formation in tansition elements is due to the presence of unpaired electron which undergoes d-d transition.
   When an electron from a lower energy *d* orbital is excited to a higher energy *d* orbital, the energy of excitation corresponds to the frequency of light absorbed. This frequency generally lies in the visible region. The colour observed corresponds to the complementary colour of the light absorbed.The colour formation in tansition elements is due to the presence of unpaired electron which undergoes d-d transition

Colours of Some of the First Row Transition Metal Ions

Ion	**Outer configuration**	**Colour of the ion**
Sc(III), Ti(IV)	$3d^0$	**Colourless**
Ti(III)	$3d^1$	**Purple**

V(IV)	3d^{1}	**Blue**
V(III)	3d^{2}	**Green**
V(II), Cr(III)	3d^{3}	**Violet**
Cr(II)	3d^{4}	**Blue**
Mn(III)	3d^{4}	**Violet**
Mn(II)	3d^{5}	**Pink**
Fe(III)	3d^{5}	**Yellow**
Fe(II)	3d^{6}	**Green**
Co(III)	3d^{6}	**Blue**
Co(II)	3d^{7}	**Pink**
Ni(II)	3d^{8}	**Green**
Cu(II)	3d^{9}	**Blue**
Cu(I)	3d^{10}	**Colourless**
Zn(II)	3d^{10}	**Colourless**

2. **Magnetic properties:** When a magnetic field is applied to substances, mainly two types ofmagnetic behaviour are observed: *diamagnetism* and *Paramagnetism*.
   Diamagnetic substances are repelled by the applied field whilethe paramagnetic substances are attracted. Substances which areattracted very strongly are said to be ferromagnetic

   The magnetic moment is determined by the number of unpairedelectrons and is calculated by using the ‘spin-only’ formula

   $\mu = \surd n(n + 2)$

   where n is the number of unpaired electrons and μ is the magnetic moment in units of Bohr magneton (BM).

   Calculated Magnetic Moments (BM)

Ion	**Outer configuration**	**No. of unpaired electrons**	**Calculate Magnetic moment (BM)**
Sc(III)	3d^{0}	0	0
Ti(III)	3d^{1}	1	1.73
Ti(II)	3d^{2}	2	2.84
V(II)	3d^{3}	3	3.87
Cr(II)	3d^{4}	4	4.90
Mn(II)	3d^{5}	5	5.92
Fe(II)	3d^{6}	4	4.90
Co(II)	3d^{7}	3	3.87
Ni(II)	3d^{8}	2	2.84
Cu(II)	3d^{9}	1	1.73
Zn(II)	3d^{10}	0	0

3. **Catalytic property:** Many transition metals and their compounds act as good catalysts for various reactions. This is due to their ability to adopt multiple oxidation states and to form complexes. A few examples are
   (i) **Iron-molybdenum** is used as a catalyst in the synthesis of ammonia by Haber's process.
   (ii) **Nickel** is used in hydrogenation reactions in organic chemistry.
   (iii) **Vanadium pentaoxide, V_2O_5** is usedfor the oxidation of SO_2 to SO_3 in the contact process for the manufacture of H_2SO_4.
   (iv) **Manganese dioxide,** MnO_2 is used to catalyze the decomposition of H_2O_2 solution.
   (v) **Cobalt salts** catalyze the decomposition of bleaching powder.
   (vi) **Pt/Rh** is used in Ostwald process during manufacture of HNO_3.
   (vii) **Pd** is used in hydrogenation reactions in organic chemistry.

4. **Interstitial compounds:** Interstitial compounds are those which are formed when small atoms like H, C or N are trapped inside the crystal lattices of metals. They are usually non stoichiometric and are neither typically ionic nor covalent, for example, TiC, Mn4N, Fe3H, VH0.56 and TiH1.7, etc. The formulas quoted do not, of course, correspond to any normal oxidation state of the metal. Because of the nature of their composition, these compounds are referred to as *interstitial* compounds. The principal physical and chemical characteristics of these compounds are as follows:
   (i) They have high melting points, higher than those of pure metals.
   (ii) They are very hard, some borides approach diamond in hardness.
   (iii) They retain metallic conductivity.
   (iv) They are chemically inert.

5. **Alloys formation:** Transition metals form a large number of alloys. Alloys are homogeneous solid solutions in which the atoms of one element are distributed randomly among the atoms of the other. Because of their similar radii and other characteristics of transition elements alloys are readily formed by these metals. The best known are ferrous alloys: chromium, vanadium, tungsten, molybdenum and manganese are used for the production of a variety of steels and stainless steel. Alloys of transition metals with non-transition metals such as brass (copper-zinc) and bronze (copper-tin), are also of considerable industrial importance.

Potassium dichromate $K_2Cr_2O_7$

Preparation: It is prepared from chromite ore ($FeCr_2O_4$).

(i) Conversion of chromite ore into sodium chromate
$4\ FeCr_2O_4 + 8\ Na_2CO_3 + 7\ O_2 \rightarrow 8\ Na_2CrO_4(\text{yellow}) + 2\ Fe_2O_3 + 8\ CO_2$

(ii) Conversion of sodium chromate into sodium dichromate
$2Na_2CrO_4 + 2\ H_2SO_4 \rightarrow Na_2Cr_2O_7 + 2\ Na_2SO_4 + H_2O$

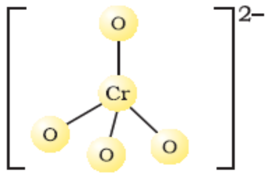
(iii) Conversion of sodium dichromate into potassium dichromate
$Na_2CrO_4 + 2\ KCl \rightarrow K_2Cr_2O_7(\text{orange}) + 2\ NaCl$

The chromates and dichromates are interconvertible in aqueous solution depending upon pH of the solution. The oxidation state of chromium in chromate and dichromate is the same.

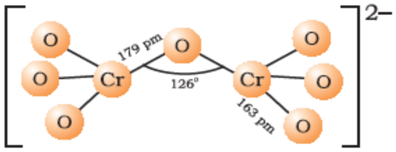
$2\,CrO_4^{2-} + 2H^+ \longrightarrow Cr_2O_7^{2-} + H_2O$

$Cr_2O_7^{2-} + 2\,OH^- \longrightarrow 2\,CrO_4^{2-} + H_2O$

The structures of chromate ion, CrO_4^{2-} and the dichromate ion, $Cr_2O_7^{2-}$. The chromate ion is tetrahedral whereas the dichromate ion consists of two tetrahedral sharing one corner with Cr–O–Cr bond angle of 126°.



Chromate ion



Dichromate ion

Properties: Sodium and potassium dichromates are strong oxidising agents; the sodium salt has a greater solubility in water and is extensively used as an oxidising agent in organic chemistry. Potassium dichromate is used as a primary standard in volumetric analysis.

In acidic solution, its oxidising action can be represented as follows:

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$ ($E^0 = 1.33V$)

Thus, acidified potassium dichromate will oxidise

(i) iodide to iodine

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

$6\,I^- \rightarrow 3I_2 + 6\,e^-$

$Cr_2O_7^{2-} + 14H^+ + 6I^- \rightarrow 3I_2 + 2Cr^{3+} + 7H_2O$

(ii) sulphide to sulphur

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

$3\,H_2S \rightarrow 6H^+ + 3S + 6e^-$

$Cr_2O_7^{2-} + 8H^+ + 3H_2S\ 3S + 2Cr^{3+} + 7H_2O$

(iii) tin(II) to tin(IV)

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

$3Sn^{2+} \rightarrow 3Sn^{4+} + 6\,e^-$

$Cr_2O_7^{2-} + 14H^+ + 3Sn^{2+}\,3Sn^{4+} + 2Cr^{3+} + 7H_2O$

(iv) iron(II) salts to iron(III).

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

$6Fe^{2+} \rightarrow 6Fe^{3+} + 6e^-$

$Cr_2O_7^{2-} + 14H^+ + 6\ Fe^{2+} 2Cr^{3+} + 6Fe^{3+} + 7H_2O$

Potassium permanganate $KMnO_4$

Potassium permanganate is prepared from mineral pyrolusite ore (MnO_2).

(i) Conversion of pyrolusite ore to potassium manganate.

$2MnO_2 + 4KOH + O_2\ 2K_2MnO_4 + 2H_2O$

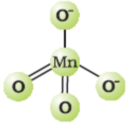
(ii) Conversion of potassium manganateto potassium permanganate.

$2K_2MnO_4 + Cl_2 \longrightarrow 2KMnO_4 + 2KCl$

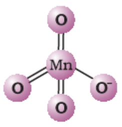
Properties: Potassium permanganate forms dark purple crystals which are isostructural with those of $KClO_4$. The salt is not very soluble in water (6.4 g/100 g of water at 293 K), but when heated it decomposes at 513 K.

$2KMnO_4 \longrightarrow K_2MnO_4 + MnO_2 + O_2$

The manganate ions (MnO_4^{2-}) and permanganate ions (MnO_4^-) are tetrahedral; the π bonding takes place by overlap of *p* orbitals of oxygen with *d* orbitals of manganese. The green manganate is paramagnetic because of one unpaired electron but the permanganate is diamagnetic due to the absence of unpaired electron.



Tetrahedral manganate ion (green)



Tetrahedral permanganate ion (purple)

Important oxidising reactions of $KMnO_4$ are given below:

1. In acid solutions:

(a) Iodine is liberated from potassium iodide:

$10I^- + 2MnO_4^- + 16H^+ \longrightarrow 2Mn^{2+} + 8H_2O + 5I_2$

(b) Fe^{2+} ion (green) is converted to Fe^{3+} (yellow):

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

(c) Oxalate ion or oxalic acid is oxidised at 333 K:

$5C_2O_4^{2-} + 2MnO_4^- + 16H^+ \longrightarrow 2Mn^{2+} + 8H_2O + 10CO_2$

(d) Hydrogen sulphide is oxidised, sulphur being precipitated:

$5S^{2-} + 2MnO_4^- + 16H^+ \longrightarrow 2Mn^{2+} + 8H_2O + 5S$

(e) Sulphurous acid or sulphite is oxidised to a sulphate or Sulphuric acid:

$5SO_3^{2-} + 2MnO4^- + 6H^+ \longrightarrow 2Mn^{2+} + 3H_2O + 5SO_4^{2-}$

(f) Nitrite is oxidised to nitrate:

$5NO_2^- + 2MnO_4^- + 6H^+ \longrightarrow 2Mn^{2+} + 5NO_3^- + 3H_2O$

2. In neutral or faintly alkaline solutions:

(a) A notable reaction is the oxidation of iodide to iodate:

$2MnO_4^- + H_2O + I^- \longrightarrow 2MnO_2 + 2OH^- + IO_3^-$

(b) Thiosulphate is oxidised almost quantitatively to sulphate:

$8MnO_4^- + 3S_2O_3^{2-} + H_2O \longrightarrow 8MnO_2 + 6SO_4^{2-} + 2OH^-$

(c) Manganous salt is oxidised to MnO2; the presence of zinc sulphate or zinc oxide catalyzes the oxidation:

$2MnO_4^- + 3Mn^{2+} + 2H_2O \longrightarrow 5MnO_2 + 4H^+$

Lanthanoids – The series involving the filling of 4f-orbitals following lanthanum La (Z=57) is called **lanthanoids series**. Cerium, Ce (Z=58) to Lutetium, Lu ((Z=71).

1. **Electronic configuration of lanthanoids:**

Element	**Symbol**	**At. No.**	**Electronic configuration**
Lanthanum	La	57	$[Xe]\ 5d^1\ 6s^2$
Cerium	Ce	58	$[Xe]\ 4f^2 5d^0\ 6s^2$
Praseodymium	Pr	59	$[Xe]\ 4f^3 5d^0\ 6s^2$
Neodymium	Nd	60	$[Xe]\ 4f^4 5d^0\ 6s^2$
Promethium	Pm	61	$[Xe]\ 4f^5 5d^0\ 6s^2$
Samarium	Sm	62	$[Xe]\ 4f^6 5d^0\ 6s^2$
Europium	Eu	63	$[Xe]\ 4f^7 5d^0\ 6s^2$
Gadolinium	Gd	64	$[Xe]\ 4f^8 5d^0\ 6s^2$
Terbium	Tb	65	$[Xe]\ 4f^9 5d^0\ 6s^2$
Dysprosium	Dy	66	$[Xe]\ 4f^{10} 5d^0\ 6s^2$
Holmium	Ho	67	$[Xe]\ 4f^{11} 5d^0\ 6s^2$
Erbium	Er	68	$[Xe]\ 4f^{12} 5d^0\ 6s^2$
Thulium	Tm	69	$[Xe]\ 4f^{13} 5d^0\ 6s^2$
Ytterbium	Yb	70	$[Xe]\ 4f^{14} 5d^0\ 6s^2$
Lutetium	Lu	71	$[Xe]\ 4f^{14} 5d^1\ 6s^2$

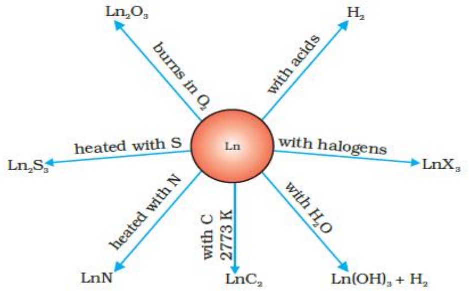
Oxidation states: All lanthanoids exhibit a common stable oxidation state of +3.In addition some lanthanoids show +2 and +4 oxidation states also in solution or in solid compounds.

(i) Cerium(Ce) and Terbium(Tb) exhibit +4 oxidation states.
Ce^{4+}: $[Xe]\ 4f^0$
Tb^{4+}: $[Xe]\ 4f^7$

(ii) Europium(Eu)and Ytterbium(Yb)exhibit +2 oxidation states.
Eu^{2+}: $[Xe]\ 4f^7$
Yb^{2+}: $[Xe]\ 4f^{14}$

(iii) Lanthanum(La),Gadolinium(Gd) andLutetium(Lu)exhibit only +3 oxidation states.
La^{3+}: $[Xe]\ 5d^0\ 6s^0$
Gd^{3+}: $[Xe]\ 4f^7\ 5d^0\ 6s^0$
Lu^{3+}: $[Xe]\ 4f^{14}\ 5d^0\ 6s^0$

Chemical reactivity:



Lanthanide contraction and its Consequences: The steady decrease in atomic and ionic sizes of lanthanide elements with increasing atomic number is called Lanthanide contraction.

Cause of Lanthanide contraction:

In the lanthanide series, as we move from one element to another, the nuclear charge increases by one unit and one electron is added. The new electrons are added to the same inner 4f-subshells. However, theshielding of one 4 *f* electron by another is lessthan one *d* electron by another with the increasein nuclear charge along the series. There isregular decrease in the sizes withincreasing atomic number.

Consequences of Lanthanide contraction: The important consequences of Lanthanide contraction are:

1. **Resemblance of second and third transition series**: As a result of Lanthanide contraction, the elements of second and third transition series resemble each other much more than the elements of first and second transition series.
2. **Similarities among lanthanoids**: Because of very small change in radii of lanthanoids, their chemical properties are quite similar. Thus, it is very difficult to separate the elements in pure state.
3. **Basicity differences**: Due to Lanthanide contraction, the size of the lanthanoids ions decreases regularly with increase in atomic number. As a result of decrease in size, their covalent character between lanthanoids ion and OH^- ions increases from La^{3+} to Lu^{3+}. Therefore, **the basic strength of the hydroxides decreases with increase in atomic number. Thus, La $(OH)_3$ is most basic while $Lu(OH)_3$ is the least basic.**

Actinoids -The Actinoids includes the fourteen elements from Th to Lr .The name ,symbol and electronic configuration of these elements are given below

Electronic configuration of Actinoids:

Element	**Symbol**	**At. No.**	**Electronic configuration**
Actinium	Ac	89	[Rn] $6d^1 7s^2$
Thorium	Th	90	[Rn] $5f^1 6d^1 7s^2$ or $6d^2 7s^2$
Protactinium	Pa	91	[Rn] $5f^2 6d^1 7s^2$
Uranium	U	92	[Rn] $5f^3 6d^1 7s^2$
Neptunium	Np	93	[Rn] $5f^4 6d^1 7s^2$

Plutonium	Pu	94	[Rn] $5f^{6}6d^{0}7s^{2}$
Americium	Am	95	[Rn] $5f^{7}d^{0}7s^{2}$
Curium	Cm	96	[Rn] $5f^{7}6d^{1}7s^{2}$
Berkelium	Bk	97	[Rn] $5f^{9}6d^{0}7s^{2}$
Californium	Cf	98	[Rn] $5f^{10}6d^{0}7s^{2}$
Einsteinium	Es	99	[Rn] $5f^{11}6d^{0}7s^{2}$
Fermium	Fm	100	[Rn] $5f^{12}6d^{0}7s^{2}$
Mendelevium	Md	101	[Rn] $5f^{13}6d^{0}7s^{2}$
Nobelium	No	102	[Rn] $5f^{14}6d^{0}7s^{2}$
Lawrencium	Lr	103	[Rn] $5f^{14}6d^{1}7s^{2}$

Oxidation states: Actinoids show different oxidation state such as +2, +3, +4, +5, +6 and +7. However, +3 oxidation states are most common among all the actinoids. The greater range of oxidation state is due to the fact that 5f, 6d and 7s levels are of comparable energies.

Comparison with lanthanoids:

Some of the important points of similarities and differences are given below:

Similarities between lanthanoids and actinoids:

1. Both exhibits +3 oxidation state.
2. Both involve the filling of f-orbitals.
3. Both having same number of unpaired electrons have quite similar spectra. In the absorption spectra of the elements of both the series, sharp lines like bands appear due to f-f transition.
4. Both are electropositive and have high reactivity.
5. Like lanthanoids contraction, there is actinoids contraction. These contractions are due to poor shielding of 5f and 4f electrons in lanthanoids and actinoids respectively.

Differences between lanthanoids and actinoids:

Property	Lanthanoids	Actinoids
Oxidation state	Show mainly +3, except in a few cases where it is +2 and +4	+3 and also show higher oxidation state +4, +5, +6 and +7.
Shielding effect	4f electrons have greater shielding effect. Contraction in their ionic radii is less.	5f electrons have poor shielding effect. Contraction in their ionic radii is more.
Basic character	Less basic	More basic
Tendency to form Oxo ions	They do not form Oxo ions	They form Oxo ions UO_2^+, NpO_2^+, PuO_2^+
Colours	Most of their ions are colourless.	Most of the actinoids ions are coloured. UO_2^+ (yellow)

ASSIGNMENTS:

Q1. The number of unpaired electrons in gaseous species of Mn^{3+}, Cr^{3+} and V^{3+} respectively are:

(a) 4, 4 and 2
(b) 3, 3 and 2
(c) 4, 3 and 2

(d) 3, 3 and 3

Ans. (c)

Q2. Gun metal is an alloy of:

(a) Cu and Al
(b) Cu and Sn
(c) Cu, Zn and Sn
(d) Cu, Zn and Ni

Ans. (c)

Q3. Which one of the following elements shows the maximum number of different oxidation states in its compounds?

(a) Eu
(b) La
(c) Cd
(d) Am

Ans. (d)

Q4. Which of the following characteristics of transition elements is associated with their catalytic activities?

(a) Paramagnetic nature
(b) Colour of hydrated ion
(c) High enthalpy of atomisation
(d) Variable oxidation state

Ans. (d)

Q5. Zinc and mercury do not show variable valency like d-block elements because

(a) they are soft
(b) their d-shells are complete
(c) they have only two electrons in the outermost subshell.
(d) their d-shells are incomplete

Ans. (b)

Q6. $KMnO_4$ acts as an oxidising agent in alkaline medium. when alkaline $KMnO_4$ is treated with KI , iodide ion is oxidised to.......

a) I_2
b) IO^-
c) IO_3^-
d)IO_4^-

Ans. (c)

Q7. The pair that has similar atomic radii is

(a) Mn and Re
(b) Ti and Hf
(c) Sc and Ni
(d) Mo and W

Ans. (d)

Q8. The most common oxidation state of lanthanoid is

(a) +3
(b) +2
(c) +4
(d) +6

Ans. (a)

Q9. Lanthanoid contraction is due to increase in

(a) atomic number
(b) effective nuclear charge
(c) atomic radius
(d) valence electrons

Ans. (b) effective nuclear charge

Q10. Generally transition elements form coloured salts due to the presence of unpaired electron .which of the following compounds are coloured in solid state.

(a) Ag_2SO_4
(b) CuF_2
(c) ZnF_2
(d) Cu_2Cl_2

Ans. (b)

Q11. Why is Cr^{2+} reducing and Mn^{3+} oxidising when both have d^4 configuration?

Ans. Cr^{2+} is reducing as its configuration changes from d^4 to d^3, the latter having a half-filled t_{2g} level. On the other hand, the change from Mn^{3+} to Mn^{2+} results in the half-filled (d^5) configuration which has extra stability.

Q12. (i) Explain why Cu+ ion is not stable in aqueous solutions?

(ii) How would you account for the increasing oxidising power in the series?

$VO_2^+ < Cr_2O_7^{2-} < MnO_4^-$?

Ans. (i) because less negative enthalpy of hydration than of Cu^{2+}.

(ii) This is due to the increasing stability of the lower species to which they are reduced.

Q13. Why is the E^0value for the Mn^{3+}/Mn^{2+} couple much more positivethan that for Cr^{3+}/Cr^{2+} or Fe^{3+}/Fe^{2+}? Explain.

Ans. Much larger third ionization energy of Mn (where the required change is d^5 to d^4) is mainly responsible for this.

Q14. Calculate the magnetic moment of a divalent ion in aqueous solution if its atomic number is 25.

Ans. With atomic number 25, the divalent ion in aqueous solution will have d^5 configuration (five unpaired electrons). The magnetic moment, μ is $\mu = \sqrt{5(5+2)} = 5.92$BM

Q15. What is meant by 'disproportionation' of an oxidation state? Give an example.

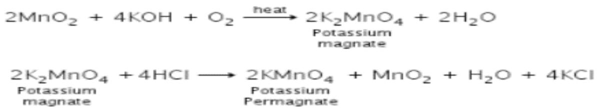
Ans. When a particular oxidation state becomes less stable relative to other oxidation states, one lower, one higher, it is said to undergo disproportionation.
For example, manganese (VI) becomes unstable relative to manganese (VII) and manganese (IV) in acidic solution.
$3\,Mn^{VI}O_4^{2-} + 4\,H^+ \rightarrow 2\,Mn^{VII}O_4^{-} + Mn^{IV}O_2 + 2H_2O$

Q16. What are interstitial compounds? Why are such compounds well known for transition metals?
Ans. The small atoms (H, B, C, N) get trapped in vacant spaces of the lattices of the transition metal atoms.

Q17. (i) Name a member of the lanthanoids series which is well known to exhibit +4 oxidation state.
(ii) Actinoids contraction is greater from element to element than lanthanoids contraction. Why?
(iii) Which out of Lu $(OH)_3$ and $La(OH)_3$ is more basic and why?
Ans. (i) Cerium ($Z = 58$)
(ii) This is because of poor shielding by 5f electrons in actinoids in comparison with shielding of 4f electrons in lanthanoids.
(iii) La $(OH)_3$ is more basic than Lu $(OH)_3$ due to lanthanoids contraction.

Q18. (a)Indicate the steps in the preparation of $K_2Cr_2O_7$ from chromite ore.
(b) What is the effect of increasing pH on a solution of potassium dichromate?
(c) Describe the oxidising action of potassium dichromate and write the ionic equations for its reaction with: (i) Iodide (ii) iron(II) solution and (iii) H_2S
Write the ionic equations for the reactions.
Ans. (a) Give preparation
(b) $Cr_2O_7^{2-} + H_2O \rightleftharpoons 2CrO_4^{2-} + 2H^+$
(c) Give equations

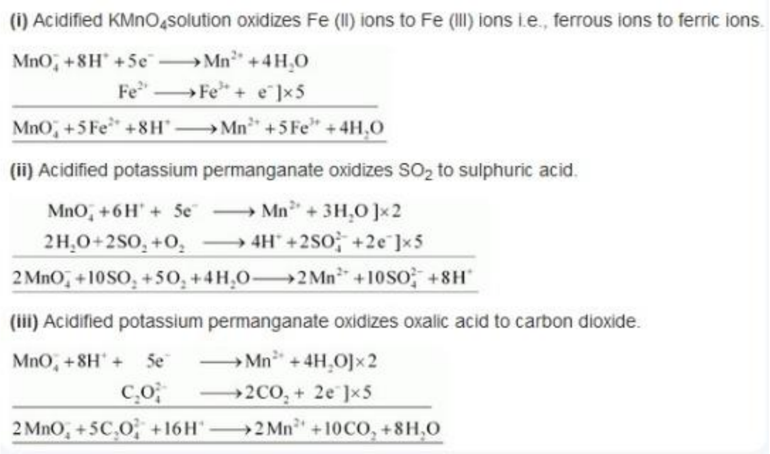
Q19. (a)Indicate the steps in the preparation of $KMnO_4$ from pyrolusite ore.
(b) Describe the preparation of potassium permanganate. How does the acidified permanganate solution react with (i) iron(II) ions (ii) SO_2 and (iii) oxalic acid?
Write the ionic equations for the reactions.
Ans. (a)



$2MnO_2 + 4KOH + O_2 \xrightarrow{heat} \underset{\text{Potassium magnate}}{2K_2MnO_4} + 2H_2O$

$\underset{\text{Potassium magnate}}{2K_2MnO_4} + 4HCl \longrightarrow \underset{\text{Potassium Permagnate}}{2KMnO_4} + MnO_2 + H_2O + 4KCl$

(b)



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

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

(ii) Acidified potassium permanganate oxidizes SO_2 to sulphuric acid.

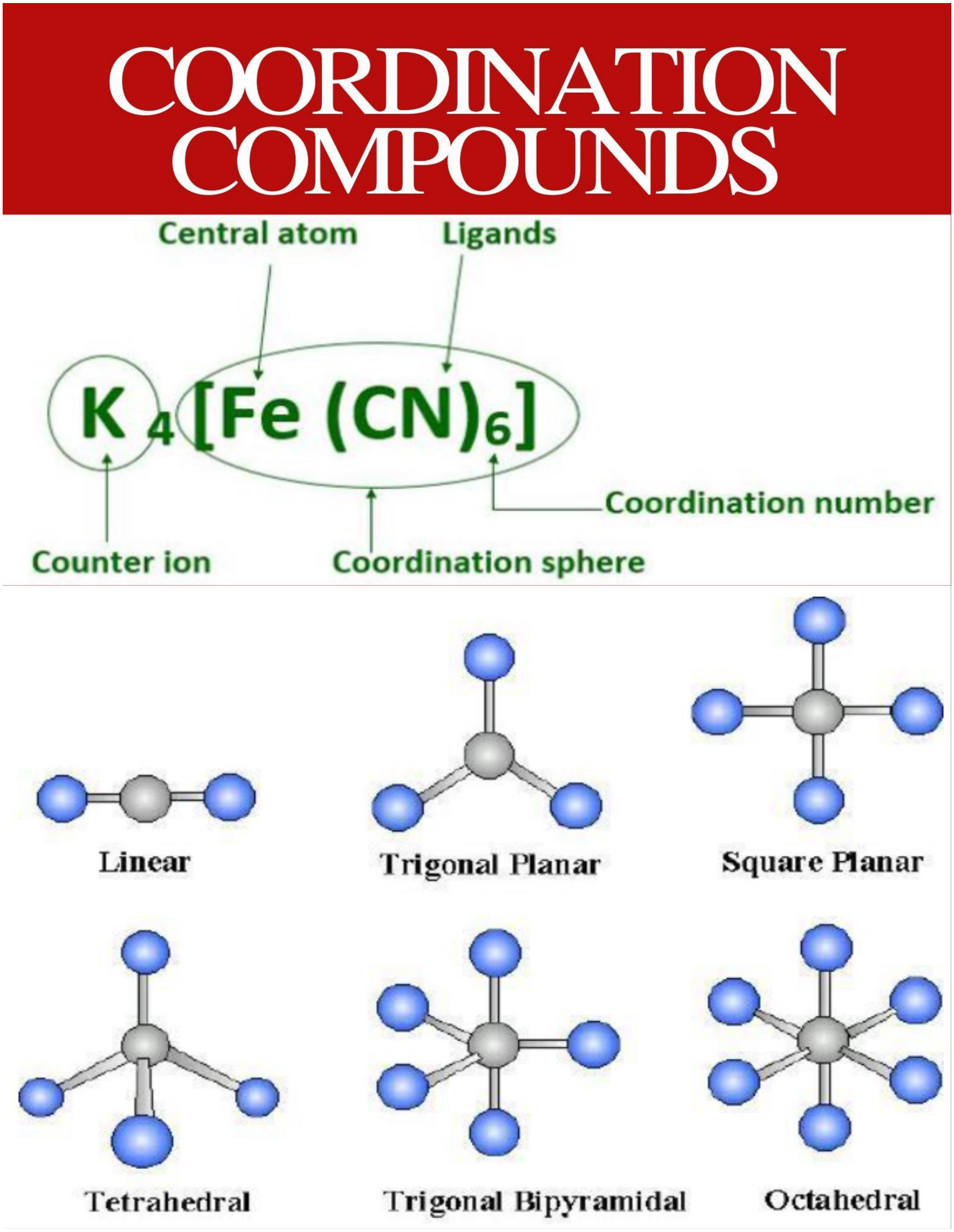
$$MnO_4^- + 6H^+ + 5e^- \longrightarrow Mn^{2+} + 3H_2O]\times 2$$
$$2H_2O + 2SO_2 + O_2 \longrightarrow 4H^+ + 2SO_4^{2-} + 2e^-]\times 5$$
$$\underline{2MnO_4^- + 10SO_2 + 5O_2 + 4H_2O \longrightarrow 2Mn^{2+} + 10SO_4^{2-} + 8H^+}$$

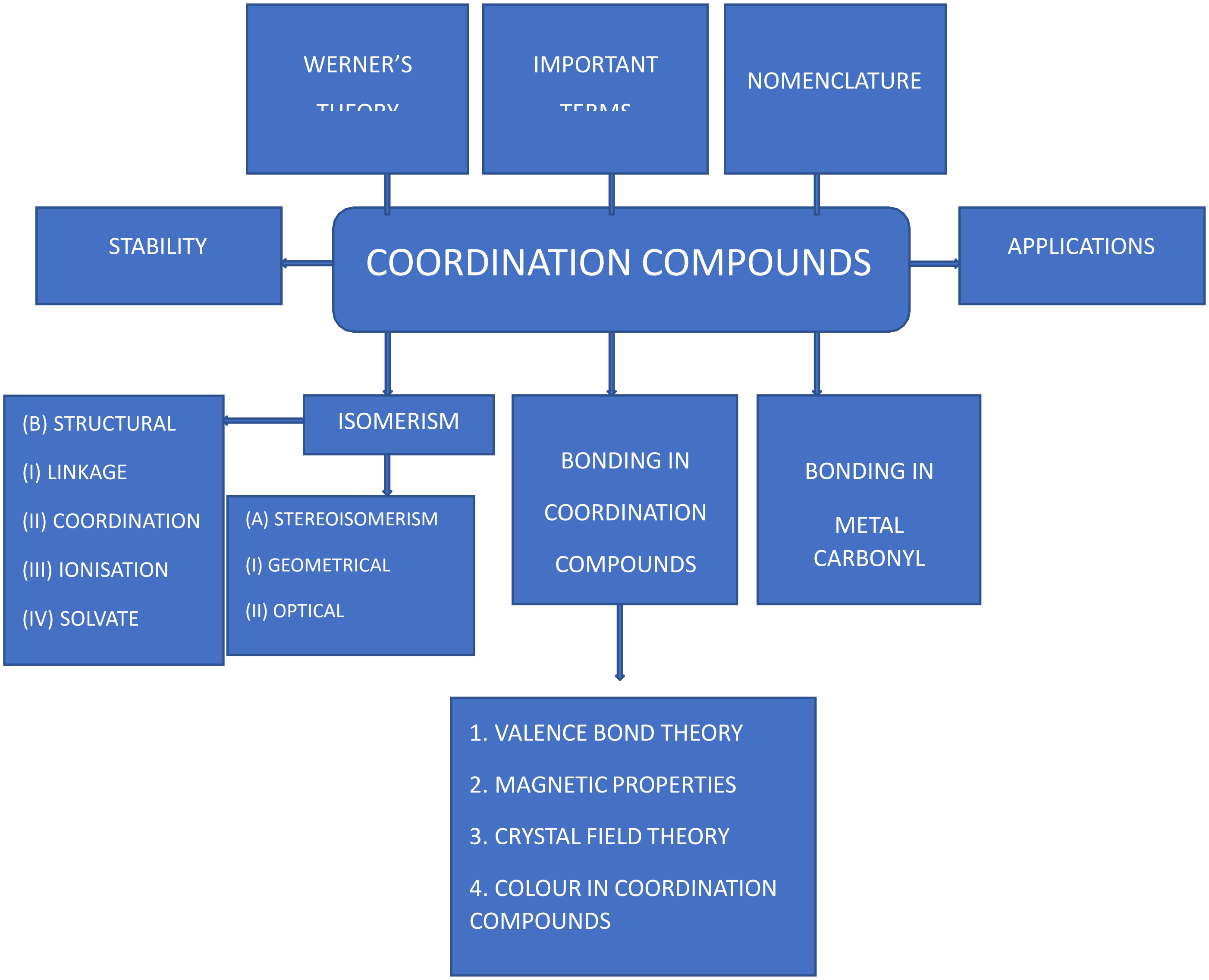
(iii) Acidified potassium permanganate oxidizes oxalic acid to carbon dioxide.

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O]\times 2$$
$$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-]\times 5$$
$$\underline{2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O}$$

Q20. Explain giving reasons:
(i) Transition metals and many of their compounds show paramagnetic behaviour.
(ii) The enthalpies of atomization of the transition metals are high.
(iii) The transition metals generally form coloured compounds.
(iv)Transition metals and their many compounds act as good catalyst.
(v) Scandium ($Z = 21$) is a transition element but zinc ($Z = 30$) is not?

Ans. (i) due to unpaired d-electrons.
(ii) Because of large number of unpaired electrons in their atoms they have stronger interatomic interaction and hence stronger bonding between atoms resulting in higher enthalpies of atomization.
(iii) unpaired d-electron which undergoes d-d transition
(iv) Due to the presence of vacant orbitals or their tendency to form variable oxidation state.
(v) On the basis of incompletely filled 3*d* orbitals in case of scandium atom in its ground state ($3d^1$), it is regarded as a transition element. On the other hand, zinc atom has completely filled *d* orbitals ($3d^{10}$) in its ground state as well as in its oxidised state; hence it is not regarded as a transition element.


COORDINATION COMPOUNDS
Central atom
Ligands
K
4
[Fe (CN)
6
]
Coordination number
Counter ion
Coordination sphere
Linear
Trigonal Planar
Square Planar
Tetrahedral
Trigonal Bipyramidal
Octahedral



Coordination compounds are a special class of compounds in which the central metal atom is surrounded by ions or molecules beyond their normal valency. These compounds are widely present in the minerals, plants and animals and play many important functions. Many biologically important compounds are Coordination compounds in which complicated organic species are bound to metal ions. The common examples are: **Haemoglobin** which is a Coordination compound of **Iron**, **Chlorophyll** which is a Coordination compound of **Magnesium** and **Vitamin B_{12}** which is a Coordination compound of **Cobalt** etc.The Coordination compounds are also finding extensive applications in metallurgical processes, analytical chemistry, industrial catalysts, textile dyeing, electroplating and medicinal chemistry.

Coordination compounds are molecular compounds which are formed from the combination of two or more simple stable compounds and retain their identity in the solid as well as in the dissolved state. For example, when aqueous ammonia is added to green solution of nickel chloride, $NiCl_2$, the colour changes to $[Ni (NH_3)_6] Cl_2$ purple crystals. Such a compound is called Coordination compounds.

$NiCl_2$ (Green) + $6NH_3$ ---------------------- > $[Ni (NH_3)_6] Cl_2$ (Purple)

When the compound $[Ni (NH_3)_6] Cl_2$ is dissolved in water it ionizes to give a new species. Such an ion is called complex ion $[Ni (NH_3)_6]^{2+}$.

$[Ni (NH_3)_6] Cl_2$----------------------- > $[Ni (NH_3)_6]^{2+} + 2Cl^-$

Coordination compounds are the compounds in which the central metal atom is bound to a number of anions or neutral molecules by coordinate bonds.

Coordination entity and Coordination sphere:

Coordination entity: A coordination entity constitutes a central metal atom or ion bounded to a fix number of oppositely charged ions or neutral molecules. For example, $[Co Cl_3 (NH_3)_3]$

Coordination sphere: The central metal atom or ion and the molecules or ions bonded to it are enclosed ina square bracket and a collectively called the **Coordination sphere.**

Central atom or ion and Ligands:

Central atom or ion: The atom or ion to which a fixed number of neutral molecules or ions are attached inthe coordination entity is called **Central atom or ion.**

Ligands: The neutral molecules or ions bonded to the central atom or ion in the coordination entity are called **ligands.** For example,

$[Ni (NH_3)_6]^{2+}$: Central atom = Ni^{2+}, ligands = NH_3 molecules

Types of ligands:

(i) **Unidentate or monodentate ligands:** When a ligand is bound to a metal ion through a singledonor atom, as with Cl^-, H_2O or NH_3, the ligand is said to be **Unidentate ligands**.

(ii) **Didentate** or **Bidentate ligands:** When a ligand can bind through two donor atoms as in $H_2NCH_2CH_2NH_2$ (ethane-1, 2-diamine) or $C_2O_4^{2-}$ (oxalate), the ligand is said to be **Didentateligands.**

(iii) **Polydentate ligands:** Ligands having more the two donor atoms present in the **molecule,** theligands are said to be **Polydentate ligands**.
Diethylene triamine acts as **tridentate ligand** having three donor N atoms. Triethylene tetra amine acts as **tetradentate ligand** having four donor N atoms.

Ethylenediamine triacetate ion acts as **Pentadentate ligand** having two N atoms and three O atoms. Ethylenediaminetetraacetate ion ($EDTA^{4-}$) is an important **hexadentate ligand**. It can bind through two nitrogen and four oxygen atoms to a central metal ion.

When a di- or Polydentate ligand uses its two or more donor atoms simultaneously to bind a single metal ion, it is said to be a **chelate ligand**. The number of such ligating groups is called the denticity of the ligand. Such complexes, called chelate complexes tend to be more stable than similar complexes containing Unidentate ligands.

Ligand which has two different donor atoms and either of the two ligates in the complex is called

ambidentate ligand.

Examples of such ligands are the NO_2^- and SCN^- ions. NO_2^- ion can coordinate either through nitrogen or through oxygen to a central metal atom/ion.
Similarly, SCN^- ion can coordinate through the sulphur or nitrogen atom.
Coordination number: The total number of ligands attached to a central metal atom or ion is called the Coordination number of that metal atom or ion. For example,
$[Ni(NH_3)_4]^{2+}$: C.N. of $Ni^{2+} = 4$
$[CoCl_3(NH_3)_3]$: C.N. of $Co^{3+} = 6$

TYPES OF COMPLEX IONS

The complex ions can be grouped into three classes depending upon the nature of charge they carry : Co – ordination Compounds
1. Complex cation : A complex ion that has a net positive charge is called a complex cation, e.g., tetraamminecopper (II), $[Cu(NH_3)_4]^{2+}$

2. Complex anion : A complex ion that has a net negative charge is called a complex anion, e.g., hexacyanoferrate (II), $[Fe(CN)_6]^{-4}$
.
3. Neutral Complex : A complex that has no net charge is called a neutral complex, e.g.,hexacarbonyl chromium(0), $[Cr(CO)_6]$.

IUPAC nomenclature of coordination compounds: Write the IUPAC names of the followingcoordination compounds:

1. The positive part of a coordination compound is named first and is followed by the negative

part.

2. The ligands are named first followed by the central metal. The prefixes di- tri-, tetra- etc,

are used to indicate the number of each kind of ligand present. The prefixes bis (two ligands) tris (three ligands) etc. are used when the polydentate ligands surround the central atom.

3. The ligands are named in alphabetical order. Names of the anionic ligands end in O, those

of cationic in ium. Neutral ligands have their regular names except that H_2O is named aqua;

NH_3 ammine; NO nitrosyl; and CO carbonyl.

4. There are three types of Monodentate ligand (Negative) F^-, Neutral Water H_2O, Positive Nitonium (NO^+)

5. The oxidation state of the central metal is indicated in roman numbers in a bracket.

6. When a complex species has negative charge, the name of the central metal ends in –ate. For some elements, the name of ion is based on the latin name of the metal (For example, argentate for silver).

ANIONIC LIGAND	**NAME**	**CHARGE**	**BIDENTATE LIGAND**	NAME	**CHARGE**
Fluoride (F^-)	Fluorido	-1	Sulphate SO_4^{2-}	Sulphato	-2
Chloride (Cl^-)	Chlorido	-1	Oxalate $C_2O_4^{2-}$	Oxalato	-2
Bromide (Br^-)	Bromido	-1	Nitrite O-–N=O	Nitrito	-2
Iodine (I^-)	Iodoido	-1	Sulphite SO_3	Sulphito	-2
Cyanide (CN^-)	Cyano/ cyanido	-1	Oxide (O^{2-})	Oxo	-2
Hydroxide (OH^-)	Hydroxo	-1	**BIDENTATE NEUTRAL LIGAND**		
Nitrate NO_2^-	Nitro	-1	Ethylenediamine	Ethane-1,2-diamine	0
Hydride H^-	Hydrido	-1			
			POLYDENTATE LIGAND		
NEUTRAL LIGANDS	**NAME**		EDTA $^{4-}$ ION (ethylene diamine tetraacetate ion)	$(^-OOC{-}CH_2)_2\mathbf{N}{-}C_2H_4{-}\mathbf{N}(CH_2{-}COO^-)_2$	4^-
Ammonia, NH_3	Ammine	0	**Number of identical ligands**	**prefix used when the ligand name is simple**	**prefix used when the ligand is polydentate or its name already has a *di-*, *tri-*, *tetra-* etc.**
Carbon monoxide, CO	Carbonyl	0	2	di	bis
Nitric oxide, NO	Nitosyl	0	3	Tri	tris
CATIONIC LIGAND	NAME	CHARGE	4	Tetra	tetrakis
Nitrosonium NO^+		+1	5	Penta	pentakis
Nitronium NO_2^+		+1	6	Hexa	hexakis
Hydrazinium NH_2NH_2		+1			

Latin terms for select metal Ions Transition Metal

Name of the Metal	Latin Name	Symbol
Copper	Cuprate	Cu
Gold	Aurate	Au
Iron	Ferrate	Fe
Lead	Plumbate	Pb
Silver	Argentate	Ag
Tin	Stannate	Sn

(a) $[Pt(NH_3)_2Cl(NO_2)]$

(b) $K_3[Cr(C_2O_4)_3]$

(c) $[CoCl_2(en)_2]Cl$

(d) $[Co(NH_3)_5(CO_3)]Cl$

(e) $Hg[Co(SCN)_4]$

(f) $[Cr(NH_3)_3(H_2O)_3]Cl_3$

(g) $[Co(H_2NCH_2CH_2NH_2)_3]_2(SO_4)_3$

(h) $[Ag(NH_3)_2][Ag(CN)_2]$

(a) Diamminechloridonitrito-N-platinum (II)

(b) Potassium trioxalatochromate (III)

(c) Dichloridobis (ethane-1, 2-diamine) cobalt (III) chloride

(d) Pentaamminecarbonatocobalt (III) chloride

(e) Mercury (I) tetrathiocyanato-S-cobaltate (III)

(f) Triamminetriaquachromium (III) chloride

(g) Tris (ethane-1,2–diamine)cobalt(III) sulphate

(h) Diamminesilver (I) dicyanidoargentate (I)

FORMULAS OF MONONUCLEAR COORDINATION ENTITIES

The following rules are applied while writing the formulas:

(i) The central atom is listed first.

(ii) The ligands are then listed in alphabetical order. The placement of a ligand in the list does not depend on its charge.

(iii) Polydentate ligands are also listed alphabetically. In case of abbreviated ligand, the first letter of the abbreviation is used to determine the position of the ligand in the alphabetical order.

(iv) The formula for the entire coordination entity, whether charged or not, is enclosed in square brackets. When ligands are polyatomic, their formulas are enclosed in parentheses. Ligand abbreviations are also enclosed in parentheses.

(v) There should be no space between the ligands and the metal within a coordination sphere.

(vi) When the formula of a charged coordination entity is to be written without that of the counter ion, the charge is indicated outside the square brackets as a right superscript with the number before the sign. For example, [Co(CN)6]3–, [Cr(H2O)6]3+, etc.
(vii) The charge of the cation(s) is balanced by the charge of the anion(s).

Werner's theory: Werner proposed the concept of a primary valence and a secondary valence for a metal ion. Binary compounds such as $CrCl_3$, $CoCl_2$ or $PdCl_2$ have primary valence of 3, 2 and 2 respectively.
In a series of compounds of cobalt (III) chloride with ammonia, it was found that some of the chloride ions could be precipitated as AgCl on adding excess silver nitrate solution in cold but some remained in solution.1 mol $CoCl_3.6NH_3$ (Yellow) gave 3 mol AgCl
1 mol $CoCl_3.5NH_3$ (Purple) gave 2 mol AgCl
1 mol $CoCl_3.4NH_3$ (Green) gave 1 mol AgCl
1 mol $CoCl_3.4NH_3$ (Violet) gave 1 mol AgCl
Werner proposed the term secondary valence for the number of groups bound directly to the metal ion; ineach of these examples the secondary valences are six.

Formulation of Cobalt (III) Chloride-Ammonia Complexes:

Colour	Formula	Solution conductivity corresponds to
Yellow	$[Co (NH_3)_6]^{3+} 3Cl^-$	1:3
Purple	$[Co Cl (NH_3)_5]^{2+} 2Cl^-$	1:2
Green	$[Co Cl_2 (NH_3)_4]^+ Cl^-$	1:1
Violet	$[Co Cl_2 (NH_3)_4]^+ Cl^-$	1:1

The main postulates are:

1. In coordination compounds metals show two types of linkages (valences)-primary and secondary.
2. The primary valences are normally ionisable and are satisfied by negative ions.
3. The secondary valences are non-ionisable. These are satisfied by neutral molecules or negative ions. Thesecondary valence is equal to the coordination number and is fixed for a metal.
4. The ions/groups bound by the secondary linkages to the metal have characteristic spatial arrangementscorresponding to different coordination numbers.

Valence Bond Theory (VBT) for bonding in Coordination Compounds:

The main assumptions of this theory are listed below:

1. The central metal ion in the complex makes available a number of empty orbitals for the formationof coordination bonds with suitable ligands.
2. The number of empty orbitals made available for this purpose is equal to coordination number of thecentral metal ion. For example, if coordination number is 6, six empty orbitals are made available and if coordination number is 4, four empty orbitals are made available in the central metal ion.
3. The appropriate atomic orbitals (s, p and d) of the metal hybridize to give a set of equivalent orbitalsof definite geometry such as square planar, tetrahedral and octahedral and so on.

4. The d-orbitals involved in the hybridization may be either inner d-orbitals i.e. (n-1) d or outer d- orbitals i.e. nd. For example, in case of octahedral hybridization. The orbitals may be two 3d, one 4sand three 4p (d^2sp^3) or one 4s, three 4p and two 4d (sp^3d^2)
5. Each ligand has at least one orbital (of donor atom)) containing a lone pair of electrons.
6. The empty hybrid orbitals of metal ion overlap the filled orbitals of the ligand to form metal-ligandcoordinate covalent bonds.

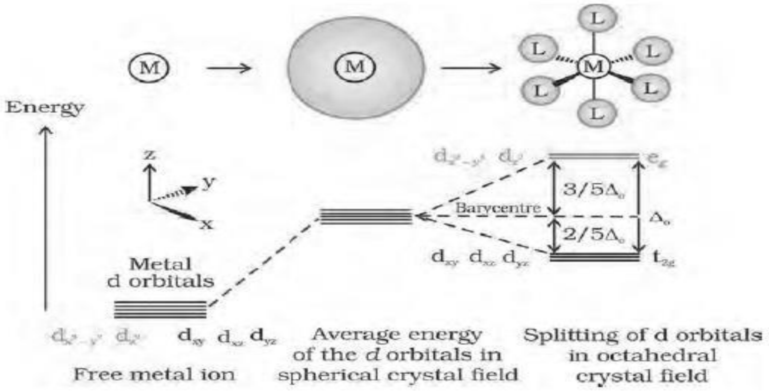
Number of Orbitals, Types of Hybridizations and Magnetic Properties of Coordination Compounds:

Coordination number	**Type of hybridization**	**Complex/ion**	**Geometry**	**No. of unpaired electrons**	**Magnetic Character**
4	sp^3	$[NiCl_4]^{2-}$	Tetrahedral	2	Paramagnetic
4	dsp^2	$[Ni(CN)_4]^{2-}$	Square planar	0	Diamagnetic
6	sp^3d^2	$[CoF_6]^{3-}$	Octahedral	4	Paramagnetic
6	d^2sp^3	$[Co(NH_3)_6]^{3+}$	Octahedral	0	Diamagnetic

CRYSTAL FIELD THEORY (CFT): The crystal field theory (CFT) is an electrostatic model which considers the metal-ligand bond to be ionic arising purely from electrostatic interactions between the metal ion and the ligand. Ligands are treated as point charges in case of anions or point dipoles in case of neutral molecules. The five *d* orbitals in an isolated gaseous metal atom/ion have same energy, *i.e.,* they are degenerate. This degeneracy is maintained if a spherically symmetrical field of negative charges surrounds the metal atom/ion. However, when this negative field is due to ligands (either anions or the negative ends of dipolar molecules like NH_3 and H_2O) in a complex, it becomes asymmetrical and the degeneracy of the *d* orbitals is lifted. It results in splitting of the *d* orbitals. The pattern of splitting depends upon the nature of the crystal field.

The conversion of five degenerate d-orbitals of the metal ion into different sets of orbitals having different energies in the presence of electric field of ligand is called **crystal field splitting**.

(a) Crystal field splitting in octahedral coordination entities:



d orbital splitting in an octahedral crystal field (fig. 9.8 ncert)

Spectrochemical series: ligands can be arranged in a series in the order of increasing field strength as givenbelow:

$I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4{}^{2-} < H_2O < NCS^- < edta^{4-} < NH_3 < en < CN^- < CO$

No light absorbed, all reflected get white color

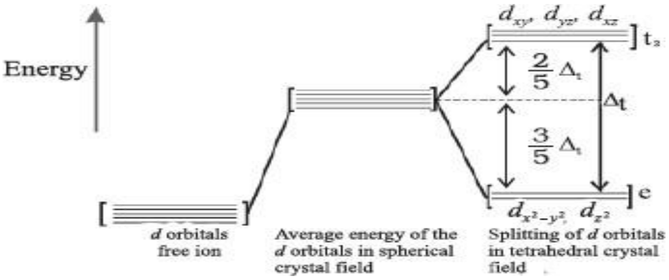
All light absorbed, none reflected get Black color

For d^4 ions, two possible patterns of electron distribution arise: (i) The fourth electron could either enter the t_{2g} level and pair with an existing electron, or

(ii) It could avoid paying the price of the pairing energy by occupying the e_g level. Which of these possibilities occurs, depends on the relative magnitude of the crystal field splitting, Δo and the pairing energy, P (P represents the energy required for electron pairing in a single orbital). The two options are: (i) If $\Delta_o < P$, the fourth electron enters one of the e_g orbitals giving the configuration $t_{2g}^3e_g^1$. Ligands for which $\Delta_o < P$ are known as ***weak field ligands*** and form **high spin complexes**.

(ii) If $\Delta_o > P$, it becomes more energetically favourable for the fourth electron to occupy a t_{2g} orbital with configuration $t_{2g}^4e_g^0$. Ligands which produce this effect are known as ***strong field ligands*** and form **low spin complexes**. Calculations show that d^4 to d^7 coordination entities are more stable for strong field as compared to weak field cases.

(b) Crystal field splitting in tetrahedral coordination entities:



d orbital splitting in a tetrahedral crystal field (fig.9.9 ncert)

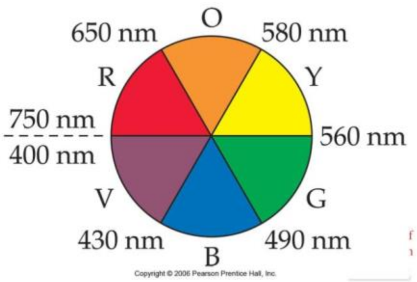
In tetrahedral coordination entity formation, the *d* orbital splitting (Fig. 9.9) is inverted and is smaller as compared to the octahedral field splitting. For the same metal, the same ligands and metal-ligand distances,it can be shown that $\Delta_t = (4/9)\ \Delta_o$.

Colour in Coordination Compounds: The crystal field theory attributes the colour of the coordinationcompounds to *d-d* transition of the electron.

Complimentary color wheel

If one color absorbed, the color opposite is perceived.

Absorb Orange
See Blue
Absorb Red
See Green



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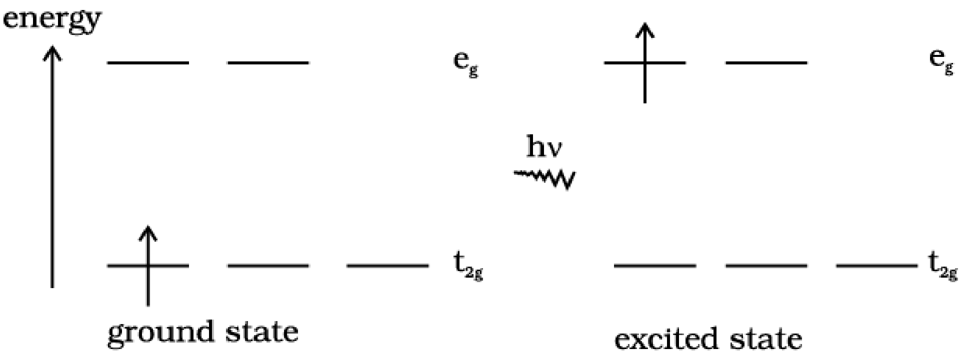


d-d Transition of an electron in $[Ti(H_2O)_6]^{3+}$

Relationship between the Wavelength of Light absorbed and the Colour observed in some Coordination Entities:

Coordination entity	Wavelength of light absorbed (nm)	Colour of light absorbed	Colour of coordination entity
$[Co(CN)_6]^{3-}$	310	Violet	Pale Yellow
$[Co(NH_3)_6]^{3+}$	475	Blue	Yellow Orange
$[Co(NH_3)_5(H_2O)]^{3+}$	500	Blue Green	Red
$[Ti(H_2O)_6]^{3+}$	510	Blue Green	Purple
$[Co\ Cl(NH_3)_5]^{2+}$	535	Yellow	Violet
$[Cu(H_2O)_4]^{2+}$	600	Red	Blue

Magnetic Properties of Complexes

1. The complex in which a central transition metal ion has unpaired electrons is paramagnetic.
2. The complex in which a central transition metal ion has no unpaired electrons is diamagnetic.
3. The magnetic moment of a complex is calculated by the spin only formula.

$M = \sqrt{[n(n+2)]}$ BM

BM = Bohr Magneton

The magnetic moment of complex compounds depends upon the following:

- Type of hybridization.
- The oxidation state of central transition metal ion.
- The number of unpaired electrons.

ISOMERISM IN COORDINATION COMPOUNDS:

Two or more compounds having the same molecular formula but different arrangement of atoms are called **isomers** and the phenomenon is called **Isomerism**

Two types of isomerism are: (a) Structural isomerism (b) Stereoisomerism

(a) STRUCTURAL ISOMERISM: The isomers which have same molecular formula but different structural arrangement of atoms or groups of atoms around the central metal ion are called **structural isomers.**

(i) **IONIZATION ISOMERISM**: The compounds which have same molecular formula but give different ions insolution are called ionization isomers. For example:
$[Co (NH_3)_5 (SO_4)]Br$ and $[Co (NH_3)_5Br] SO_4$.

(ii) **SOLVATE ISOMERISM**: The compounds which have same molecular formula but differ in the number of solvent molecules present as ligands and as free solvent molecules in the crystal lattice are called solvateisomers. This form of isomerism is known as 'hydrate isomerism' in case where water is involved as a solvent. For example:
$[Cr (H_2O)_6]Cl_3$ (violet) and its solvate isomer $[Cr (H_2O)_5 Cl]Cl_2.H_2O$ (grey-green).

(iii) **COORDINATION ISOMERISM**: This type of isomerism arises from the interchange of ligands betweencationic and anionic entities of different metal ions present in a complex. For example: $[Co (NH_3)_6][Cr(CN)_6]$, in which the NH_3 ligands are bound to Co^{3+} and the $CN^–$ ligands to Cr^{3+}. In its coordination isomer $[Cr (NH_3)_6][Co(CN)_6]$, the NH_3 ligands are bound to Cr^{3+} and the $CN^–$ ligands to Co^{3+}.

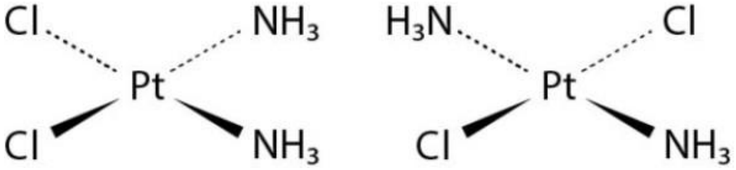
(iv) **Linkage isomerism**: The compounds which have same molecular formula but differ in the mode of attachment of a ligand to the metal atom or ion are called linkage isomers. Linkage isomerism arises in acoordination compound containing ambidentate ligand. For example:
Complexes containing the thiocyanate ligand, which may bind through sulphur to give M–SCN.
Isothiocyanate ligand through the nitrogen to give M–NCS.
$[Co (NH_3)_5 (NO_2)] Cl_2$ the ligand is bound through nitrogen (NO_2).$[Co (NH_3)_5 (ONO)] Cl_2$ the ligand is bound through oxygen (–ONO).

(b) **STEREOISOMERISM:** stereoisomers have the same chemical formula and chemical bonds but they have different spatial arrangement of atoms.

Two types of isomerism are: (a) Geometrical isomerism (b) Optical isomerism

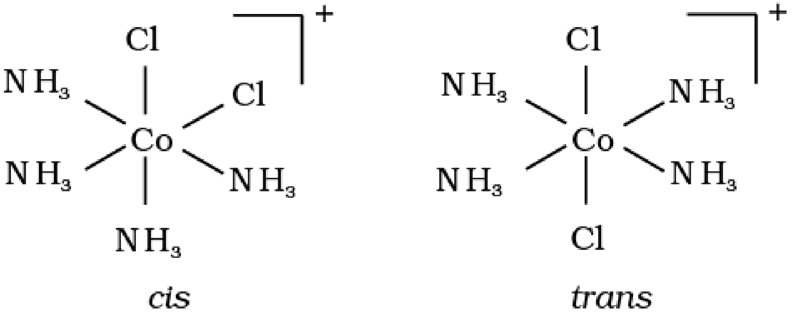
GEOMETRICAL ISOMERISM: This type of isomerism arises in heteroleptic complexes due to ligands occupying different positions around the central ion. The ligands occupy positions either adjacent to oneanother or opposite to one another. These are referred to cis- form (ligand occupy adjacent position) andtrans-form (ligand occupy opposite position). For example:

Geometrical isomers (cis and trans) of $Pt [NH_3]_2 Cl_2]$



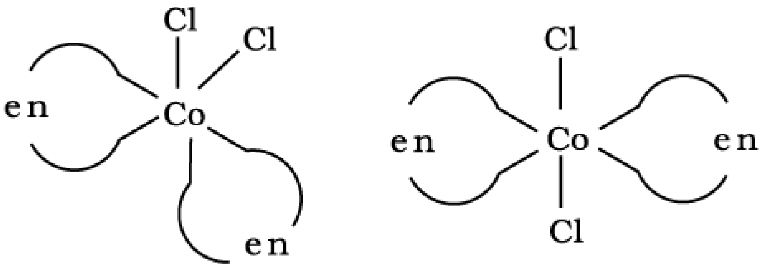
Cis- trans-

Square planar complex of the type MABXL (where A, B, X, L are unidentates) shows three isomers- two cis and one trans. Such isomerism is not possible for a tetrahedral geometry but similar behaviour is possible in octahedral complexes of formula [MX_2L_4] in which the two ligands X may be oriented cis or trans to each other



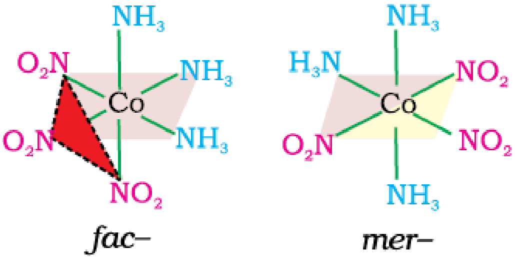
: Geometrical isomers (cis and trans) of $[Co(NH_3)_4Cl_2]^+$

This type of isomerism also arises when bidentate ligands L–L [*e.g.*, $NH_2CH_2CH_2NH_2$ (en)] are present in complexes of formula [$MX_2(L–L)_2$]



Geometrical isomers (cis and trans) of $[CoCl_2(en)_2]$

Another type of geometrical isomerism occurs in octahedral coordination entities of the type [Ma_3b_3] like [$Co(NH_3)_3(NO_2)_3$]. If three donor atoms of the same ligands occupy adjacent positions at the corners of an octahedral face, we have the **facial (fac) isomer**. When the positions are around the meridian of the octahedron, we get the **meridional (mer) isomer**



The facial (fac) and meridional (mer) isomers of $[Co(NH_3)_3(NO_2)_3]$

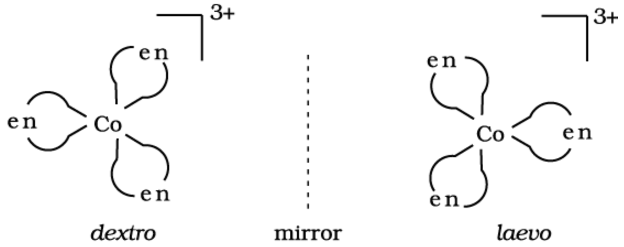
(a)* OPTICAL ISOMERISM**: Optical isomers are mirror images that cannot be superimposed on one another.These are called as ***enantiomers.

The molecules or ions that cannot be superimposed are called ***chiral.***

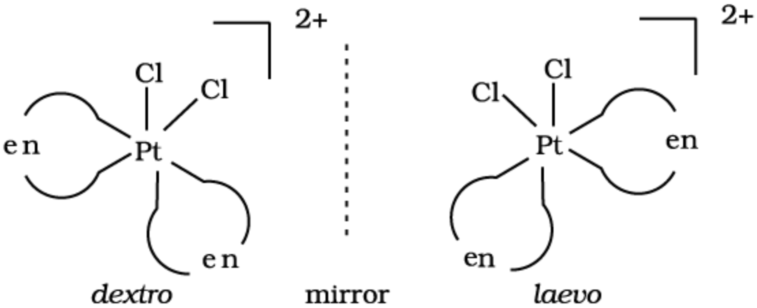
The two forms are called dextro (d) and laevo (l) depending upon the direction they rotate the plane of polarized light in a polarimeter (d rotates to the right, l to the left).

Optical isomerism is common in octahedral complexes involving Didentate ligands.Optical isomers of $[PtCl_2(en)_2]^{2+}$

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



In a coordination entity of the type $[PtCl_2(en)_2]^{2+}$, only the *cis*-isomer shows optical activity.



Optical isomers (d and l) of cis- $[PtCl_2(en)_2]^{2+}$

Importance and Applications of Coordination Compounds:

The coordination compounds are of great importance. These compounds are widely present in the mineral, plant and animal worlds and are known to play many important functions in the area of analytical chemistry, metallurgy, biological systems, industry and medicine. These are described below:

- Coordination compounds find use in many qualitative and quantitative chemical analyses. Examples ofsuch reagents include EDTA, DMG (dimethylglyoxime), etc.

Ni2+ ions are detected by adding DMG (dimethylglyoxime) in the presence of NH_4OH to nickel salt solution, red precipitates are formed.

- Hardness of water is estimated by simple titration with Na_2EDTA. The Ca^{2+} and Mg^{2+} ions form stable complexes with EDTA. The selective estimation of these ions can be done due to difference in the stabilityconstants of calcium and magnesium complexes.
- Some important extraction processes of metals, like those of silver and gold, make use of complex formation. Gold, for example, combines with cyanide in the presence of oxygen and water to form thecoordination entity $[Au(CN)_2]^-$ in aqueous solution
- Purification of metals can be achieved through formation and subsequent decomposition of their coordination compounds.

For example, impure nickel is converted to $[Ni(CO)_4]$, which is decomposed to yield pure nickel.

- Biological importance: Coordination compounds are of great importance in biological systems. The pigment responsible for photosynthesis, chlorophyll, is a coordination compound of magnesium. Haemoglobin, the red pigment of blood which acts as oxygen carrier is a coordination compound of iron. Vitamin B12, cyanocobalamin, the anti– pernicious anaemia factor, is a coordination compound of cobalt.
- In catalyst: Coordination compounds are used as catalysts for many industrial processes.

Examples include rhodium complex, $[(Ph_3P)_3RhCl]$, a Wilkinson catalyst, is used for the hydrogenation of alkenes.

- Articles can be electroplated with silver and gold much more smoothly and evenly from solutions of the complexes, $[Ag(CN)_2]^-$ and $[Au(CN)_2]^-$ than from a solution of simple metal ions.
- In black and white photography: The developed film is fixed by washing with hypo solution which

dissolves the undecomposed AgBr to form a complex ion, $[Ag(S_2O_3)_2]^{3-}$.

- In medicine: Complexing agents are used for removal of metal poisoning. A platinum complex, $[PtCl_2(NH_3)_2]$ known as cis-platin has been used in cancer therapy.

ASSIGNMENTS:

Q1. Which of the following statements about coordination compounds' bonding is incorrect?

(a) Crystal Field Theory
(b) VSEPR Theory
(c) Valence Bond Theory
(d) Molecular Orbital Theory

Ans

.(b)

Explanation: The VSEPR Theory uses electron pairs in atoms to explain the structure of particularmolecules. The theories VBT, CFT, LFT, and MOT explain the nature of bonding in coordinationcompounds.

Q2. Determine the proper name for $K_2[PdCl_4]$.

(a) Potassium tetrachlorinepalladium(II)
(b) Potassium tetrachloridopalladate(II)Potassium
(c) Potassium tetrachloridopalladium(II)
(d) tetrachlorinepalladate(II)Ans.(b)

Explanation: Because Cl is an anionic ligand, it has the suffix -o, therefore chlorido. Furthermore, becausethe complex ion is anionic, the metal must end in -ate, so palladate.

Q3. Which substance is used to determine the hardness of water using a simple titration?

(a) Mg(EDTA)
(b) Fe(EDTA)

(c) $Na_2(EDTA)$
(d) Co(EDTA)
Ans. (c)

Explanation: With EDTA, the ions Ca^{2+} and Mg^{2+} form stable complexes, and the difference in the stabilityconstants of the Ca and Mg complexes aids in the assessment of water hardness.

Q4. The core atom of which of the following biologically significant coordination molecules is magnesium?

(a) Vitamin B12
(b) Haemoglobin
(c) Chlorophyll
(d) Carboxypeptidase-A
An

s
.
(
c
)

Explanation: Chlorophyll is a coordination molecule of magnesium that is found in plants and is importantfor photosynthesis.

Q5. According to IUPAC nomenclature sodium nitroprusside dihydrate is named as

(a) Sodium pentacyanonitrosylferrate (III)
(b) Sodium nitroferrocyanide
(c) Sodium nitroferricyanide
(d) Sodium pentacyanonitrosylferrate (II)Ans.
(a)

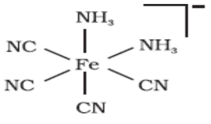
Q6. Write the formulas for the following coordination compounds:

(a) Tetraammineaquachloridocobalt (III) chloride
(b) Potassium tetrahydroxidozincate (II)
(c) Potassium trioxalatoaluminate (III)
(d) Dichloridobis (ethane-1, 2-diamine) cobalt (III) ion
(e) Tetracarbonyl nickel (0)
(a) $[Co (NH_3)_4(H_2O) Cl] Cl_2$
(b) $K_2 [Zn (OH)_4]$
(c) $K_3 [Al (C_2O_4)_3]$
(d) $[Co Cl_2 (en)_2]^+$
(e) $[Ni (CO)_4]$

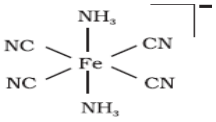
Q7. Write the IUPAC names of the following coordination compounds:

(a) $[Pt (NH_3)_2Cl (NO_2)]$
(b) $K_3 [Cr (C_2O_4)_3]$
(c) $[Co Cl_2 (en)_2] Cl$
(d) $[Co (NH_3)_5(CO_3)] Cl$
(e) $Hg [Co (SCN)_4]$
(a) Diamminechloridonitrito-N-platinum (II)
(b) Potassium trioxalatochromate (III)
(c) Dichloridobis (ethane-1, 2-diamine) cobalt (III) chloride
(d) Pentaamminecarbonatocobalt (III) chloride
(e) Mercury (I) tetrathiocyanato-S-cobaltate (III)

Q8. Draw structures of geometrical isomers of $[Fe(NH_3)_2(CN)_4]^-$



cis



trans

Q9. Indicate the types of isomerism exhibited by the following complexes and draw the structures for theseisomers:

- (i) K $[Cr(H_2O)_2(C_2O_4)_2$
- (ii) $[Co(en)_3]Cl_3$
- (iii) $[Co(NH_3)_5(NO_2)](NO_3)_2$
- (iv) $[Pt(NH_3)(H_2O)Cl_2]$

Ans. (i) Both geometrical (cis and trans) and optical isomers for cis.
(ii) Two optical isomers
(iii) Geometrical, ionization and linkage isomers.
(iv) Geometrical (cis and trans)

Q10. Give evidence that $[Co(NH_3)_5Cl]SO_4$ and $[Co(NH_3)_5(SO_4)]Cl$ are ionization isomers.Ans. $[Co(NH_3)_5Cl]SO_4 + BaCl_2 \rightarrow BaSO_4$ (white ppt)
$[Co(NH_3)_5(SO_4)]Cl + AgNO_3 \rightarrow$ AgCl (white ppt)

Q11. The spin only magnetic moment of $[MnBr_4]^{2-}$ is 5.9 BM. Predict the geometry of the complex ion? Ans. Since the coordination number of Mn^{2+} ion in the complex ion is 4, it will be either tetrahedral (sp^3 hybridization) or square planar (dsp^2 hybridization). But the fact that the magnetic moment of the complexion is 5.9 BM, it should be tetrahedral in shape rather than square planar because of the presence of five unpaired electrons in the *d* orbitals.

Q12. Predict the number of unpaired electrons in the square planar $[Pt(CN)_4]^{2-}$ ion.Ans. Pt = $5d^9\ 6s^1$
Pt (II) = $5d^8$, square planar geometry and dsp^2 hybridization.

Q13. Explain on the basis of valence bond theory that $[Ni(CN)_4]^{2-}$ ion with square planar structure isdiamagnetic and the $[NiCl_4]^{2-}$ ion with tetrahedral geometry is paramagnetic.

Ans. $[Ni(CN)_4]^{2-}$ square planar geometry and dsp^2 hybridization.$[NiCl_4]^{2-}$ Tetrahedral geometry and sp^3 hybridization.

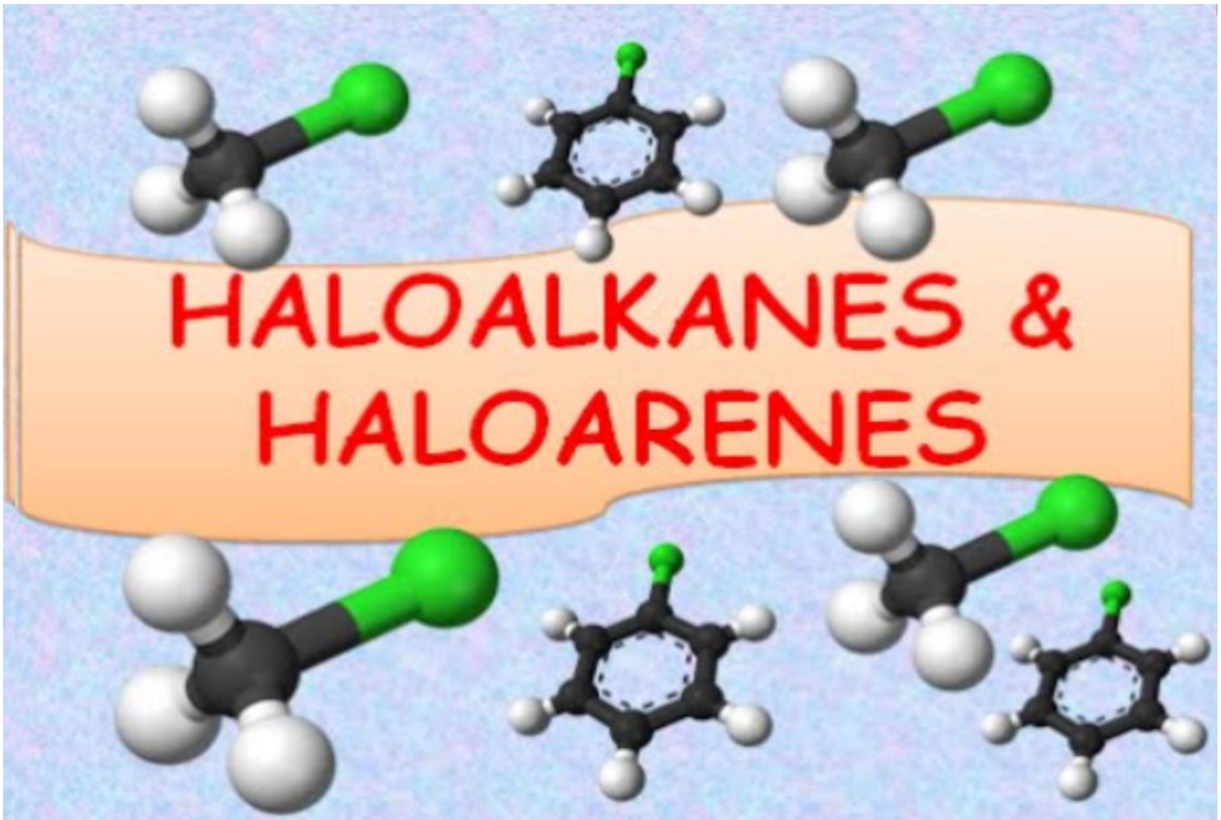
Q14. $[Fe(H_2O)_6]^{3+}$ is strongly paramagnetic whereas $[Fe(CN)_6]^{3-}$ is weakly paramagnetic. Explain.Ans. In both the complexes, Fe is in +3 oxidation state.
CN^- is strong field ligand, inner d-orbitals are involved, d^2sp^3 hybridization, one unpaired electron, weaklyparamagnetic.
H_2O is weak field ligand, outer d-orbitals are involved, sp^3d^2 hybridization, five unpaired

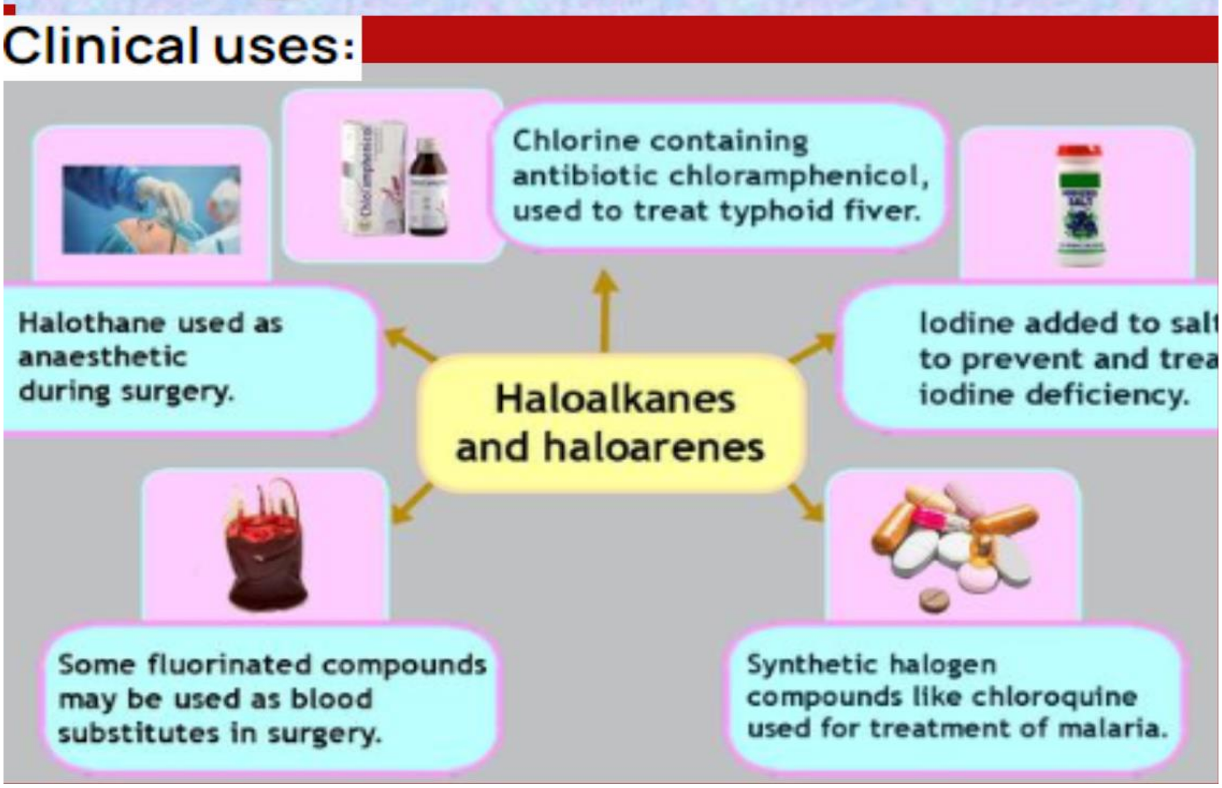
electrons, strongly paramagnetic.

Q15. Explain [Co $(NH_3)_6]^{3+}$ is an inner orbital complex whereas [Ni $(NH_3)_6]^{2+}$ is an outer orbital complex.Ans. [Co $(NH_3)_6]^{3+}$ is an inner orbital complex, d^2sp^3 hybridization.

[Ni $(NH_3)_6]^{2+}$ is an outer orbital complex, sp^3d^2 hybri

UNIT VI HALOALKANES AND HALOARENES





Clinical uses:

Haloalkanes and haloarenes

Halothane used as anaesthetic during surgery.

Chlorine containing antibiotic chloramphenicol, used to treat typhoid fiver.

Iodine added to salt to prevent and trea iodine deficiency.

Some fluorinated compounds may be used as blood substitutes in surgery.

Synthetic halogen compounds like chloroquine used for treatment of malaria.

HALOALKANES AND HALOARENES

The replacement of one or more hydrogen atoms of a hydrocarbon, aliphatic or aromatic, by an equal number of halogen atom results in the formation of alkyl halide (haloalkanes) and aryl halide (Haloarenes), respectively.

1. Haloalkanes are classified as Fluoro, Chloro, Bromo or Iodo compounds according to the type of halogen present and as mono-, di- tri- haloalkanes, etc., according to the one, two, and three halogen atoms respectively present in their molecule.

C_2H_5X

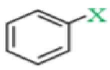
Monohaloalkane

CH_2X-CH_2X

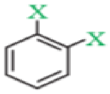
Dihaloalkane

$CH_2X-CHX-CH_2X$

Trihaloalkane

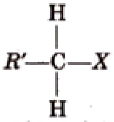


Monohaloarene



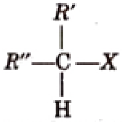
Dihaloarene

2. Alkyl halides are further classified as primary (1°), secondary (2°) and tertiary (3°) according to the halogen atom attached to primary, secondary and tertiary carbon atoms, respectively. R'CH_2X (Primary), R'R''CHX (Secondary) and R'R''R'''CX (Tertiary)



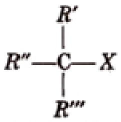
$R'-CH_2-X$

primary (1°)



$R''-CH(R')-X$

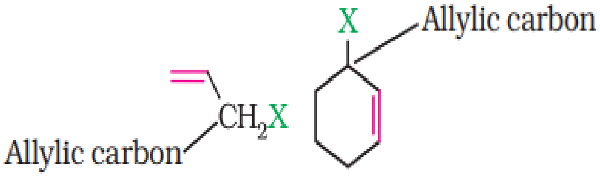
secondary (2°)



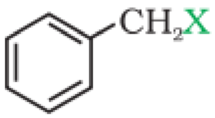
$R''-C(R')(R''')-X$

tertiary (3°)

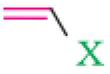
3. Allylic halides:

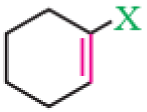


4. Benzylic halides:

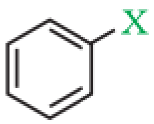


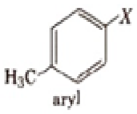
5. Vinylic halides:





6. Aryl halide:





aryl

Dihalogen Derivatives: vic-dihalides, gem-dihalides and isolated dihalides.
For examples: vic-dihalides $CH_3-CH_2-CH(Cl)-CH_2Cl$, gem-dihalides $CH_3-CH_2-CH(Cl)_2$ isolated dihalides $ClCH_2-CH_2-CH_2-CH_2Cl$.

C-X bond is a polar covalent bond due to electronegativity difference between the carbon and the halogen, the shared pair of electron lies closer to the halogen atom. As a result, the halogen carries a small negative charge, while the carbon carries a small positive charge.

Isomerism in Haloalkanes and Haloarenes:

Haloalkanes show two types of isomerism: Chain isomerism and Position isomerism
Haloarenes also show position isomerism.

Methods of Preparation of Haloalkanes:

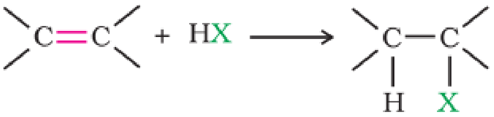
From alcohols: Haloalkanes can be prepared from displacement of alcoholic group in alkyl alcohol by halogen acid, PCl_5 or PCl_3. Haloalkanes can also be prepared by addition of halogen acids or halogens on alkene and alkyne. Alkyl halides can also be prepared by free radical halogenation of alkane.

$R – OH + HCl + ZnCl_2$⍰ $R - Cl + H_2O$
$R – OH + NaBr + H_2SO_4$ ⍰ $R – Br + NaHSO_4 + H_2O$
$R – OH + PX_3$ $R - X + H_3PO_3$
$R – OH + PCl_5$ $R - Cl + POCl_3 + HCl$
$R – OH +$ Red P/X2 $R - Cl + H_2O$
$R – OH + SOCl_2$ $R - Cl + SO_2 + HCl$

Free Radical Halogenation of Alkanes:

$CH_3CH_2CH_2CH_3$ Cl2 , UV $CH_3CH_2CH_2CH_2Cl + CH_3CH_2CH(Cl)\ CH_3$

Addition of Hydrogen Halides or halogen acids on Alkenes:



During the addition of halogen acids to unsymmetrical alkenes, **Markovnikov rule** is followed, According to this rule during the addition across unsymmetrical double bond, the negative part of the attacking reagent attaches itself to the carbon atom carrying lesser number of hydrogen atoms while the positive part goes to the carbon atom with more number of hydrogen atoms.
Propene + HBr ▯ 2-bromopropane (major product)

Anti-Markovnikov rule or Kharasch effect: In this case of addition of HBr to unsymmetrical alkenes, the negative part of the attacking reagent (Br) will join to the carbon atom carrying more number of hydrogen atoms while H-atom will go to the other carbon atom containing lesser number of hydrogen atoms in the presence of organic peroxide such as benzoyl peroxide ($C_6H_5CO-O-O-COC_6H_5$)
Propene + HBr ▯ 1-bromopropane (major product)

1. Finkelstein Reaction: $R – X + NaI$ Acetone $R – I + NaX$ (X = Cl, Br)
2. Swarts Reaction: $H_3C – Br + AgF \rightarrow H_3C – F + AgBr$
3. Hunsdiecker Reaction: $CH_3COOAg + Br_2$ CCl4 $CH_3Br + AgBr + CO_2$

Physical Properties of Haloalkanes:

1. Boiling point orders
   1. $R – I > R – Br > R – CI > R – F$
   2. $CH_3 – (CH_2)_2 – CH_2Br > (CH_3)_2\ CHCH_2Br > (CH_3)_3CBr$

3. $CH_3CH_2CH_2X > CH_3CH_2X > CH_3X$

2. Bond enthalpy of haloalkanes decreases as the size of the halogen atom increases. Thus, the order of bond strength is $CH_3F > CH_3Cl > CH_3Br > CH_3I$

3. Dipole moment decreases as the electronegativity of the halogen decreases.

4. Haloalkanes though polar but are insoluble in water as they do not form hydrogen bonding with water.

5. Density: n-C_3H_7I > n-C_3H_7 Br > n-C_3H_7Cl, $CH_3I > C_2H_5I > C_3H_7I$

5. Chemical reactions of haloalkanes:

KCN is predominantly ionic and provides cyanide ions in solution, which is ambident nucleophile and bind with carbon side to form as the major product, while AgCN is covalent and form isocyanide as the major product.

CH_3CH_2Br +KCN CH_3CH_2CN + KBr

CH_3CH_2Br +AgCN CH_3CH_2NC + KBr

Like KCN, KNO_2 form R-ONO while $AgNO_2$ produces R-NO_2 as product.

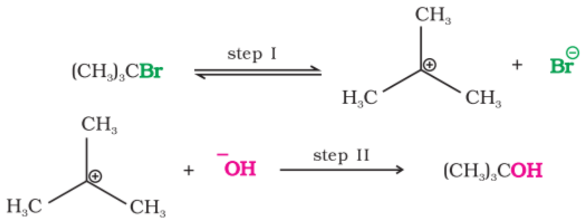
Nucleophilic substitution reactions: These are of two types:

(1) S_N1 (Substitution, Nucleophilic, Unimolecular): In such type of reactions, rate = k [RX] i.e., rate is independent of concentration of nucleophile and occurs in two steps. Such reactions are favoured by polar solvents.

(2) S_N2 (Substitution, Nucleophilic, bimolecular): (i) In such type of reactions, rate = k [RX] $[Nu]^-$, i.e., rate of reaction depends on concentration of nucleophile and take place in one step.

(ii) A S_N2 reaction proceeds with complete Stereochemical inversion while a S_N1 reaction proceeds with racemisation.

(a) S_N1 type (Unimolecular Nucleophilic reactions proceed in two steps: ref. ncert

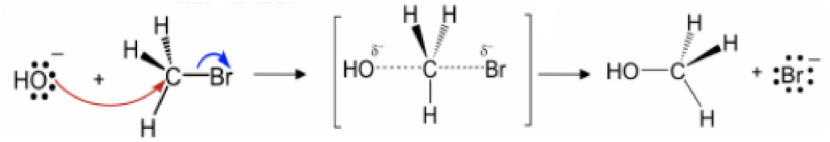


Rate, r = k [RX]. It is a first order reaction.

Reactivity order of alkyl halide towards S_N1 mechanism 3° > 2° > 1° Polar solvents, low concentration of nucleophiles and weak nucleophiles favour S_N1 mechanism.

In S_N1 reactions, partial racemisation occurs due to the possibility of frontal as well as backside attack on planar carbocation.

(b) S_N2 type (Bimolecular Nucleophilic substitution): These reactions proceed in one step.



It is a second order reaction with r = k[RX] [Nu].

During S_N2 reaction, inversion of configuration occurs (Walden inversion) i.e., starting with dextrorotatory halide a laevo product is obtained and vice-versa, e.g.,

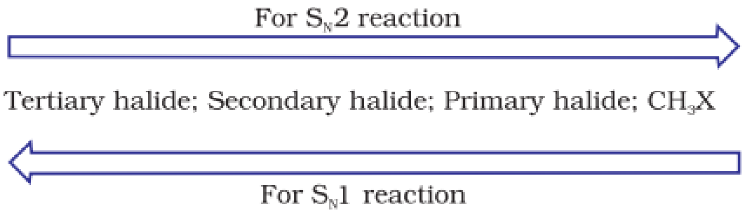
Reactivity of halides towards S_N2 mechanism is 1° > 2° > 3°

Rate of reaction in S_N2 mechanism depends on the strength of the attacking nucleophile. Strength of some common nucleophiles is

$: CN^- >: I^- >: OR^- >: OH^- > CH_3COO: > H_2O > F^-$

Non-polar solvents, strong nucleophiles and high concentration of nucleophiles favour S_N2 mechanism.

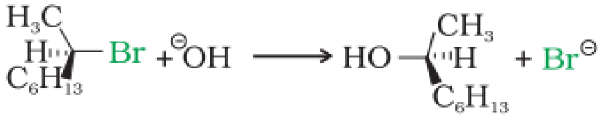
Order of reactivity of alkyl halides towards SN1 and SN2 as follows: ref. ncert



Stereochemical Aspects of Nucleophilic Substitution Reactions

a. Stereochemical Aspects of SN2 reaction:

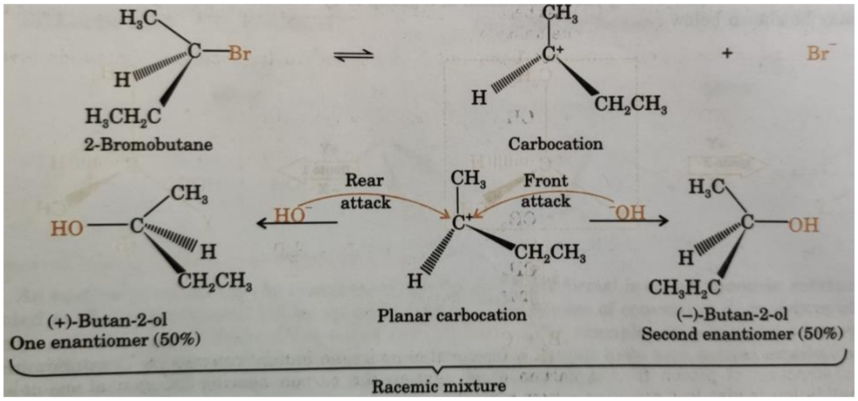
In case of optically active alkyl halides, the product formed as a result of SN2 mechanism has the inverted configuration as compared to the reactant. This is because the nucleophile attaches itself on the side opposite to the one where the halogen atom is present. When (–)-2-bromooctane is allowed to react with sodium hydroxide, (+)-octan-2-ol is formed with the –OH group occupying the position opposite to what bromide had occupied. (Ref. ncert)



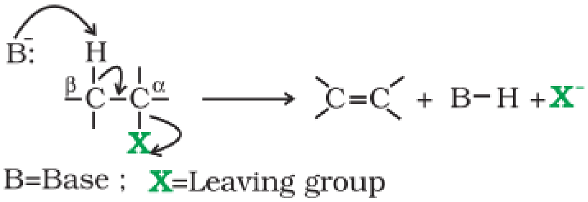
Thus, SN 2 reactions of optically active halides are accompanied by inversion of configuration.

b. Stereochemical Aspects of SN1 reaction:

In case of optically active alkyl halides, SN1 reactions are accompanied by racemization. Actually, the carbocation formed in the slow step being sp^2 hybridized is planar (achiral). The attack of the nucleophile may be accomplished from either side of the plane of carbocation resulting in a mixture of products, one having the same configuration (the –OH attaching on the same position as halide ion) and the other having opposite configuration (the –OH attaching on the side opposite to halide ion). This may be illustrated by hydrolysis of optically active 2-bromobutane, which results in the formation of (±)-butan-2-ol. (Ref. ncert)



(b) Elimination reaction: When a haloalkanes with β-halogen atom is heated with alcoholic solution of potassium hydroxide, there is elimination of hydrogen atom from α-carbon and a halogen atom from the a-carbon atom.



Ease of dehydrohalogenation among halides 3° > 2° > 1°

Reaction with metals:

CH_3CH_2Br + Mg dry ether CH_3CH_2MgBr (Grignard reagent)

$CH_3CH_2MgBr + H_2O$ CH_3CH_3 + Mg (OH)Br

Wurtz reaction: 2RX + 2Na RR + 2NaX

Isomerisation: $CH_3CH_2CH_2 – Cl$ 573 K $CH_3 – CH(Cl) – CH_3$

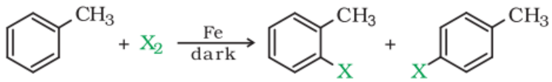
Relative reactivity of alkyl halides for same alkyl group is: RI > RBr > RCI > RF

Methods of preparation of Haloarenes. Haloarenes can be prepared by side chain halogenation or nuclear halogenation of aromatic hydrocarbons.

1. By Halogenation of Aromatic Hydrocarbons:

$C_6H_6 + Cl_2$ FeCl3, dark $C_6H_5Cl + HCl$

It is an electrophilic substitution reaction.



o-Halotoluene *p*-Halotoluene

2. By Side Chain Halogenation:

$C_6H_5CH_3 + Cl_2 \xrightarrow{sunlight} C_6H_5CH_2Cl + Cl_2 \xrightarrow{sunlight} C_6H_5CHCl_2 + Cl_2 \xrightarrow{sunlight} C_6H_5CCl_3$

(It involves free radical mechanism.)

3. From diazonium salts:

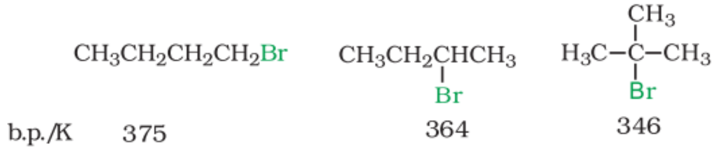
(i) By Sandmeyer reaction: $C_6H_5\,N_2^+Cl^- \xrightarrow{CuCl/HCl} C_6H_5\,Cl + N_2$

(ii) By Gattermann reaction: $C_6H_5\,N_2^+Cl^- \xrightarrow{Cu/HCl} C_6H_5\,Cl + N_2$

4. From Phenol: $C_6H_5OH + PCl_5 \longrightarrow C_6H_5Cl + HCl + POCl_3$

Physical Properties of Aryl Halides:

1. Aryl halides are colourless liquids or crystalline solids..
2. Boiling point generally increases with increase in the size of aryl group or halogen atom. Boiling point order Ar – I > Ar – Br > Ar – Cl > Ar – F, the boiling points of isomeric haloalkanes decrease with increase in branching (ncert)



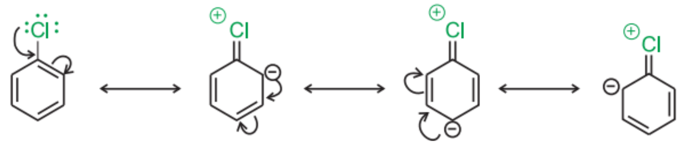
3. The melting point of p -isomer is more than o- and m-isomer. This is because of more symmetrical nature of p-isomer.
4. Due to resonance in Chlorobenzene, C-CI bond is shorter and hence, its dipole moment is less than that of cyclohexyl chloride.

Chemical Properties of Aryl Halides:

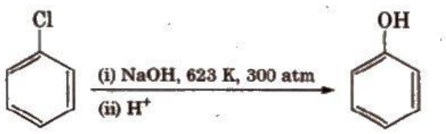
1. Nucleophilic Substitution Reaction

Aryl halides are less reactive towards Nucleophilic substitution reaction. Their low reactivity is attributed due to the following reasons:

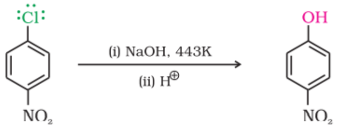
1. Due to resonance, C-X bond has partial double bond character.
2. Stabilisation of the molecule by delocalisation of electrons.
3. Instability of phenyl carbocation.

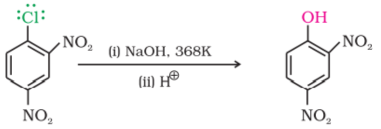


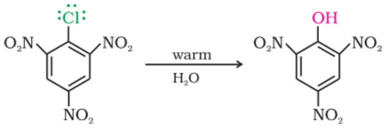
However, aryl halides having electron withdrawing groups (like – NO_2, -SO_3H, etc.) at ortho and para positions undergo Nucleophilic substitution reaction easily.



Presence of electron withdrawing group (-NO_2) increases the reactivity. (ref. ncert)



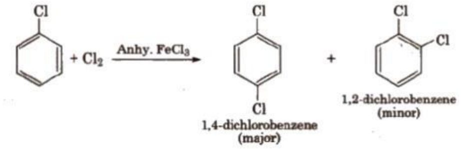




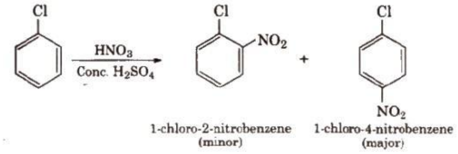
2. Electrophilic Substitution Reactions

Halogens are deactivating but o, p-directing. Thus, chlorination, nitration, Sulphonation and Friedel Craft's reaction give a mixture of o- and p- Chloro substituted derivatives.

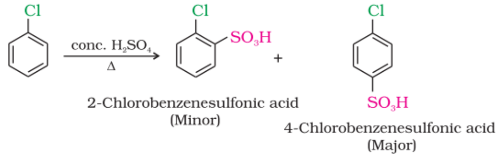
(i) Halogenation:



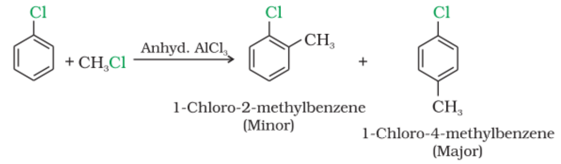
(ii) Nitration:

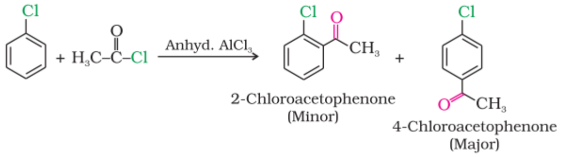


(iii) Sulphonation:



(iv) Friedel-Crafts reaction: Alkylation and Acylation:

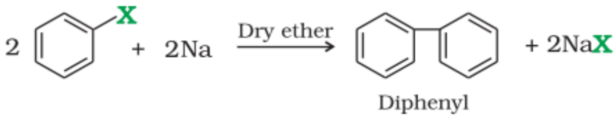




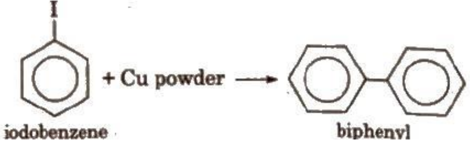
3. Reaction with Metals:

(i) Wurtz Fittig reaction:

(ii) Fitting reaction:

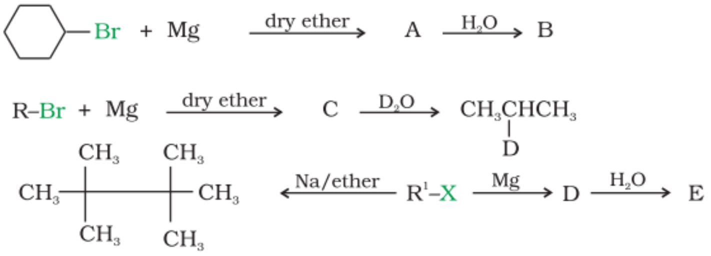


(iii) Ullmann reaction: Iodobenzene reacts with copper powder to form biphenyl



Example:

10.9 Identify A, B, C, D, E, R and R^1 in the following:



A = Cyclohexyl magnesium bromide, B = Cyclohexane, C = RMgBr

D = $(CH_3)_3MgBr$, E = 2-Methyl propane, R' = $(CH_3)_3C$ -

Polyhalogen Compounds:

Dichloromethane (Methylene chloride), CH_2Cl_2: It is a colourless, sweet smelling liquid.

It is widely used as a solvent as a paint remover, as a propellant in aerosols, and as a process solvent in the manufacture of drugs.

It is also used as a metal cleaning and finishing solvent.

Methylene chloride harms the human central nervous system. Exposure to lower levels of methylene chloride in air can lead to slightly impaired hearing and vision. Higher levels of methylene chloride in air cause dizziness, nausea, tingling and numbness in the fingers and toes.

In humans, direct skin contact with methylene chloride causes intense burning and mild redness of the skin. Direct contact with the eyes can burn the cornea.

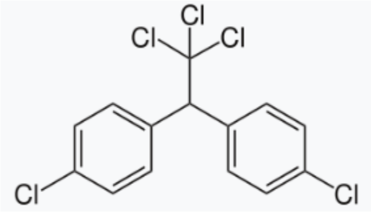
Trichloromethane (Chloroform) $CHCl_3$: It is a colourless oily liquid with a peculiar sickly smell and a burning taste. It is heavier than water. It is sparingly soluble in water but readily soluble in organic solvent such as ethanol and ether. It is poisonous compound. The vapour when inhaled cause consciousness. Due to this reason, chloroform is used as anaesthetic. It is used in medicine and used in the production of Freon refrigerant. It is used as a laboratory reagent.
Chloroform is slowly oxidised by air in the presence of light to an extremely poisonous gas, carbonyl chloride, also known as phosgene. It is therefore stored in closed dark coloured bottles completely filled so that air is kept out.
$2CHCl_3 + O_2 \qquad 2COCl_2 + 2HCl$
Carbonyl chloride (phosgene)

Tetrachloromethane (Carbon tetrachloride) CCl_4: It is a colourless oily liquid with sickly smell. It is insoluble in water but soluble in organic solvent such as ethanol and ether. It is inflammable.
It is used in the manufacture of refrigerants and propellants for aerosol cans.
It is also used as feedstock in the synthesis of chlorofluorocarbons (Freons) and other chemicals.
It is also used as a solvent in manufacturing of pharmaceuticals.
It was also widely used as a cleaning fluid, both in industry, as a degreasing agent, and in the home, as a spot remover and as fire extinguisher.
When carbon tetrachloride is released into the air, it rises to the atmosphere and depletes the ozone layer. Depletion of the ozone layer is believed to increase human exposure to ultraviolet rays, leading to increased skin cancer, eye diseases and disorders, and possible disruption of the immune system.

Triiodomethane (Iodoform) CHI_3: It is a yellow coloured crystalline solid. It is insoluble in water but soluble in organic solvent such as ethanol and ether.
It is used as an antiseptic but the antiseptic properties are due to the liberation of free iodine and not due to Iodoform itself.
It is used in the manufacturing of pharmaceuticals.

Freons: The chlorofluorocarbon compounds of methane and ethane are collectively known as freons. They are extremely stable, unreactive, non-toxic, noncorrosive and easily liquefiable gases.
Freon 12 (CCl_2F_2) is one of the most common freons in industrial use. It is manufactured from tetrachloromethane by Swarts reaction. These are usually produced for aerosol propellants, refrigeration and air conditioning purposes.

p, p'-Dichlorodiphenyltrichloroethane (DDT): DDT, the first chlorinated organic insecticides, was originally prepared in 1873.Paul Muller was awarded the Nobel Prize in Medicine and Physiology in 1948 for this discovery.
It is synthesized by heating a mixture of chloral (1 mol) with Chlorobenzene (2 mol) in the presence of conc. H_2SO_4.
$Cl_3C\text{-}CHO + C_6H_5\,Cl \quad \text{conc. H2SO4} \quad DDT$



DDT is a powerful insecticide. It is widely used as an insecticide for killing mosquitoes and other insects.

ASSIGNMENTS:
Q1. What is the common name of 3-Bromopropene?
(a) Allyl bromide
(b) Vinyl bromide
(c) Tert-Butyl bromide
(d) Propylidene bromide
Ans. (a)
Q2. IUPAC name of $CH_3CH_2C(Br) = CH—Cl$ is
(a) 2-bromo-1-chloro butene
(b) 1-chloro-2-bromo butene
(c) 3-chloro-2-bromo butene
(d) None of the above
Ans. (a)
Q3. Which of the following will have the maximum dipole moment?
(a) CH_3F
(b) CH_3Cl
(c) CH_3Br
(d) CH_3I
Ans. (b) CH3Cl has higher dipole moment than CH3F due to much longer C–Cl bond length than the C–F bond. The much longer bond length of the C–C bond outweighs the effect produced by lower electronegativity of Cl than that of F.
Q4. Phosgene is a common name for
(a) phosphoryl chloride
(b) thionyl chloride
(c) carbon dioxide and phosphine
(d) carbonyl chloride
Ans. (d)
Q5. In the preparation of chlorobenzene from aniline, the most suitable reagent is
(a) Chlorine in the presence of ultraviolet light
(b) Chlorine in the presence of $AlCl_3$
(c) Nitrous acid followed by heating with Cu_2Cl_2
(d) HCl and Cu_2Cl_2

Ans. (c)
Q6. The decreasing order of boiling points of alkyl halides is
(a) RF > RCl > RBr > RI

(b) RBr > RCl > RI > RF
(c) RI > RBr > RCl > RF
(d) RCl > RF > RI > RBr
Ans. (c) For the same alkyl group, the boiling points of alkyl halides decrease in the order :
RI > RBr > RCl > RF
This is because with the increase in size and mass of halogen atom, the magnitude of van der Waal's forces increases.

Q7. Chlorobenzene is prepared commercially by
(a) Raschig process
(b) Wurtz Fittig reaction
(c) Friedel-Craft's reaction
(d) Grignard reaction
Ans. (a)
Q8. Finkelstein reaction for the preparation of alkyl iodide is based upon the fact that
(a) Sodium iodide is soluble in methanol, while sodium chloride is insoluble in methanol
(b) Sodium iodide is soluble in methanol, while NaCl and NaBr are insoluble in methanol
(c) Sodium iodide is insoluble in methanol, while NaCl and NaBr are soluble
(d) The three halogens differ considerably in their electronegativity
Ans. (b)
Q9. Which of the following statements about SN_2 mechanisms is incorrect?
(a) The transition state is stable
(b) The complete mechanism takes place in a single step
(c) The rate of the reaction depends on the concentration of both reactants
(d) There is an inversion of configuration
Ans. (a)
Q10. Which of the following catalyst in the chloroalkane reaction of a primary alcohol with HCl?
(a) red phosphorous
(b) concentrated H_2SO_4
(c) anhydrous $ZnCl_2$
(d) pyridine
Ans. (c)
Q11. $C_2H_5OH + PCl_5$ $C_2H_5Cl + HCl +$ ______.
(a) Phosphorus acid
(b) Phosphoryl chloride
(c) Phosphorus trichloride
(d) Phosphoric acid
Ans. (b)
Q12. Which of the following substances has the highest melting point?
(a) Chloromethane (CH_3Cl)
(b) Tetrachloromethane (CCl_4)
(c) Trichloromethane (CHCl3)
(d) Dichloromethane (CH_2Cl_2)
Ans. (b)
Q13. Which sequence should isomeric dichlorobenzenes be boiled in?

(a) p-dichlorobenzene > o-dichlorobenzene > m-dichlorobenzene
(b) m-dichlorobenzene > o-dichlorobenzene > p-dichlorobenzene
(c) o-dichlorobenzene > m-dichlorobenzene > p-dichlorobenzene
(d) p-dichlorobenzene > m-dichlorobenzene > o-dichlorobenzene

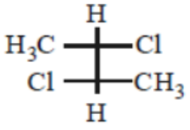
Ans**.** (a) Because para isomers have the highest melting temperatures due to their symmetry and ease of fitting into a crystal lattice.

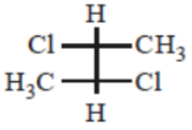
Q14. Which of the following statements about the interaction between C_2H_4 and Cl_2 in CCl_4 is incorrect?

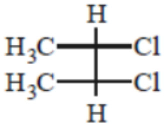
(a) It results in the formation of a vicinal dihalide
(b) It results in the discharge of a reddish-brown colour
(c) It results in the formation of a colourless compound
(d) It results in the breaking of the C-C double bond

Ans. (b)

Q15. Which of the following is optically inactive?

(a)


(b)


(c)


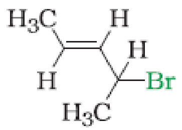
(d) none of these.

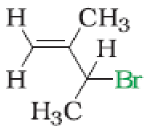
Ans. (c)

Q16. Draw the structures of all the eight structural isomers that have the molecular formula $C_5H_{11}Br$. Name each isomer according to IUPAC system and classify them as primary, secondary or tertiary bromide.

Ans. $CH_3CH_2CH_2CH_2CH_2Br$ 1-Bromopentane (primary)
$CH_3CH_2CH_2CH$ (Br) CH_3 2-Bromopentane (secondary)
CH_3CH_2CH (Br) CH_2 CH_3 3-Bromopentane (secondary)
$(CH_3)_2CHCH_2CH_2Br$ 1-Bromo-3-methylbutane (primary)
$(CH_3)_2CHCHBrCH_3$ 2-Bromo-3-methylbutane (secondary)
$(CH_3)_2CBrCH_2CH_3$ 2-Bromo-2-methylbutane (tertiary)
CH_3CH_2CH (CH_3) CH_2Br 1-Bromo-2-methylbutane (primary)
$(CH_3)_3CCH_2Br$ 1-Bromo-2, 2-dimethylpropane (primary)

Q17. Write IUPAC names of the following:

(i)


(ii)


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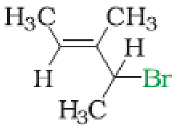

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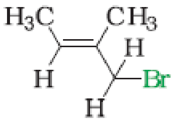
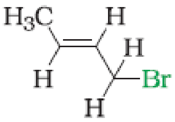


(v)


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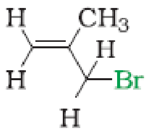


Ans.

i. 4-Bromopent-2-ene
ii. 3-Bromo-2-methylbut-1-ene
iii. 4-Bromo-3-methylpent-2-ene
iv. 1-Bromo-2-methylbut-2-ene
v. 1-Bromobut-2-ene
vi. 3-Bromo-2-methylpropene

Q18. Why is Sulphuric acid not used during the reaction of alcohols with KI?

Ans. Sulphuric acid is an oxidising agent. It will oxidise HI produced during the reaction to I_2 and therefore, will prevent reaction between an alcohol and HI to form alkyl halide.

Q19. Write structures of different dihalogen derivatives of propane.

Ans. 1,1-dibromopropane, 1,2-dibromopropane, 1,3-dibromopropane, 2,2-dibromopropane

Q20. Arrange each set of compounds in order of increasing boiling points.

(i) Bromomethane, Bromoform, Chloromethane, Dibromomethane.

(ii) 1-Chloropropane, Isopropyl chloride, 1-Chlorobutane.

Ans. (i) Chloromethane < Bromomethane < Dibromomethane < Bromoform

(ii) Isopropyl chloride < 1-Chloropropane < 1-Chlorobutane

Q21. Haloalkanes react with KCN to form alkyl cyanides as main product while AgCN forms isocyanides as the chief product. Explain.

Ans. KCN is predominantly ionic and provides cyanide ions in solution. Although both carbon and nitrogen atoms are in a position to donate electron pairs, the attack takes place mainly through carbon atom and not through nitrogen atom since C—C bond is more stable than C—N bond. However, AgCN is mainly covalent in nature and nitrogen is free to donate electron pair forming isocyanide as the main product.

Q22. In the following pairs of halogen compounds, which would undergo SN^2 reaction faster?

i. C_6H_{11}-CH_2Cl and C_6H_{11}-Cl
ii. $CH_3CH_2CH_2CH_2I$ and $CH_3CH_2CH_2CH_2Cl$

Ans. (i) C_6H_{11}-CH_2Cl is primary halide and therefore undergoes SN^2 reaction faster.

(ii) $CH_3CH_2CH_2CH_2I$ will undergoes SN^2 reaction faster because iodide ion is a better leaving group because of its large size, it will be released at a faster rate in the presence of incoming nucleophile.

Q23. Predict the order of reactivity of the following compounds in SN^1 and SN^2 reactions:

(i) The four isomeric bromobutanes
(ii) $C_6H_5CH_2Br$, $C_6H_5CH\ (C_6H_5)\ Br$, $C_6H_5\ CH\ (CH_3)\ Br$, $C_6H_5\ C\ (CH_3)\ (C_6H_5)\ Br$

Ans. In SN^1 reaction, stability of carbocation decreases, tertiary > secondary > primary
(i) $CH_3CH_2CH_2CH_2Br < (CH_3)_2CHCH_2Br < CH_3CH_2CH\ (Br)\ CH_3 < (CH_3)_3CBr\ (SN^1)$
$CH_3CH_2CH_2CH_2Br > (CH_3)_2CHCH_2Br > CH_3CH_2CH\ (Br)\ CH_3 > (CH_3)_3CBr\ (SN^2)$
(ii) $C_6H_5C\ (CH_3)\ (C_6H_5)\ Br > C_6H_5CH\ (C_6H_5)\ Br > C_6H_5CH\ (CH_3)\ Br > C_6H_5CH_2Br\ (SN^1)$
$C_6H_5\ C\ (CH_3)\ (C_6H_5)\ Br < C_6H_5\ CH\ (C_6H_5)\ Br < C_6H_5\ CH\ (CH_3)\ Br < C_6H_5CH_2Br\ (SN^2)$

Q24. Explain why (i) the dipole moment of Chlorobenzene is lower than that of cyclohexyl chloride?

(ii) Alkyl halides, though polar, are immiscible with water?

(iii) Grignard reagents should be prepared under anhydrous conditions?

Ans. (i) Due to magnitude of negative charge (δ-) is less on Cl atom of Chlorobenzene than in cyclohexyl chloride.

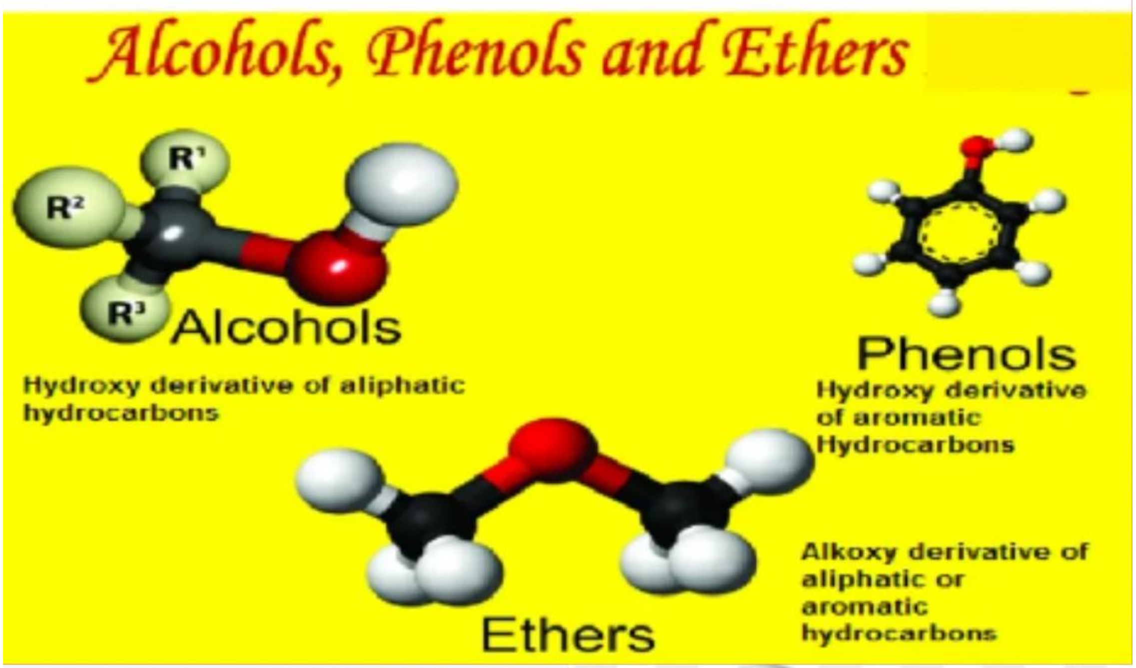
(ii) Alkyl halides, though polar, are immiscible with water because the molecules of water are held together by hydrogen bonds.

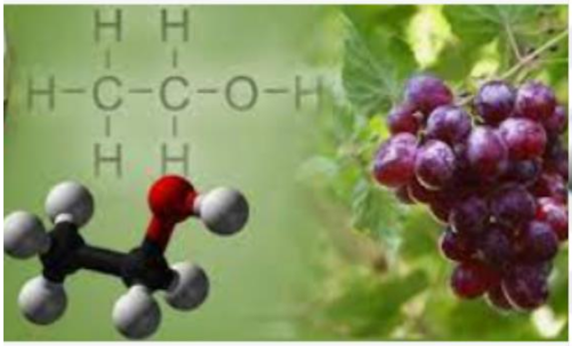
(iii) Grignard reagents are very reactive.

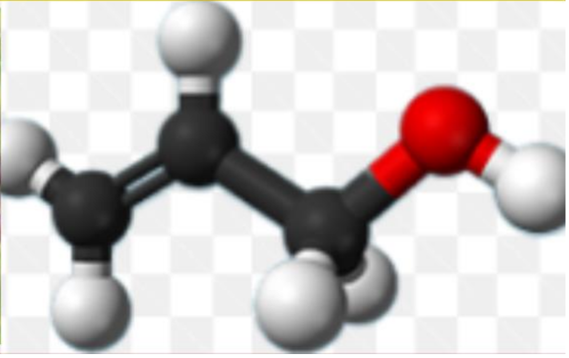
Q25. Primary alkyl halide C_4H_9Br (a) reacted with alcoholic KOH to give compound (b). Compound (b) is reacted with HBr to give (c) which is an isomer of (a). When (a) is reacted with sodium metal it gives compound (d), C_8H_{18} which is different from the compound formed when n-butyl bromide is reacted with sodium. Give the structural formula of (a) and write the equations for all the reactions.

Ans. (a) isobutyl bromide
(b) 2-methyl prop-1-ene
(c) t-butyl bromide
(d) 2, 5-dimethyl hexane.

UNIT VII ALCOHOLS, PHENOLS AND ETHERS







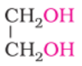
Alcohols and Phenols

Alcohols and phenols are formed when a hydrogen atom in hydrocarbon (aliphatic and aromatic) is replaced by hydroxyl group (-OH group).

1. Alcohols and phenols may be classified as monohydric, dihydric, trihydric or polyhydric according to number of hydroxyl groups they contain one, two, three or many respectively in their molecules. Alcohols may be

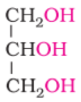
C_2H_5OH

Monohydric



CH_2OH-CH_2OH

Dihydric

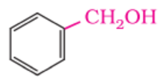


$CH_2OH-CHOH-CH_2OH$

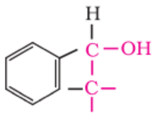
Trihydric

2.In phenols, -OH group is attached to Sp^2 hybridized carbon. These may also be monohydric, dihydric, etc. The dihydric phenol be ortho, Meta' or para derivative.

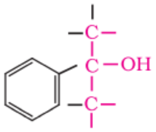
3.In Allylic alcohols, – OH group is attached to sp^3 hybridized carbon but next to C=C bond. e.g., $CH_2 = CH - CH_2OH$, Benzyl alcohol ($C_6H_5CH_2OH$).



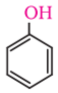
Primary



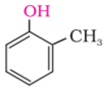
Secondary



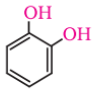
Tertiary



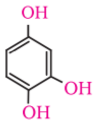
Monohydric



Monohydric



Dihydric



Trihydric

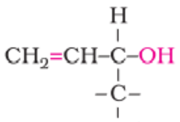
Classification of Alcohols and Phenols

In alcohols, -OH group is attached to Sp^3 hybridized carbon. These alcohols are usually classified as primary, secondary and tertiary alcohols.

Allylic alcohols: classified as primary, secondary and tertiary alcohols.

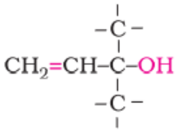
$CH_2=CH-CH_2-OH$

Primary



$CH_2=CH-\underset{|}{\overset{H}{C}}-OH$

Secondary



$CH_2=CH-\underset{|}{\overset{|}{C}}-OH$

Tertiary

Structures of Methanol, Phenols and Methoxymethane (Dimethyl ether)

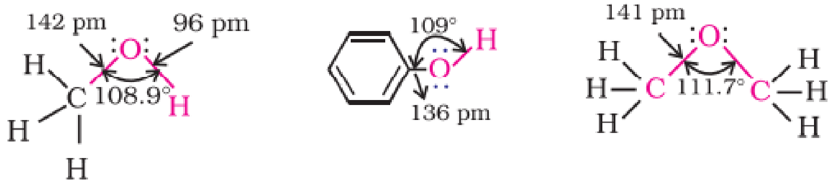


Fig. 11.1: Structures of methanol, phenol and methoxymethane

Isomerism in Alcohols: Alcohols exhibits four types of structural isomers:

(i)Chain isomer: $C_4H_{10}O$ Butan-1-ol, 2-methylpropan-1-ol

(ii)Position isomerism: C_3H_8O Propan-1-ol, propan-2-ol
(iii)Functional isomerism: C_2H_6O Ethanol, methoxy methane
(iv)Optical isomerism: Monohydric alcohols containing chiral carbon atoms exhibit optical isomerism. E.g. Butan-2-ol, Pentan-2-ol

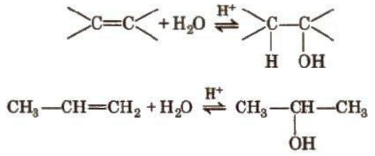
Nomenclature of Alcohols and Phenol:

In IUPAC, system, alcohol or alkanols are named by replacing the last word 'e' of the corresponding alkane by 'ol'. e.g., Propan-1, 2, 3-triol, 2-methyl phenol and 2, 4-dimethylcyclopentanol.

Preparation of Alcohols

(i) **From alkenes**

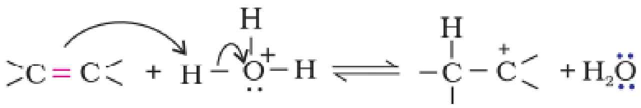
(a) By acid catalyzed hydration in accordance with Markovnikov's rule.



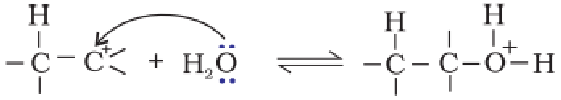
Mechanism

Step I Protonation of alkene to form carbocation by electrophilic attack of H_3O^+

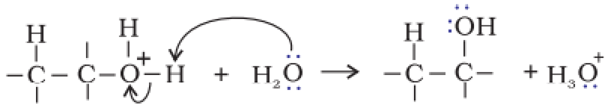
$$H_2O + H^+ \rightarrow H_3O^+$$



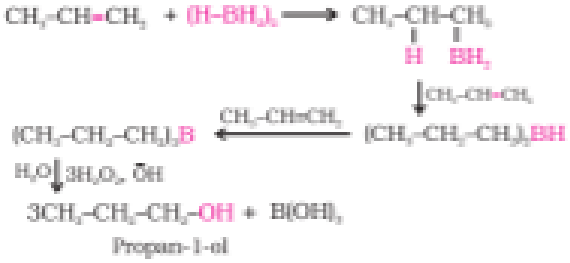
Step II Nucleophilic attack of water on carbocation forming protonated alcohol.



Step III Deprotonation to form an alcohol.



(b) **By hydroboration-oxidation:** Diborane B_2H_6 reacts with alkenes (prop-1-ene) to give trialkyl boranes as addition product. This is oxidised to alcohol (Propan-1-ol) by hydrogen peroxide in the presence of aqueous sodium hydroxide.



(ii) **From carbonyl compounds**

. By reduction of aldehydes and ketones:

R – CHO + H_2 Pd R – CH_2 – OH

R CO R' NaBH4 R –CH (OH) – R'

b. By reduction of carboxylic acids and ester

$R-COOH$ LiAlH4 /H2O $R-CH_2-OH$

(iii) **From haloalkanes:**

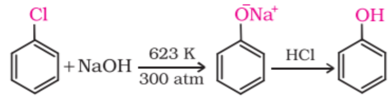
$R-X + KOH(aq) \rightarrow ROH + KX$

(iv) **From primary amines** by treatment with nitrous acid.

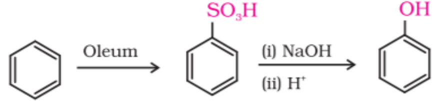
$R-NH_2 + HONO$ NaNO + HCl $R-OH + N_2 + H_2O$

Preparation of Phenols

(i) **From Haloarenes (Dow's process)**



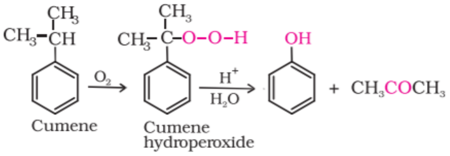
(ii) **From benzene sulphonic acid**



(iii) **From diazonium salts: Aniline to Phenol**

$C_6H_5-NH_2$ $NaNO_2 + HCl$ $C_6H_5-N_2^+Cl^-$ H2O $C_6H_5-OH + N_2 + H_2O$

(iv) **From cumene**



Physical Properties of Alcohols

1. The hydroxyl groups in alcohols can form H-bonds with water, so alcohols are miscible with water. The solubility decreases with increase in molecular mass.

2. Boiling points of alkanes are higher than expected because of the presence of intermolecular hydrogen bonding in the polar molecules. The boiling point decreases in the order 1° > 2° > 3°, This is due to the fact that with branching, the surface area decreases and therefore, Vander walls forces decrease, consequently, boiling point also decreases.

Physical Properties of Phenols

1. These are colourless liquids or crystalline solids but become coloured due to slow oxidation with air.

2. Phenol is also called carbolic acid.

3. Because of the presence of polar -OH bond, phenols form intermolecular H-bonding with other phenol molecules and with water.

4. Boiling point of phenols are higher than the boiling points of aromatic hydrocarbons, due to the presence of intermolecular hydrogen bonding in phenols.

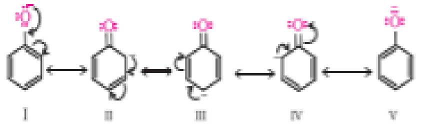
Chemical Reactions of Alcohols and Phenols

(i) **Reactions involving cleavage of O – H Bond**

(a) Acidity of alcohols and phenols: $R-OH + 2Na$ $2R-ONa + H_2$

$C_6H_5-OH + 2Na$ $2C_6H_5-ONa + H_2$

Alcohols are weaker acids than water due to (+I effect) group present in alcohols, which decreases the polarity of -O-H bond.
Acid strength of alcohols: 1° > 2° > 3°
Electron releasing group increases electron density on oxygen to decrease the polarity of – OH bond.
Order of acidity is: $RCOOH > H_2CO_3 > C_6H_5OH > H_2O > R - OH$.
Phenol is more acidic than alcohols due to stabilization of phenoxide ion through resonance.



Presence of electron withdrawing groups ($-NO_2$, -CN, -X) increases the acidity of phenol by stabilizing phenoxide ion while presence of electron releasing groups (-R, $-NH_2$, -OR) decreases the acidity of phenol by destabilizing phenoxide ion.
Thus, increasing acidic strength is
o-cresol < p-cresol < m-cresol < phenol < o-nitrophenol < 2, 4, 6 Trinitrophenol (picric acid)
Higher K_a and lower pK_a value correspond to the stronger acid.

(b) **Esterification:** The reaction with R'COOH and $(R'CO)_2O$ is reversible, so cone, H_2SO_4 is used to remove water.
The reaction with R' COCI is carried out in the presence of pyridine so as to neutralize HCI which is formed during the reaction.

$$Ar/ROH + R'-COOH \overset{H^+}{\rightleftharpoons} Ar/ROCOR' + H_2O$$
$$Ar/R-OH + (R'CO)_2O \overset{H^+}{\rightleftharpoons} Ar/ROCOR' + R'COOH$$
$$R/ArOH + R'COCl \xrightarrow{Pyridine} R/ArOCOR' + HCl$$

The introduction of acetyl (CH_3CO-) group in phenols is known as acetylation.
Acetylation of salicylic acid produces aspirin.

(ii) **Reaction involving cleavage of C-O bond in alcohols** in these reactions, the reactivity order of alcohols: 3° > 2° > 1°
Alkyl group due to +1 effect increases the electron density on the carbon and oxygen atom of C-O bond. As a result, the bond cleavage becomes easy. Greater the number of alkyl groups present; more will be the reactivity of alcohol. 3° > 2° > 1° (Reactivity decreases)
(a) **Reaction with halogen acids:** Alcohols can be converted into haloalkanes by the action of halogen acids.
In this reaction anhydrous $ZnCl_2$ is used, $R - OH + HCI \rightarrow R\text{-}Cl + H_2O$
In this reaction conc. H_2SO_4 & reflux, $R - OH + HBr \rightarrow R\text{-}Br + H_2O$
In this reaction Red P at 423 K, $R - OH + HI \rightarrow R\text{-}H + I_2 + H_2O$
For a given alcohol order of reactivity of HX is H-1 > H-Br > H-Cl
This is because I^- ion is a better nucleophile than Br^- ion,
For a given halogen acid order of reactivity of alcohols: Tertiary > Secondary > Primary
(b) **Reaction with phosphorus halides:**

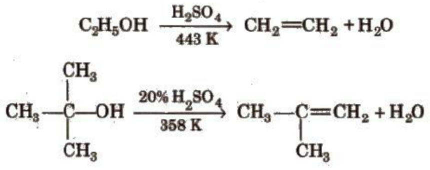
$ROH + PCl_5$ ⍰ $RCl + POCl_3 + HCl$

(c) **Reaction with thionyl chloride:**

$ROH + SOCl_2$ ⍰ $RCl + SO_2 + HCl$

d) **Dehydration of alcohols** It requires acid catalyst and the reaction proceeds via intermediate carbonium ion. Acidic catalyst converts hydroxyl group into a good leaving group. Since, the rate determining step is the formation of carbocation, the ease of dehydration

$3° > 2° > 1°$

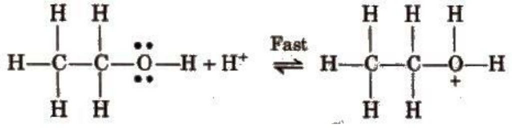


$$C_2H_5OH \xrightarrow[443\ K]{H_2SO_4} CH_2{=}CH_2 + H_2O$$

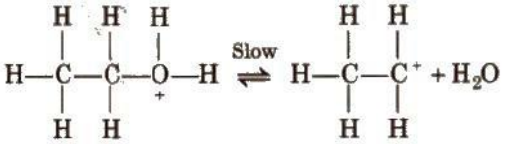
$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-OH \xrightarrow[358\ K]{20\%\ H_2SO_4} CH_3-\underset{CH_3}{C}{=}CH_2 + H_2O$$

Mechanism

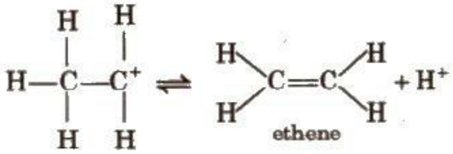
Step I Formation of protonated alcohol



Step II Formation of carbocation

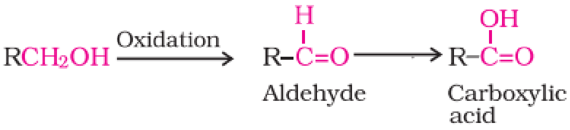


Step III Formation of Ethene by elimination of a proton



In dehydration reaction, highly substituted alkene is the major product and if the major product is capable of showing cis-trans isomerism, trans-product is the major product. (Saytzeff rule).

(iii) Oxidation reactions: Oxidizing reagents used for the oxidation of alcohols are neutral, acidic or alkaline $KMnO_4$ and acidified $K_2Cr_2O_7$.



$$RCH_2OH \xrightarrow{Oxidation} R-\overset{H}{C}{=}O \longrightarrow R-\overset{OH}{C}{=}O$$

Aldehyde

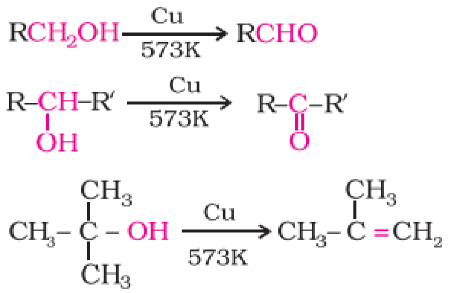
Carboxylic acid

$$RCH_2OH \xrightarrow{CrO_3} RCHO$$

A common reagent that selectively oxidizes a primary alcohol to an aldehyde (and no further) is pyridinium chlorochromate (PCC).

$$CH_3-CH=CH-CH_2OH \xrightarrow{PCC} CH_3-CH=CH-CHO$$

(iv) **Dehydrogenation:**



$$RCH_2OH \xrightarrow[573K]{Cu} RCHO$$

$$R\text{-}\underset{OH}{CH}\text{-}R' \xrightarrow[573K]{Cu} R\text{-}\underset{O}{\overset{}{C}}\text{-}R'$$

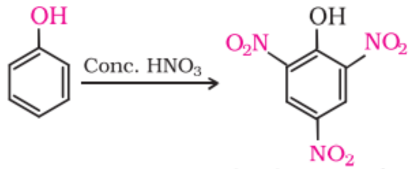
$$CH_3\text{-}\underset{CH_3}{\overset{CH_3}{C}}\text{-}OH \xrightarrow[573K]{Cu} CH_3\text{-}\overset{CH_3}{C}=CH_2$$

Distinction among 1°,2° and 3° Alcohols:
1°, 2° and 3° alcohols are distinguished by Lucas test. In this test with an equimolar concentrated HCl and anhydrous $ZnCl_2$.The alcohols get converted into alkyl halides. Since the alkyl halides are insoluble in water, their formation is indicated by the appearance of turbidity in the reaction mixture.
If turbidity appears immediately, the alcohol is tertiary.
If turbidity appears within five minutes, the alcohol is secondary.
If turbidity appears only upon heating, the alcohol may be primary.
Victor Meyer's test is also used to distinguish them. This test involves the following steps:
(i)The given alcohol is treated with red phosphorous and iodine resulting in the formation of alkyl iodide.
(ii)The alkyl iodide is treated with silver nitrate to form nitroalkane.
(iii)The nitroalkane finally reacted with nitrous acid and resulting solution is made alkaline.
Formation of a blood red colour indicates the primary alcohol.
Formation of a blue colour shows the original alcohol to be secondary.
A colourless solution means that alcohol is tertiary alcohol.

Reactions of Phenols
1. Electrophilic substitution reactions The -OH group attached to the benzene ring activates it towards electrophilic substitution at ortho and para positions.

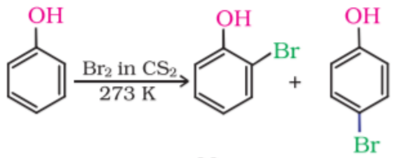
(i)(a)**Nitration:** With dilute nitric acid at low temperature (298 K), phenol yields a mixture of ortho and para nitrophenol.

The ortho and para isomers can be separated by steam distillation. This is because o-nitrophenol is steam volatile due to intramolecular hydrogen bonding while p nitrophenol is less volatile due to intermolecular hydrogen bonding which causes the association of molecules.
(b)With concentrated nitric acid, phenol is converted to 2, 4, 6-trinitrophenol (Picric acid)



2,4,6-Trinitrophenol
(Picric acid)

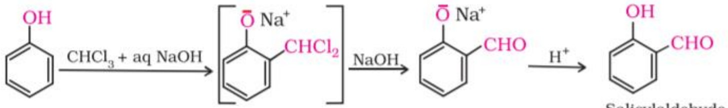
(ii) (a)**Halogenation:** With calculated amount of Br_2 in CS_2 or $CHCl_3$ it gives ortho and para product



Minor Major

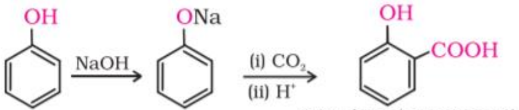
(b)When phenol is treated with bromine water, 2, 4, 6-tribromophenol is formed as white precipitate.

(d) **Reimer-Tiemann reaction:** On treating phenol with chloroform in the presence of sodium hydroxide, a –CHO group is introduced at ortho position of benzene ring. This reaction is known as Reimer - Tiemann reaction.



Intermediate Salicylaldehyde

(ii) **Kolbe's reaction:**

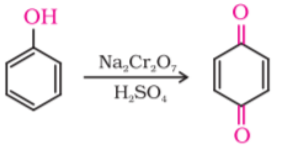


2-Hydroxybenzoic acid
(Salicylic acid)

(iii) **Reaction with zinc dust:** Phenol is converted to benzene on heating with zinc dust.

$C_6H_5OH + Zn \rightarrow C_6H_6 + ZnO$

(iv) **Oxidation:** Oxidation of phenol with chromic acid produces a conjugated diketone known as benzoquinone.



benzoquinone

ETHERS: Structure of Ether

Ethers Classifications

Ethers can be classified into two categories; they are listed below.

- **Symmetrical Ethers**

If two identical groups are attached to either side of an oxygen atom, then it is referred to as symmetrical ethers. These are also known as Simple Ethers.
Examples are diethyl ether, dipropyl ether, dimethyl ether, and more.

- **Asymmetrical Ethers**

If two different groups are attached to either side of an oxygen atom, it is said to be asymmetrical ethers. These are also known as Mixed Ethers.
Examples are methyl phenyl ether, ethyl methyl ether, and more.

Nomenclature of Ethers:

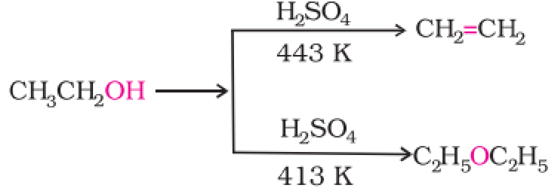
CH_3OCH_3 is named as "Dimethyl ether."
$CH_3OC_2H_5$ is named as "Ethyl methyl ether." "1-methoxy ethane."
$CH_3OC_6H_5$ is named as "Methyl phenyl ether."
$C_6H_5OC_2H_5$ is named as ''Ethyl phenyl ether'' & also, known as phenetole.

Physical Properties of Ethers

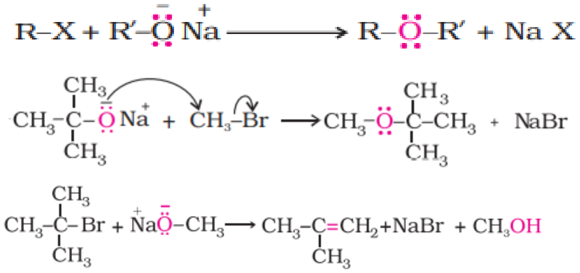
Ethers are polar but insoluble in H_2O and have low boiling point than alcohols of comparable molecular masses because ethers do not form hydrogen bonds with water.

Preparation of Ethers: Ethers can be prepared

(a) by dehydration of alcohols

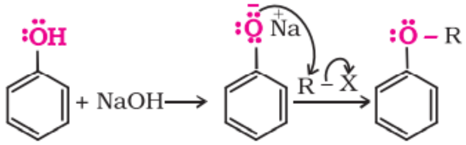


(b)Williamson's synthesis: Only primary alkyl halides when react with sodium alkoxide give ether while tertiary alkyl halides give alkene due to steric hindrance.



2-Methylpropene

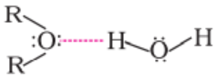
(c)For Aryl ethers, Phenol converted into ether.



Physical properties of ether: The C – O bond in ethers are polar. The boiling point of alkanes, alcohols and ethers as follows:

Formula	$CH_3(CH_2)_3CH_3$ n-Pentane	C_2H_5-O-C_2H_5 Ethoxyethane	$CH_3(CH_2)_3$-OH Butan-1-ol
b.p./K	309.1	307.6	390

The miscibility of ethers with water due to hydrogen bond with water.



Chemical properties:

(a) Cleavage of C-O bond in ethers:

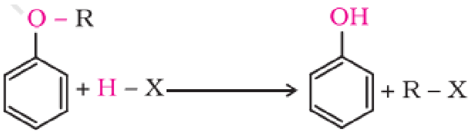
R – O – R' + HX ⍰ RX + R' – OH

R' – OH + HX ⍰ R' – X + H_2O

(b) Electrophilic substitution: In this, the alkoxy group activates the aromatic ring and directs the incoming group to ortho and para positions.

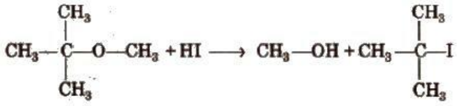
(i) **Reaction with HX:**

R – O – R + HX ⍰ RX + R – OH



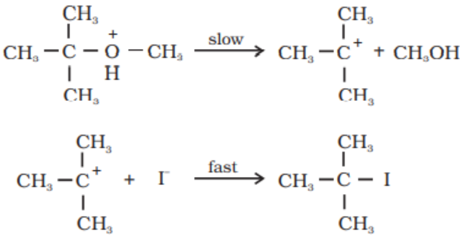
The order of reactivity of hydrogen halides is as follows: HI > HBr > HCl

In ethers if one of the alkyl groups is a tertiary group, the halide formed is a tertiary halide by $S_{N}{}^{1}$ mechanism.



$$CH_3-C(CH_3)_2-O-CH_3 + HI \longrightarrow CH_3-OH + CH_3-C(CH_3)_2-I$$

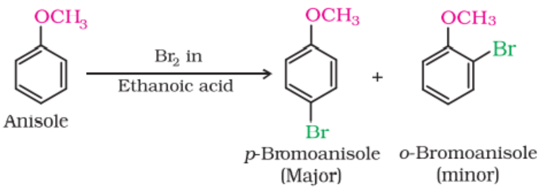
Mechanism:



$$CH_3-C(CH_3)_2-\overset{+}{O}(H)-CH_3 \xrightarrow{slow} CH_3-\overset{+}{C}(CH_3)_2 + CH_3OH$$

$$CH_3-\overset{+}{C}(CH_3)_2 + I^- \xrightarrow{fast} CH_3-C(CH_3)_2-I$$

(ii)Halogenation: Bromination of Anisole**:**



(iii)Reaction with PCl_5:

Ethers on heating give alkyl halides

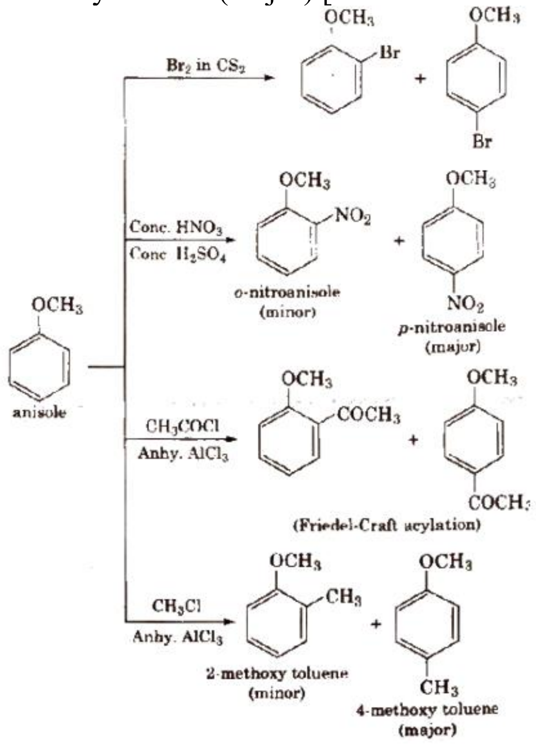
$R - O - R + PCl_5 \rightarrow RCl + POCl_3$

(iv)Reaction with CO:

$R - O - R + CO \rightarrow RCOOR$

(v) Electrophilic substitution reactions in ethers, -OR is ortho, para directing group and activate. the aromatic ring towards electrophilic substitution reaction.

1. Anisole reacts with Br_2 to give ortho- and para-bromo anisole (major)
2. Anisole reacts with concentrated nitric acid and concentrated Sulphuric acid to give ortho- and para-nitro anisole (major)
3. Anisole reacts with CH_3COCl in the presence of anhydrous $AlCl_3$ to give 2-methoxy acetophenone and 4-methoxy acetophenone (major) [Friedal Craft acylation]
4. Anisole reacts with CH_3Cl in the presence of anhydrous $AlCl_3$ to give 2-methoxy toluene and 4-methoxy toluene (major) [Friedal Craft alkylation]



Uses of Ethers

1. Dimethyl ether is used as refrigerant and as a solvent at low temperature.
2. Diethyl Ether is used as an anaesthesia in surgery.

ASSIGNMENTS:

Q1. Benzene diazonium chloride on reaction with phenol in weakly basic medium gives

. diphenyl ether
a. p-hydroxy azobenzene
b. chlorobenzene
c. Benzene

Ans. (b)

Q2. Phenol reacts with bromine in CS_2 at low temperature to give

. m-bromophenol

a. o-and p-bromophenol

b. p-bromophenol

c. 2,4,6-tribromophenol

Ans. (b)

Q3. Dehydration of alcohol is an example of

. addition reaction

a. elimination reaction

b. substitution reaction

c. redox reaction

Ans. (b)

Q4. Which of the following is formed when phenol is exposed to air?

. o-Benzoquinone

a. p-Benzoquinone

b. Phenoquinone

c. o-and p-Benzoquinone

Ans. (d)

Q5. The alcohol which does not react with Lucas's reagent is

. isobutyl alcohol

a. n-butanol

b. tert-butyl alcohol

c. sec-butyl alcohol

Ans. (b)

Q6. Give the structures and IUPAC names of the products expected from the following reactions:

(a) Catalytic reduction of butanal.

(b) Hydration of propene in the presence of dilute Sulphuric acid.

(c) Reaction of Propanone with methyl magnesium bromide followed by hydrolysis.

Ans. (a) Butan-1-ol

(b) Propan-2-ol

(c)2-methyl Propan-2-ol

Q7. Arrange the following sets of compounds in order of their increasing boiling points:

(a) Pentan-1-ol, butan-1-ol, butan-2-ol, ethanol, propan-1-ol, methanol.

(b) Pentan-1-ol, n-butane, pentanal, ethoxyethane.

Ans. (a) Methanol, ethanol, propan-1-ol, butan-2-ol, butan-1-ol, pentan-1-ol.

(b) n-Butane, ethoxyethane, pentanal and pentan-1-ol.

Q8. Arrange the following compounds in increasing order of their acid strength:

Propan-1-ol, 2, 4, 6-trinitrophenol, 3-nitrophenol, 3, 5-dinitrophenol, phenol, 4-methylphenol.

Ans. Propan-1-ol, 4-methylphenol, phenol, 3-nitrophenol, 3,5-dinitrophenol, 2,4, 6-trinitrophenol.

Q9. Give structures of the products you would expect when each of the following alcohol reacts with (a) HCl –$ZnCl_2$ (b) HBr and (c) $SOCl_2$.

.Butan-1-ol
i.2-Methylbutan-2-ol

Ans. (a) HCl –$ZnCl_2$, it is a Lucas reagent.

(i) Turbidity appears upon heating (ii) white turbidity formed

(b) With HBr to give alkyl halides.

(c) Both alcohols react to give alkyl chlorides.

Q10. Predict the major product of acid catalyzed dehydration of

.1-methylcyclohexanol
i.butan-1-ol

Ans. (i) 1- Methyl cyclohexene (ii) But-2-ene.

Q11. Ortho and para nitrophenols are more acidic than phenol. Draw the resonance structures of the corresponding phenoxide ions.

Ans. Draw the resonance structures of o- & p- phenoxide ions.

Due to –I and –R effect of –NO_2 group, o- & p- phenoxide ions are more stable. Hence, Ortho and para nitrophenol are more acidic than phenol.

Q12. Write the equations involved in the following reactions:

.Reimer - Tiemann reaction
i.Kolbe’s reaction

Ans. (i) Reimer - Tiemann reaction – when phenol reacts with chloroform in the presence of aqueous sodium hydroxide, salicylaldehyde is formed.

(ii) Kolbe’s reaction- when sodium phenoxide is heated with carbon dioxide at about 400K and under

4 to 7 atmospheric pressure, sodium salicylate is formed. On acidification gives salicylic acid.

Q13. The following is not an appropriate reaction for the preparation of t-butyl ethyl ether.

$C_2H5Na + (CH_3)_3 – Cl \qquad (CH_3)_3 – OC_2H_5$

.What would be the major product of this reaction?
i.Write a suitable reaction for the preparation of t-butyl ethyl ether.

Ans. (i) The major product of the given reaction is 2-methylprop-1-ene. It is because sodium ethoxide is a strong nucleophile as well as a strong base. Thus, elimination reaction predominates over substitution.

(ii) $(CH_3)_3 - O^- Na^+ + CH_3CH_2Cl$ $(CH_3)_3 - OC_2H_5$

Q14. Write the mechanism of hydration of Ethene to yield ethanol.

Ans. It is an example of electrophilic addition.

$CH_2 = CH_2 + H^+$ CH_3CH_2OH

Q15. Write the names of reagents and equations for the preparation of the following ethers by Williamson's synthesis:

.1-Propoxypropane
i.Ethoxy benzene
ii.2-Methoxy-2-methylpropane
iii.1-Methoxyethane

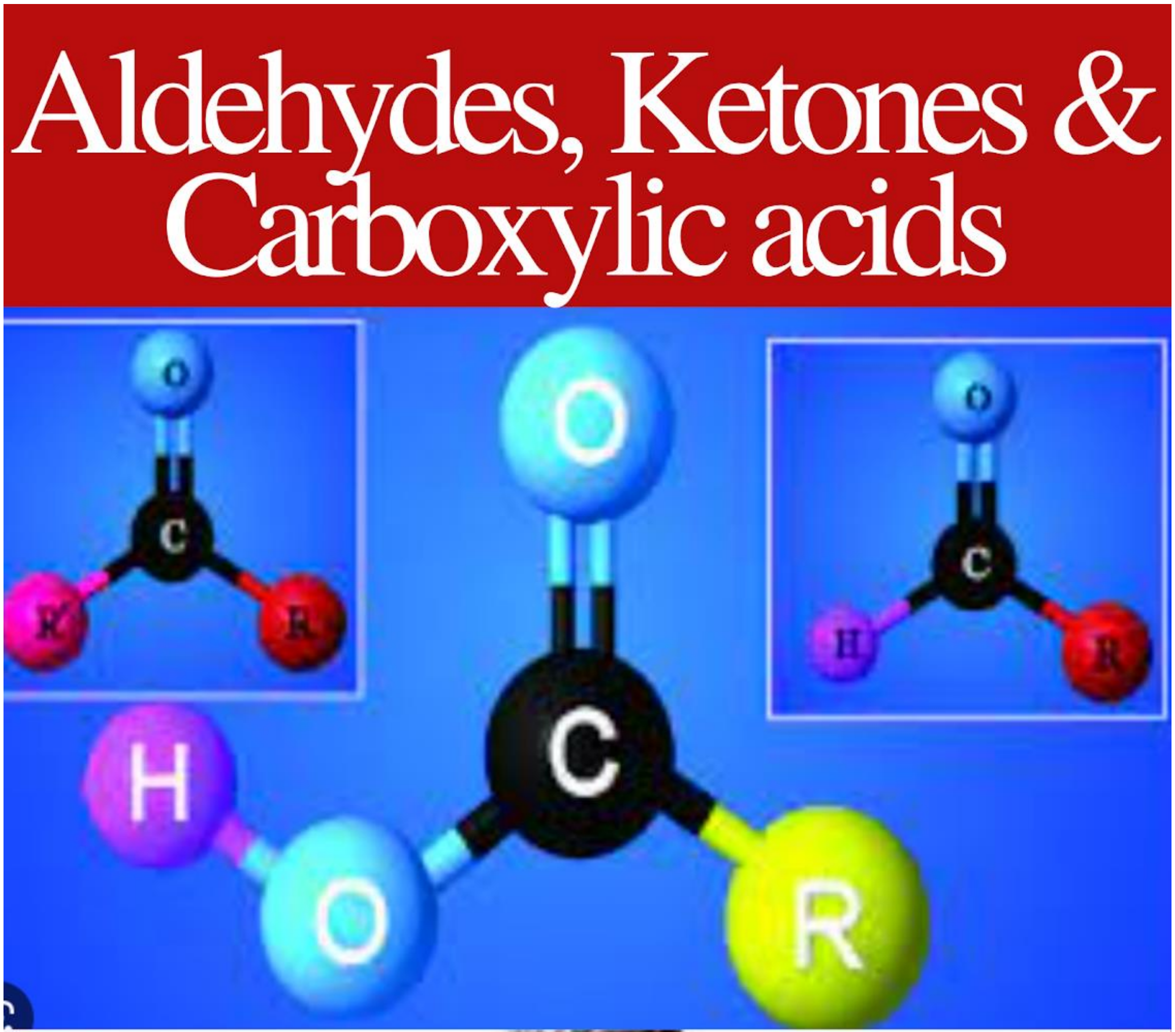
Ans. (i) Sodium propoxide + 1-bromopropane

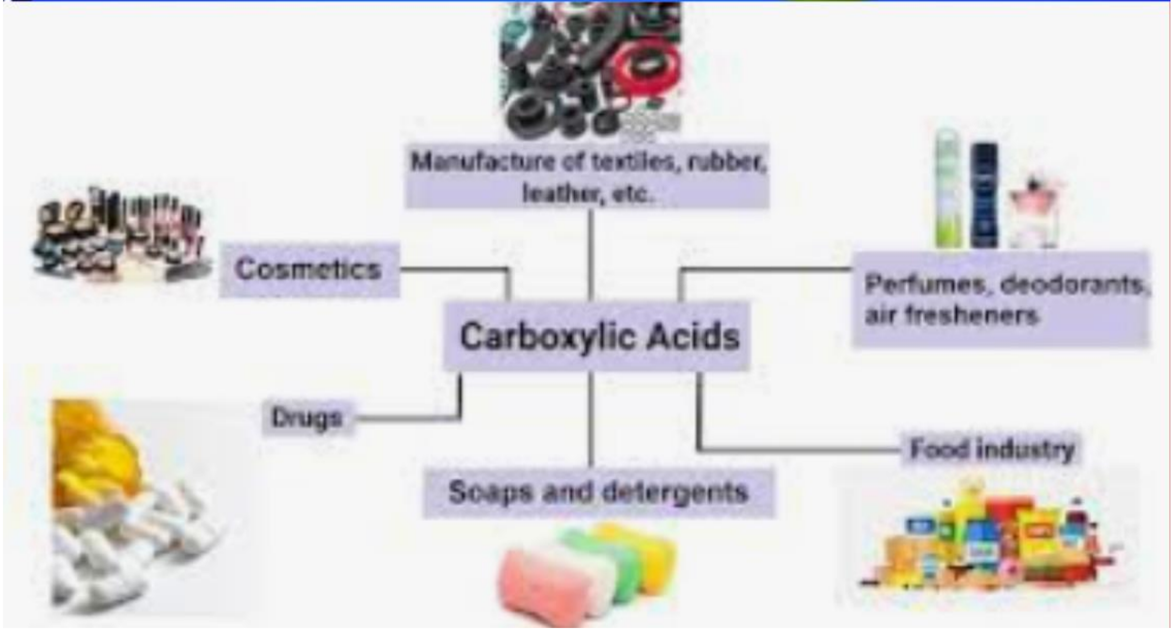
(ii) Sodium phenoxide + ethyl bromide

(iii)Sodium 2-methyl-2-propoxide + Bromomethane

(iv)Sodium ethoxide + Bromomethane

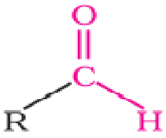
UNIT VIII ALDEHYDES, KETONES AND CARBOXYLIC ACIDS



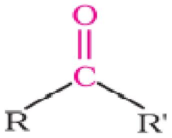


Aldehydes and Ketones: The organic compounds containing carbon-oxygen double bond (>C=O) called carbonyl group, which is one of the most important functional groups in organic chemistry.

In aldehydes, the carbonyl group is bonded to a carbon and hydrogen while in the ketones; it is bonded to two carbon atoms.



Aldehyde



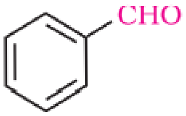
Ketone

Nomenclature: There are two systems of nomenclature of aldehydes and ketones.

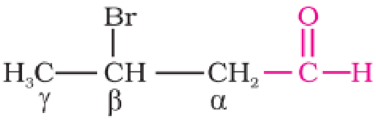
(a) Common names: Acetaldehyde, Benzaldehyde and β-Bromo-butyraldehyde

CH_3CHO

Acetaldehyde



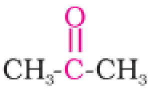
Benzaldehyde



$\underset{\gamma}{H_3C}-\underset{\beta}{\overset{Br}{\overset{|}{CH}}}-\underset{\alpha}{CH_2}-\overset{O}{\overset{\|}{C}}-H$

β-Bromobutyraldehyde

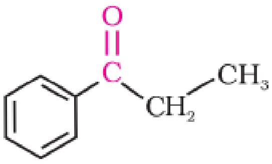
Acetone, Acetophenone, Propiophenone and Benzophenone



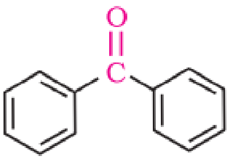
$CH_3-\overset{O}{\overset{\|}{C}}-CH_3$

Acetone

Acetophenone

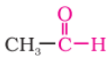


Propiophenone



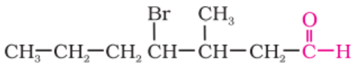
Benzophenone

(b) IUPAC names: The IUPAC names of open chain aliphatic aldehydes and ketones are derived from the names of the corresponding alkanes by replacing the ending –e with –al and –one respectively.



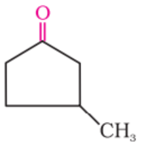
$CH_3-\overset{\overset{O}{\|}}{C}-H$

Ethanal

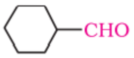


$CH_3-CH_2-CH_2\ \underset{}{\overset{\overset{Br}{|}}{CH}}-\overset{\overset{CH_3}{|}}{CH}-CH_2-\overset{\overset{O}{\|}}{C}-H$

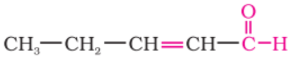
4-Bromo-3-methylheptanal



3-Methylcyclopentanone

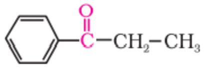


Cyclohexanecarbaldehyde

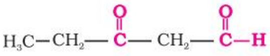


$CH_3-CH_2-CH=CH-\overset{\overset{O}{\|}}{C}-H$

Pent-2-enal

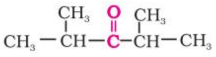


1-Phenylpropan-1-one



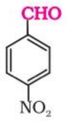
$H_3C-CH_2-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-H$

3-Oxopentanal

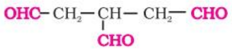


$CH_3-\overset{\overset{CH_3}{|}}{CH}-\overset{\overset{O}{\|}}{C}-\overset{\overset{CH_3}{|}}{CH}-CH_3$

2,4-Dimethylpentan-3-one



4-Nitrobenzenecarbaldehyde
or
4-Nitrobenzaldehyde



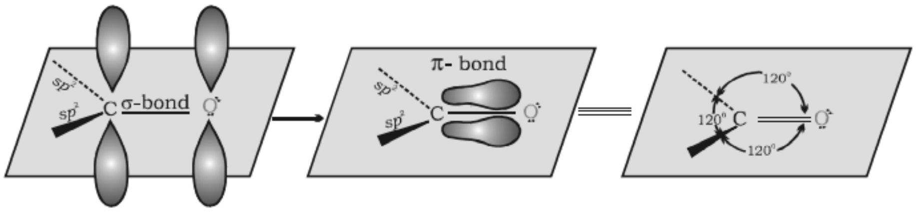
$OHC-CH_2-\underset{\underset{CHO}{|}}{CH}-CH_2-CHO$

Propane–1,2,3-tricarbaldehyde

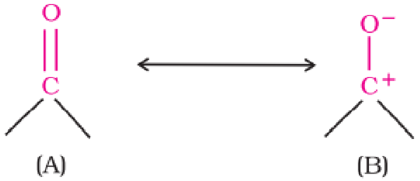
Note: To give identical treatment to all aldehydic groups, the compound is named as shown above.

Structure of the Carbonyl Group: The carbonyl carbon atom is sp^2 -hybridized and forms three sigma (σ) bonds. The fourth valence electron of carbon remains in its p-orbital and forms a π-bond with oxygen by overlap with p-orbital of oxygen. In addition, the oxygen atom also has two nonbonding electron pairs. Thus, the carbonyl carbon and the three atoms attached to it lie in the same plane and the π-electron cloud is above and below this plane. The bond angles are approximately 120° as expected of a Trigonal coplanar structure.

Orbital diagram for the formation of carbonyl group:



The carbon-oxygen double bond is polarized due to higher electronegativity of oxygen relative to carbon. Hence, the carbonyl carbon is an electrophilic (Lewis acid), and carbonyl oxygen, a Nucleophilic (Lewis base) centre. Carbonyl compounds have substantial dipole moments and are polar than ethers. The high polarity of the carbonyl group is explained on the basis of resonance involving a neutral (A) and a dipolar (B) structure as shown.



Preparation of Aldehydes and Ketones:

1. **By oxidation of alcohols:** Aldehydes and ketones are generally prepared by oxidation of primary and secondary alcohols, respectively.

CH_3CH_2OH K2Cr2O7 + dil H2SO4 CH_3CHO

By dehydrogenation of alcohols: This method is suitable for volatile alcohols and is of industrial application. In this method alcohol vapours are passed over heavy metal catalysts (Ag or Cu). Primary and secondary alcohols give aldehydes and ketones, respectively and Tertiary alcohol gives 2-methyl propene.

CH_3CH_2OH Cu, 573 K $CH_3CHO + H_2$

$CH_3CH\ (OH)\ CH_3$ Cu, 573 K $CH_3COCH_3 + H_2$

$(CH_3)_3COH$ Cu, 573 K $(CH_3)_2C = CH_2 + H_2$

2. **From hydrocarbons:**

   i. By ozonolysis of alkenes: Ozonolysis of alkenes followed by reaction with zinc dust and water gives aldehydes, ketones or a mixture of both depending on the substitution pattern of the alkene.

   $CH_2 = CH_2 + O_3$ □ Ethene ozonide Zn, H2O $2HCHO + H_2O_2$

   $CH_3CH = CH_2 + O_3$ □ Propene ozonide Zn, H2O $CH_3CHO + HCHO$

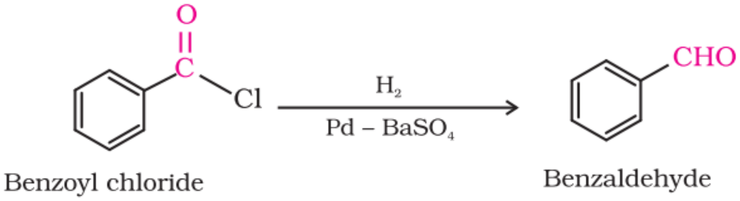
   ii. By hydration of alkynes: Addition of water to Ethyne in the presence of H_2SO_4 and $HgSO_4$ gives acetaldehyde. All other alkynes give ketones in this reaction.

   Ethyne + H_2O H2SO4 (dil), HgSO4 CH_3CHO

   Propyne + H_2O H2SO4 (dil), HgSO4 CH_3COCH_3

Preparation of Aldehydes:

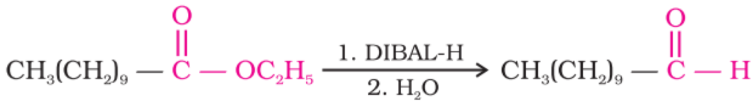
1. From acyl chloride (acid chloride): Acyl chloride (acid chloride) is hydrogenated over catalyst, palladium on barium sulphate. This reaction is called **Rosenmund's reduction.**



2. From nitriles: Nitriles are reduced to corresponding imine with stannous chloride in the presence of hydrochloric acid, which on hydrolysis give corresponding aldehyde. This reaction is called **Stephen reaction.**

$RCN + SnCl_2 + HCl$ --------> $RCH = NH$ ----------> $RCHO$

3. From esters: Esters are reduced to aldehydes with DIBAL-H.

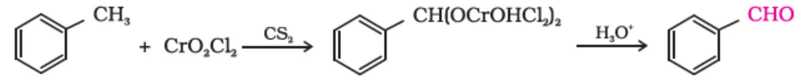


$$CH_3(CH_2)_9-\overset{O}{\overset{\|}{C}}-OC_2H_5 \xrightarrow[2.\ H_2O]{1.\ DIBAL\text{-}H} CH_3(CH_2)_9-\overset{O}{\overset{\|}{C}}-H$$

4. **From hydrocarbons:**

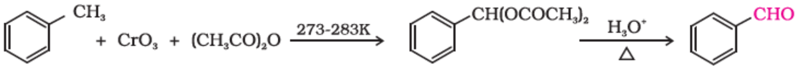
(i) By oxidation of methylbenzene

(a) Use of chromyl chloride (CrO_2Cl_2): This reaction is called Etard reaction.



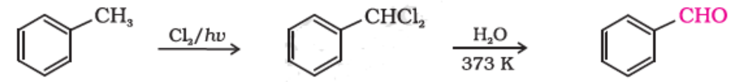
Toluene Chromium complex Benzaldehyde

(b) Use of chromic oxide (CrO_3):



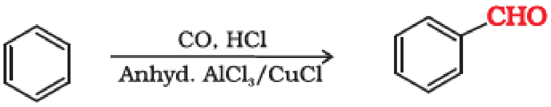
Benzaldehyde

(ii) By side chain chlorination followed by hydrolysis:



Toluene Benzal chloride Benzaldehyde

(iii) By Gatterman – Koch reaction:



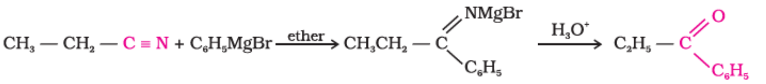
Preparation of Ketones:

1. **From acyl chlorides:**

$2RMgX + CdCl_2$ ------> $R_2Cd + 2Mg(X)Cl$

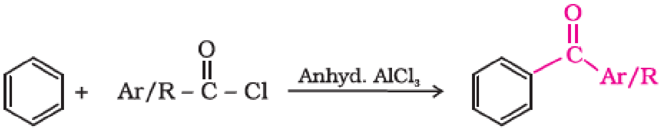
$2R'COCl + R_2Cd$ ------> $2R'COR + CdCl_2$

2. **From nitriles:**



Propiophenone
(1-Phenylpropanone)

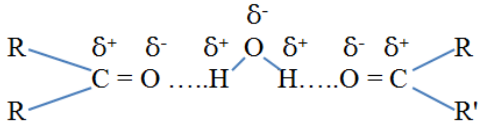
3. **From benzene or substituted benzenes:**



This reaction is known as Friedel-Crafts acylation reaction.

Physical Properties:

The boiling points of aldehydes and ketones are higher than hydrocarbons and ethers of comparable molecular masses. It is due to weak molecular association in aldehydes and ketones arising out of the dipole-dipole interactions. Also, their boiling points are lower than those of alcohols of similar molecular masses due to absence of intermolecular hydrogen bonding.
n-Butane < Methoxyethane < Propanal < Acetone < Propan-1-ol
The following compounds of molecular masses 72 and 74 are ranked in order of increasing boiling points.
$CH_3CH_2CH_2CH_3 < H_5C_2\text{-O-}C_2H_5 < CH_3CH_2CH_2CHO < CH_3CH_2CH_2CH_2OH$
The lower members of aldehydes and ketones such as Methanal, Ethanal and Propanone are miscible with water in all proportions, because they form hydrogen bond with water.

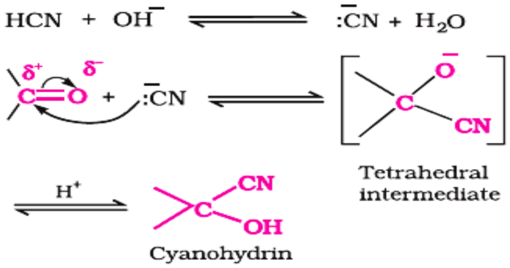


However, the solubility of aldehydes and ketones decreases rapidly on increasing the length of alkyl chain. All aldehydes and ketones are fairly soluble in organic solvents like benzene, ether, methanol, chloroform, etc.
The lower aldehydes have sharp pungent odours. As the size of the molecule increases, the odour becomes less pungent and more fragrant. In fact, many naturally occurring aldehydes and ketones are used in the blending of perfumes and flavouring agents.

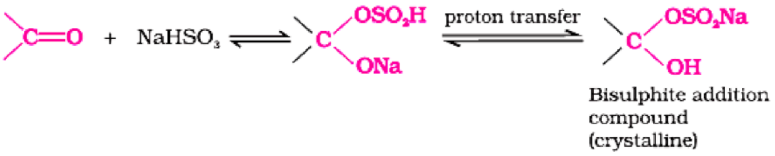
Chemical Properties:

1. Nucleophilic addition and Nucleophilic addition-elimination reactions:

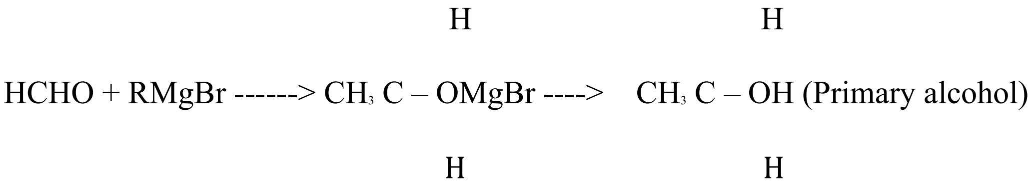
a. Addition of hydrogen cyanide (HCN):



b. Addition of sodium hydrogensulphite:

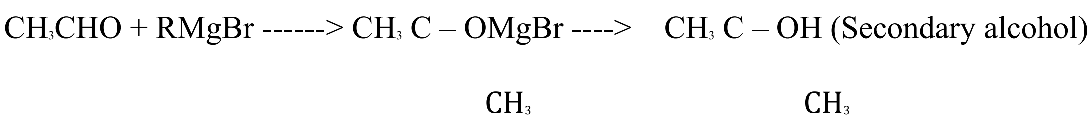


c. Addition of Grignard reagents:



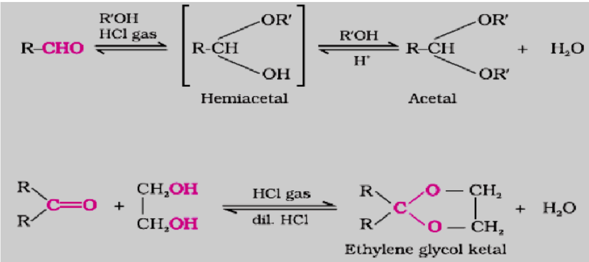
$$HCHO + RMgBr \text{------>} CH_3\,\overset{H}{\underset{H}{C}} - OMgBr \text{---->} CH_3\,\overset{H}{\underset{H}{C}} - OH \text{ (Primary alcohol)}$$

H H

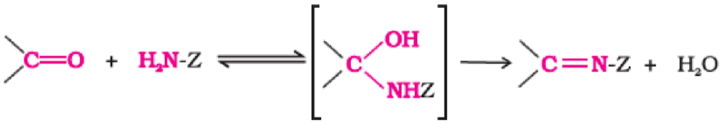


$$CH_3CHO + RMgBr \text{ ------> } CH_3\underset{CH_3}{C} - OMgBr \text{ ----> } CH_3\underset{CH_3}{C} - OH \text{ (Secondary alcohol)}$$

d. Addition of alcohols:



(e) Addition of ammonia and its derivatives:



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

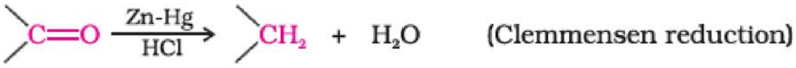
2. Reduction

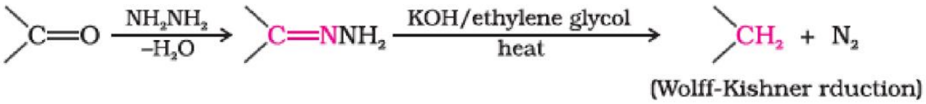
(i) Reduction to alcohols:

RCHO H2(Ni or Pt or Pd) Na/C2H5OH, LiAlH4 or NaBH4 RCH_2OH (Primary alcohol)

RCOR' H2(Ni or Pt or Pd) Na/C2H5OH, LiAlH4 or NaBH4 RCH(OH)R' (Secondary alcohol)

(ii) Reduction to hydrocarbons:





3. Oxidation:

RCHO [O] RCOOH

The mild oxidising agents mainly Tollen's' reagent and Fehling's' reagent are used to distinguish aldehydes from ketones:

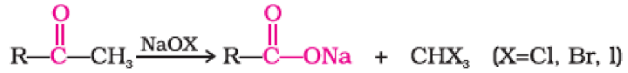
(i) Tollen's' test: On warming an aldehyde with freshly prepared ammoniacal silver nitrate solution (Tollen's' reagent), a bright silver mirror is produced due to the formation of silver metal.

$$RCHO + 2[Ag(NH_3)_2]^+ + 3\,\bar{O}H \longrightarrow RCO\bar{O} + 2Ag + 2H_2O + 4NH_3$$

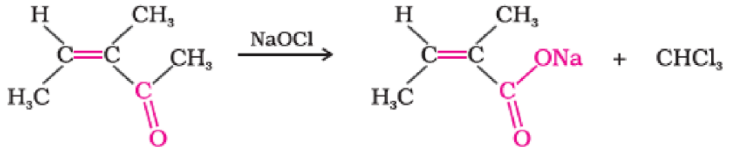
(ii) Fehling's test: On heating an aldehyde with Fehling's reagent, a reddish brown precipitate is obtained.

$$R\text{-}CHO + 2Cu^{2+} + 5\bar{O}H \longrightarrow RCO\bar{O} + \underset{\text{Red-brown ppt}}{Cu_2O} + 3H_2O$$

(iii) Oxidation of methyl ketones by haloform reaction:



$$R-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{NaOX} R-\overset{\overset{O}{\|}}{C}-ONa + CHX_3 \quad (X{=}Cl, Br, I)$$



4. Reactions due to a-hydrogen: (i) Aldol condensation: Aldehydes and ketones having at least one α-hydrogen undergo a reaction in the presence of dilute alkali as catalyst to form β-hydroxy aldehydes (Aldol) or β-hydroxy ketones (ketol), respectively. This is known as Aldol reaction.

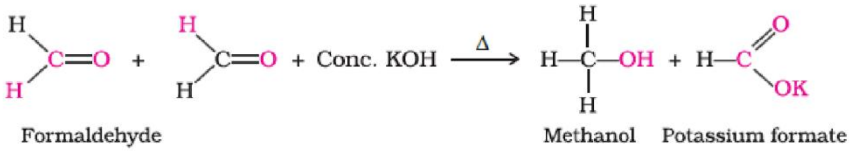
$2CH_3CHO$ dil.NaOH $CH_3–CH\ (OH)\ \text{-}CH_2\text{-}CHO$ (Aldol) heat $CH_3\ \text{-}CH = CH\ \text{-}CHO$

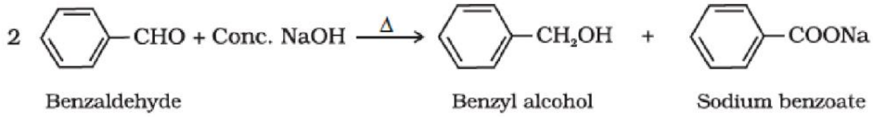
$2CH_3COCH_3$ $Ba(OH)2$ $CH_3–C\ (CH_3)\ (OH)\ \text{-}CH_2\text{-}CO\ \text{-}CHO$ heat $CH_3\ –C(CH_3) = CH\ –CO\ –CHO$
(Ketol)

(ii) Cross Aldol condensation: When Aldol condensation is carried out between two different aldehydes and / or ketones; it is called cross Aldol condensation.

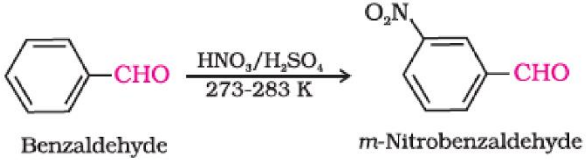
5. Other reactions

(i) Cannizzaro reaction:





(ii) Electrophilic substitution reaction: Aromatic aldehydes and ketones undergo electrophilic substitution at the ring in which the carbonyl group acts as a deactivating and meta-directing group.



Uses of Aldehydes and Ketones:

Formaldehyde is well known as formalin (40%) solution used to preserve biological specimens and to prepare bakelite (a phenol-formaldehyde resin), urea-formaldehyde glues and other polymeric products.

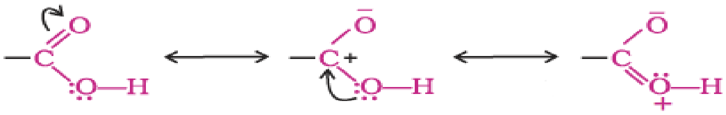
Acetone and ethyl methyl ketone are common industrial solvents.

Many aldehydes and ketones, e.g., butyraldehyde, vanillin, acetophenone, camphor, etc. are well known for their odours and flavours.

Carboxylic Acids:

Carbon compounds containing a carboxyl functional group, –COOH are called carboxylic acids. The carboxyl group consists of a carbonyl group attached to a hydroxyl group, hence its name carboxyl. Carboxylic acids may be aliphatic (RCOOH) or aromatic (Ar COOH) depending on the group, (R, alkyl or Ar, aryl group) attached to carboxylic carbon.

Structure of Carboxyl Group: In carboxylic acids, the bonds to the carboxyl carbon lie in one plane and are separated by about 120°. The carboxylic carbon is less electrophilic than carbonyl carbon because of the possible resonance structure shown below:



Methods of Preparation of Carboxylic Acids:

1. From primary alcohols:

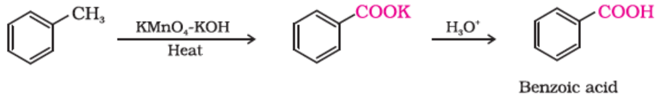
$$RCH_2OH \xrightarrow[2.\ H_3\overset{+}{O}]{1.\ \text{alkaline } KMnO_4} RCOOH$$

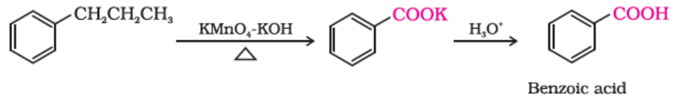
$$\underset{\text{1-Decanol}}{CH_3(CH_2)_8CH_2OH} \xrightarrow[\text{Jones reagent}]{CrO_3\text{-}H_2SO_4} \underset{\text{Decanoic acid}}{CH_3(CH_2)_8COOH}$$

2. From aldehydes:

RCHO [O] RCOOH

3. From alkyl benzenes:



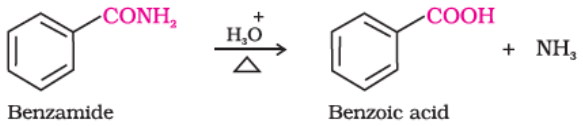


4. From nitriles:

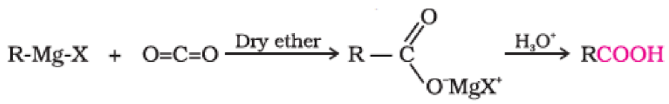
RCN H+ or OH- $RCONH_2$ H+ or OH- $RCOOH$

5. From amides:

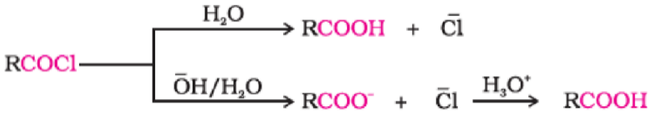
CH_3CONH_2 H3O+ $CH_3COOH + NH_3$



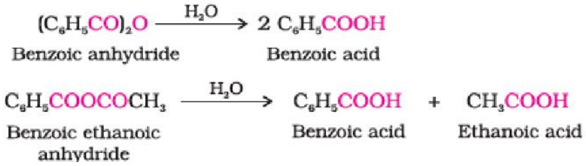
6. From Grignard reagents:



7. From acyl halides:



8. From anhydrides:

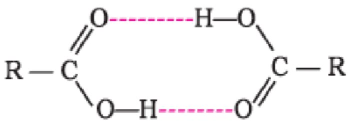


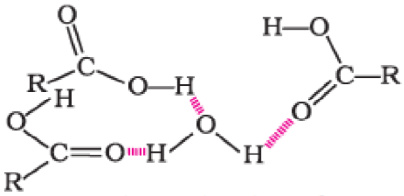
6. From esters: Acidic hydrolysis of ethyl benzoate gives benzoic acid.

$C_6H_5COO\ C_2H_5 \quad H3O+ \quad C_6H_5\ COOH + C_2H_5OH$

Physical Properties:

Carboxylic acids are higher boiling liquids than aldehydes, ketones and even alcohols of comparable molecular masses. This is due to more extensive association of carboxylic acid molecules through intermolecular hydrogen bonding. The hydrogen bonds are not broken completely even in the vapour phase.
In fact, most carboxylic acids exist as dimer in the vapour phase or in the aprotic solvents.

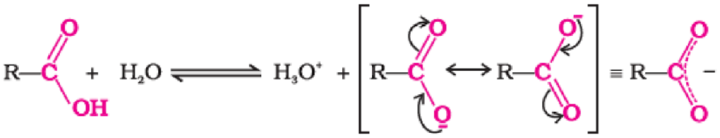

dimer


Hydrogen bonding of $RCOOH$ with H_2O

Simple aliphatic carboxylic acids having up to four carbon atoms are miscible in water due to the formation of hydrogen bonds with water. The solubility decreases with increasing number of carbon atoms. Higher carboxylic acids are practically insoluble in water due to the increased hydrophobic interaction of hydrocarbon part. Benzoic acid, the simplest aromatic carboxylic acid is nearly insoluble in cold water. Carboxylic acids are also soluble in less polar organic solvents like benzene, ether, alcohol, chloroform, etc.

Chemical Reactions:
Reactions Involving Cleavage of O–H Bond:
Acidity:
Reactions with metals: $2RCOOH + 2Na \text{ ---> } 2RCOO^-Na^+ + H_2$
Reactions with alkalies: $RCOOH + NaOH \text{ ---> } RCOO^-Na^+ + H_2O$

Carboxylic acids dissociate in water to give resonance stabilized carboxylate anions and hydronium ion.



For the above reaction:

$$K_{eq} = \frac{[H_3\overset{+}{O}]\,[RCO\overset{-}{O}]}{[H_2O]\,[RCOOH]} \qquad K_a = K_{eq}\,[H_2O] = \frac{[H_3\overset{+}{O}]\,[RCO\overset{-}{O}]}{[RCOOH]}$$

where K_{eq}, is equilibrium constant and K_a is the acid dissociation constant.

The dissociation constant is called acidity constant. The stronger the acid, the larger will be its K_a value.

$$pK_a = -\log K_a$$

Smaller the value of pKa, stronger the acid is.

The acids have pKa values < 1. Strong acids.

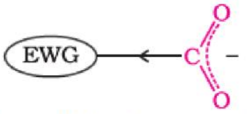
The acids with pKa values between 1 and 5 are considered to be moderately strong acids.

The acids have pKa values between 5 and 15 are extremely weak acids have pKa values >15.

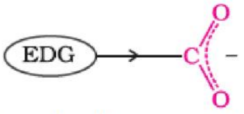
Effect of substituents on the acidity of carboxylic acids:

Electron withdrawing group's increase the acidity of carboxylic acids by stabilizing the conjugate base through delocalization of the negative charge by inductive and/or resonance effects.

Conversely, electron donating groups decrease the acidity by destabilizing the conjugate base.



Electron withdrawing group (EWG) stabilises the carboxylate anion and strengthens the acid



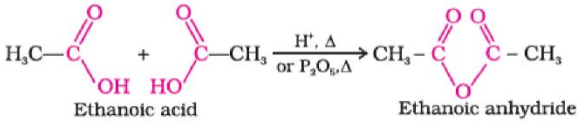
Electron donating group (EDG) destabilises the carboxylate anion and weakens the acid

The effect of the following groups in increasing acidity order is

Phenyl < I < Br < Cl < F < CN < NO_2 < CF_3

Reactions Involving Cleavage of C–OH Bond:

1. Formation of anhydride:



2. Esterification:

RCOOH + R'OH ----> RCOOR' + H_2O

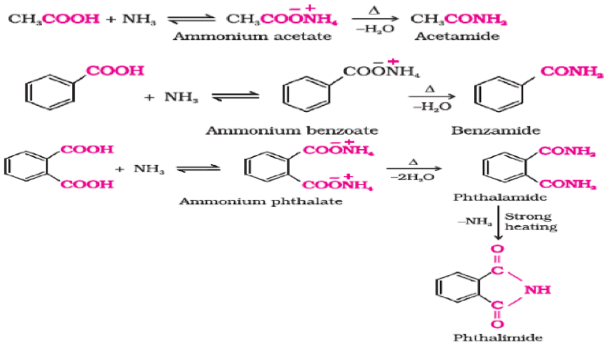
3. Reactions with PCl_5, PCl_3 and $SOCl_2$:

RCOOH + PCl_5 ---> RCOCl + $POCl_3$ + HCl

3RCOOH + PCl_3 ---> 3RCOCl + H_3PO_3

RCOOH + $SOCl_2$ ---> RCOCl + SO_2 + HCl

4. Reaction with ammonia:



Reactions Involving –COOH Group:

1. Reduction:

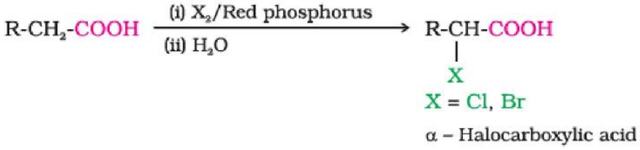
$$\mathrm{RCOOH} \xrightarrow{\text{(i) LiAlH4/Ether or B2H6 (ii) H3O+}} \mathrm{RCH_2OH}$$

2. Decarboxylation:

$$\mathrm{RCOONa} \xrightarrow{\text{NaOH \& CaO, heat}} \mathrm{R - H + Na_2CO_3}$$

Substitution Reactions in the Hydrocarbon Part:

Hell-Volhard-Zelinsky reaction

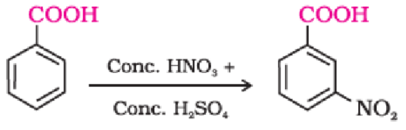


$$\mathrm{R\text{-}CH_2\text{-}COOH} \xrightarrow[\text{(ii) } H_2O]{\text{(i) } X_2\text{/Red phosphorus}} \mathrm{R\text{-}\underset{\displaystyle X}{\underset{|}{C}H}\text{-}COOH}$$

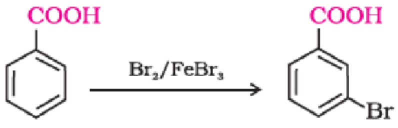
X = Cl, Br

α – Halocarboxylic acid

2. Ring substitution:



m-Nitrobenzoic acid



m-Bromobenzoic acid

Uses of Carboxylic Acids:

Methanoic acid is used in rubber, textile, dyeing, leather and electroplating industries.
Ethanoic acid is used as solvent and as vinegar in food industry.
Hexanedioic acid is used in the manufacture of nylon-6, 6.
Esters of benzoic acid are used in perfumery.
Sodium benzoate is used as a food preservative.
Higher fatty acids are used for the manufacture of soaps and detergents.

ASSIGNMENTS:

Q1. Which of these has the least unpleasant Odour?

a) Methanal
b) Butanal
c) Propanal
d) Ethanal
Ans. (b) Because the Odour gets less strong and more fragrant as the size of the aldehyde molecule grows.
Q2. Reactions occur between aldehydes and alcohol.
(a) nucleophilic addition
(b) electrophilic substitution
(c) electrophilic addition
(d) nucleophilic substitution
Ans. (a)
Q3. Which of the following is not a formaldehyde application?
(a) Preservation of biological specimens
(b) Preparation of acetic acid
(c) Silvering of mirrors
(d) Manufacturing of Bakelite
Ans. (b)
Explanation: Because formaldehyde has only one carbon atom, it cannot be employed as a starting material for the production of acetic acid. It is, nevertheless, utilized to make Bakelite, glues, and polymeric items. In the silvering of mirrors, it also works as a reducing agent.
Q4. Which of the following compounds is formed when benzyl alcohol is oxidized with $KMnO_4$?
(a) CO_2 and H_2O
(b) Benzoic acid
(c) Benzaldehyde
(d) Benzophenone
Ans. (b)
Q5. The Rosenmund reaction can produce which of the following carbonyl compounds?
(a) Methanal
(b) Benzaldehyde
(c) Butanone
(d) Acetone
Ans. (b) Benzoyl chloride produces benzaldehyde.

Q6. Name the following compounds according to IUPAC system of nomenclature:

i. $CH_3CH(CH_3)\ CH_2CH_2CHO$
ii. $CH_3CH_2COCH(C_2H_5)\ CH_2CH_2Cl$
iii. $CH_3CH=CHCHO$
iv. $CH_3COCH_2COCH_3$
v. $CH_3CH(CH_3)\ CH_2C(CH_3)_2COCH_3$
vi. $(CH_3)_3CCH_2COOH$
vii. $OHCC_6H_4CHO$-p

Ans. (i) 4-methyl pentanal

(ii)6-chloro-4-ethyl hexan-3-one

i.But-2-enal
ii.Pentane-2,4-dione
iii.3,3,5-trimethyl hexane-2-one
iv.3,3-dimethyl butanoic acid
v.Benzene-1,4-dicarbaldehyde

Q7. Give names of the reagents to bring about the following transformations:

i.Hexan-1-ol to hexanal
ii.Cyclohexanol to cyclohexanone
iii.p-Fluor toluene to p-Fluoro benzaldehyde
iv.Ethanenitrile to ethanal
v.Allyl alcohol to propenal
vi.But-2-ene to ethanal

Ans.

i.$C_5H_5NH+CrO_3Cl^-$ (PCC)
ii.Anhydrous CrO_3 or $K_2Cr_2O_7$ in acidic medium
iii.CrO_3 in the presence of acetic anhydride or 1. CrO_2Cl_2 2. H_2O
iv.(Di isobutyl) Aluminium hydride (DIBAL-H)
v.PCC
vi.O_3 /H_2O-Zn dust

Q8. Arrange the following compounds in the increasing order of their boiling points: $CH_3CH_2CH_2CHO$, $CH_3CH_2CH_2CH_2OH$, H_5C_2 -O-C_2H_5 and CH3CH2CH2CH3

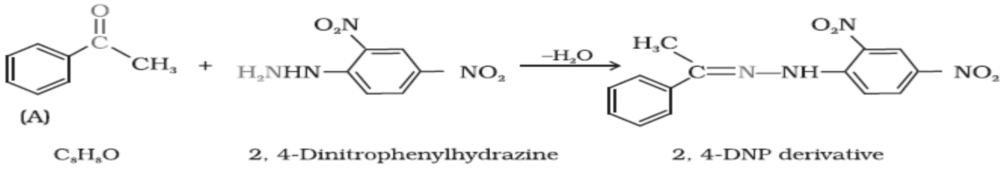
Ans. Increasing order of boiling points of the given compounds is as follows:

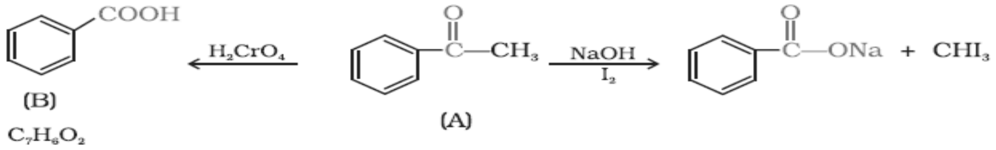
$CH_3CH_2CH_2CH_3$ < H_5C_2 -O-C_2H_5 < $CH_3CH_2CH_2CHO$ < $CH_3CH_2CH_2CH_2OH$

Q9. Although phenoxide ion has a greater number of resonating structures than carboxylate ion, carboxylic acid is a stronger acid than phenol. Why?
Ans. The electronic charge in the carboxylate ion is more dispersed in comparison to phenate ion. Carboxylate ion is more stable as compared to phenate ion. The release of H^+ ion is easier from carboxylic acid. It behaves as stronger acid than phenol.

Q10. An organic compound (A) with molecular formula C_8H_8O forms an orange-red precipitate with 2,4-DNP reagent and gives yellow precipitate on heating with iodine in the presence of sodium hydroxide. It neither reduces Tollens' or Fehling's reagent, nor does it decolourise bromine water or Baeyer's reagent. On drastic oxidation with chromic acid, it gives a carboxylic acid (B) having molecular formula C_7H_6O2. Identify the compounds (A) and (B) and explain the reactions involved.

Ans. Reactions are as follows:





Q11. Arrange the following compounds in increasing order of their reactivity in nucleophilic addition reactions.

i. Ethanal, Propanal, Propanone, Butanone.
ii. Benzaldehyde, p-Tolualdehyde, p-Nitro benzaldehyde, Acetophenone.

Ans. (i) Butanone < Propanone < Propanal < Ethanal

(ii) Acetophenone < p-Tolualdehyde < Benzaldehyde < p-Nitro benzaldehyde

Q12. An organic compound with the molecular formula $C_9H_{10}O$ forms 2, 4-DNP derivative, reduces Tollens' reagent and undergoes Cannizzaro reaction. On vigorous oxidation, it gives 1,2-benzenedicarboxylic acid. Identify the compound.

Ans. 2-Ethyl benzaldehyde

Q13. An organic compound (A) (molecular formula $C_8H_{16}O_2$) was hydrolyzed with dilute Sulphuric acid to give a carboxylic acid (B) and an alcohol (C). Oxidation of (C) with chromic acid produced (B). (C) on dehydration gives but-1-ene. Write equations for the reactions involved.

Ans. A = Butyl butanoate, B = Butanoic acid, C = Butanol

Q14. Arrange the following compounds in increasing order of their property as indicated:

i. Acetaldehyde, Acetone, Di-tert-butyl ketone, Methyl tert-butyl ketone (reactivity towards HCN)
ii. $CH_3CH_2CH(Br)COOH$, $CH_3CH(Br)CH_2COOH$, $(CH_3)_2CHCOOH$, $CH_3CH_2CH_2COOH$ (acid strength)
iii. Benzoic acid, 4-Nitrobenzoic acid, 3,4-Dinitrobenzoic acid, 4-Methoxybenzoic acid (acid strength)

Ans. (i) Acetaldehyde > Acetone > Methyl tert-butyl ketone > Di-tert-butyl ketone

(ii) $(CH_3)_2CHCOOH < CH_3CH_2CH_2COOH < CH_3CH(Br)CH_2COOH < CH_3CH_2CH(Br)COOH$

(iii) 4-Methoxybenzoic acid < Benzoic acid < 4-Nitrobenzoic acid < 3, 4-Dinitrobenzoic acid

Q15. Give plausible explanation for each of the following:

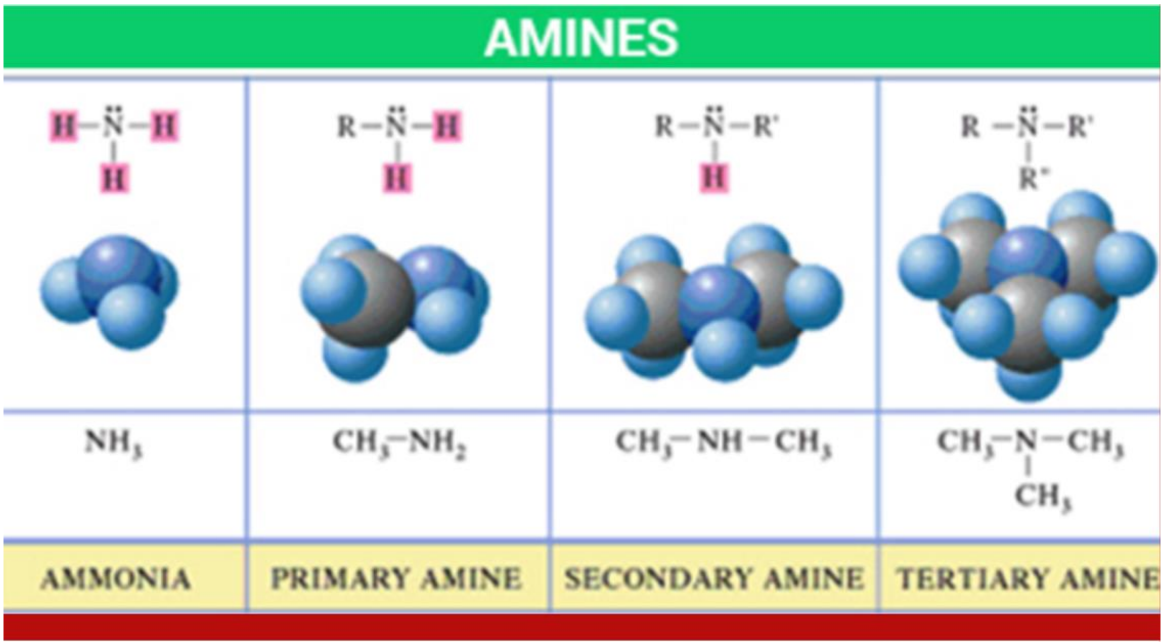
i. Cyclohexanone forms cyanohydrin in good yield but 2,2,6-trimethylcyclohexanone does not.
ii. There are two –NH_2 groups in semi carbazide. However, only one is involved in the formation of semi carbazones.
iii. During the preparation of esters from a carboxylic acid and an alcohol in the presence of an acid catalyst, the water or the ester should be removed as soon as it is formed.

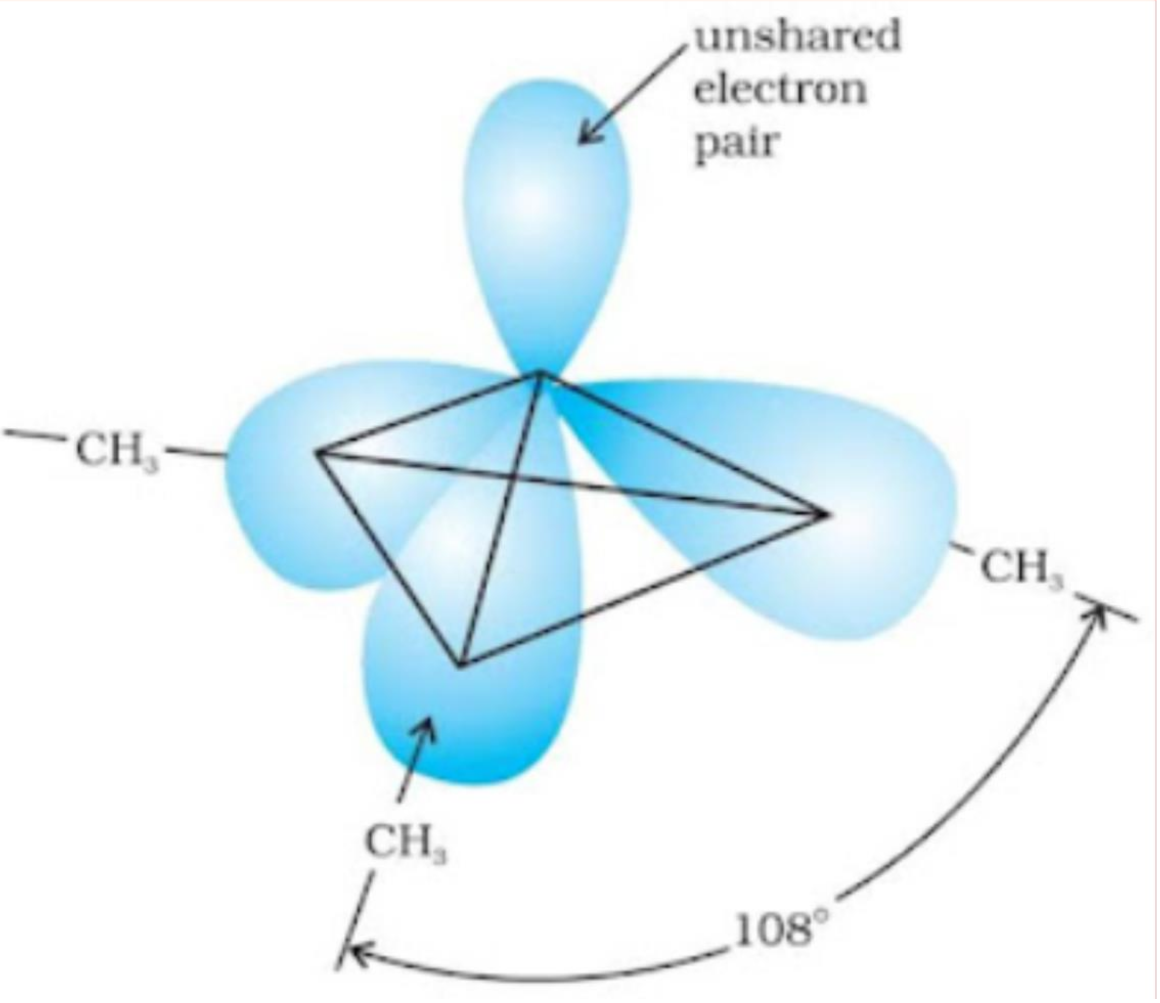
Ans. (i) Cyclohexanone forms cyanohydrin in good yield but 2, 2, 6-trimethylcyclohexanone does not because of presence of three methyl groups at α-position w.r.t carbonyl group which hinder the Nucleophilic attack of CN^- group due steric hindrance. No such steric hindrance in Cyclohexanone.

(ii) Semi carbazide has two –NH_2 groups but one of these which is directly attached to C=O is involved in resonance. Electron density on NH_2 group decreases hence it does not act as nucleophile.

(iii)It is a reversible reaction. Therefore, to shift the equilibrium in the forward direction, the water or the ester should be removed as fast as it is formed.

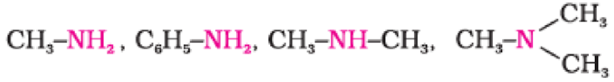
UNIT IX AMINES





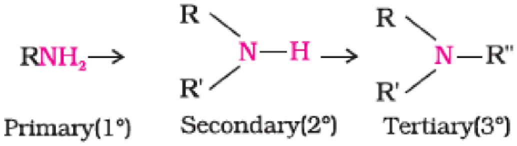
Amines: Nomenclature, classification, structure, methods of preparation, physical and chemical properties, uses, identification of primary, secondary and tertiary amines.

Amines can be considered as derivatives of ammonia, obtained by replacement of one, two or all the three hydrogen atoms by alkyl and/or aryl groups.
For example: Methylamine, Aniline, Dimethylamine, and Trimethylamine

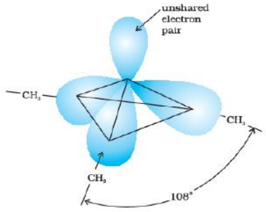


$CH_3–NH_2$, $C_6H_5–NH_2$, $CH_3–NH–CH_3$, $CH_3–N(CH_3)_2$

Classification: Amines are classified as primary (1°), secondary (2°) and tertiary (3°) depending upon the number of hydrogen atoms replaced by alkyl or aryl groups in ammonia molecule.



Structure of Amines:



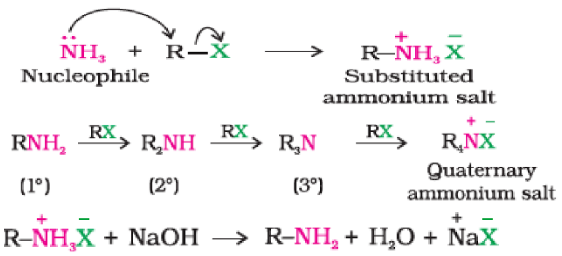
Preparation of Amines:

1. Reduction of nitro compounds:

(i) $C_6H_5\ NO_2$ H2/Pd, ethanol $C_6H_5\ NH_2$

(ii) $C_6H_5\ NO_2$ Sn + HCl or Fe + HCl $C_6H_5\ NH_2$

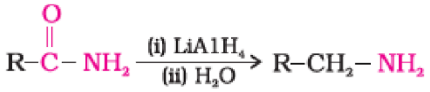
2. Ammonolysis of alkyl halides:



3. Reduction of nitriles:

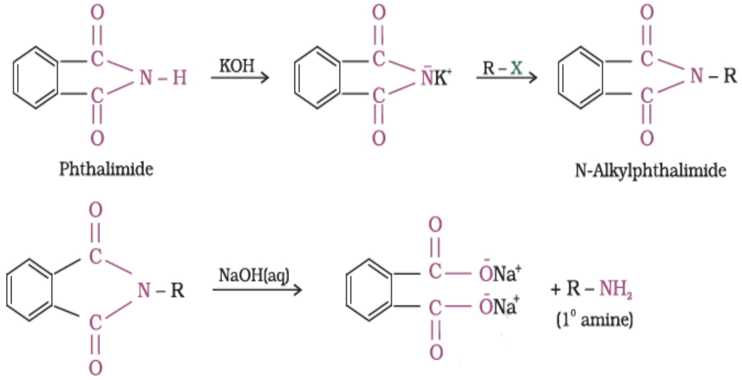
$$R-C\equiv N \xrightarrow[Na(Hg)/C_2H_5OH]{H_2/Ni} R-CH_2-NH_2$$

4. Reduction of amides:



$$R-\overset{\overset{\large O}{\|}}{C}-NH_2 \xrightarrow[(ii)\ H_2O]{(i)\ LiAlH_4} R-CH_2-NH_2$$

5. Gabriel phthalimide synthesis:



6. Hoffmann bromamide degradation reaction:

$RCONH_2 + Br_2 + 4NaOH \text{ ---> } R\text{-}NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$

Physical Properties:

The lower aliphatic amines are gases with fishy odour.

Primary amines with three or more carbon atoms are liquid and still higher ones are solid.

Lower aliphatic amines are soluble in water because they can form hydrogen bonds with water molecules. However, solubility decreases with increase in molar mass of amines due to increase in size of the hydrophobic alkyl part.

Higher amines are essentially insoluble in water.

Primary and secondary amines are engaged in intermolecular association due to hydrogen bonding between nitrogen of one and hydrogen of another molecule. This intermolecular association is more in primary amines than in secondary amines as there are two hydrogen atoms available for hydrogen bond formation in it. Tertiary amines do not have intermolecular association due to the absence of hydrogen atom available for hydrogen bond formation.

Therefore, the order of boiling points of isomeric amines is as follows:

Primary > Secondary > Tertiary

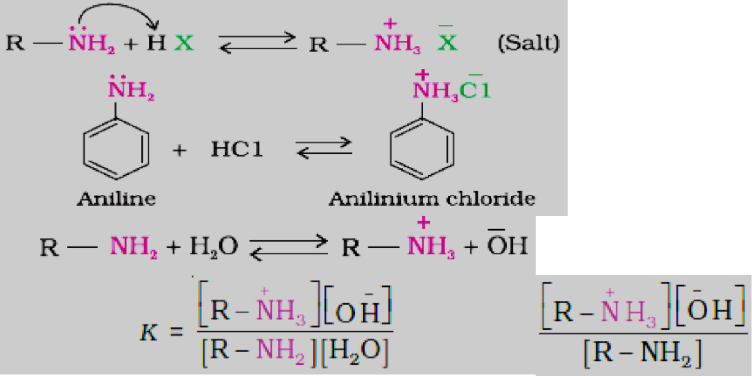
Boiling Points of Amines of Similar Molecular Masses:

S.No.	COMPOUND	MOLAR MASS	BOILING POINT
1	n-$C_4H_9NH_2$ (Primary)	73	350.8

2	$(C_2H_5)_2NH$ (Secondary)	73	329.3
3	$C_2H_5N(CH_3)_2$ (Tertiary)	73	310.5

Chemical Reactions:

1. Basic character of amines: Amines, being basic in nature, react with acids to form salts.



$$K = \frac{[R-\overset{+}{N}H_3][\overset{-}{O}H]}{[R-NH_2][H_2O]}$$

K_b = $\frac{[R-\overset{+}{N}H_3][\overset{-}{O}H]}{[R-NH_2]}$

pK_b = - log K_b

Larger the value of K_b or smaller the value of pK_b, stronger is the base.

2. Alkylation: Amines undergo alkylation on reaction with alkyl halides.

C_2H_5Br NH3 $C_2H_5NH_2$ (1°) $(C_2H_5)_2NH$ (2°) $(C_2H_5)_3N$ (3°) (C_2H_5) N^+Br^-

3. Acylation: Ethanamine to N-ethyl ethanamide

$C_2H_5NH_2 + CH_3COCl$ $C_2H_5NH - CO - CH_3$

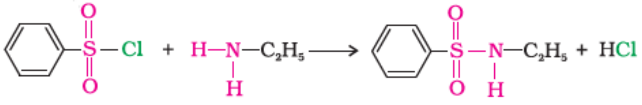
4. Carbylamine reaction: Test for primary amines (Aliphatic and aromatic)

$$R-NH_2 + CHCl_3 + 3KOH \xrightarrow{Heat} R-NC + 3KCl + 3H_2O$$

5. Reaction with nitrous acid:

$$R-NH_2 + HNO_2 \xrightarrow{NaNO_2 + HCl} [R-\overset{+}{N_2}\overset{-}{Cl}] \xrightarrow{H_2O} ROH + N_2 + HCl$$

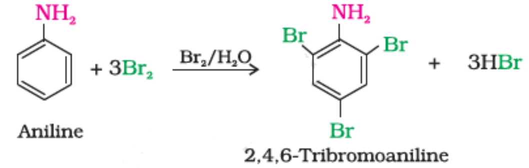
6. Reaction with arylsulphonyl chloride: Benzenesulphonyl chloride ($C_6H_5SO_2Cl$), which is also known as Hinsberg's reagent, reacts with Ethyl amine to form N-Ethylbenzenesulphonamide.



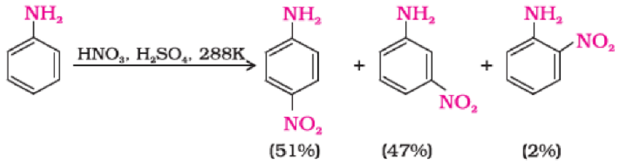
N-Ethylbenzenesulphonamide
(soluble in alkali)

7. Electrophilic substitution:

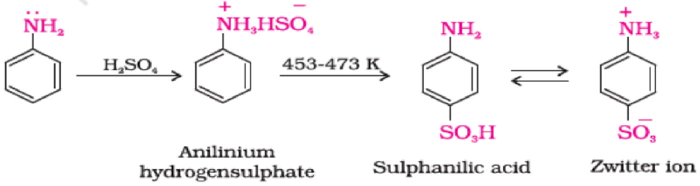
(a) Bromination: Aniline reacts with bromine water at room temperature to give a white precipitate of 2, 4, 6-tribromoaniline.



(b) Nitration: Aniline reacts with nitric acid to give o-, m- & p-nitro aniline.



(c) Sulphonation: Aniline reacts with concentrated Sulphuric acid to form anilinium hydrogensulphate which on heating with Sulphuric acid at 453-473K produces p-amino benzene sulphonic acid, known as sulphanilic acid followed by Zwitter ion structure.



USES OF AMINES: The important uses of aliphatic and aromatic amines are given below:

1. Aliphatic amines of low molecular mass are used as solvents.
2. Amines are also used as intermediates in drug manufacture and as reagents in organic synthesis.
3. Aromatic amines are used for the manufacture of polymers, dyes and as intermediates for additives in the rubber industry.
4. The quaternary ammonium salts derived from long chain aliphatic tertiary amines are widely used as detergents.
5. Aromatic amines are converted into arene Diazonium salts which are used for the preparation of variety of aromatic compounds via substitution and coupling reactions.

Identification of primary, secondary and tertiary amines.

S.No.	**Characteristic reaction**	**Primary**	**Secondary**	**Tertiary**
1	Action with nitrous acid ($NaNO_2$ + HCl)	N_2 is given out with the formation of alcohols.	Nitrosoamines are formed which give Liebermann's Nitroso test.	They remain dissolved forming amine nitrite salt which decomposes on warming to Nitrosoamines and alcohol.
2	Carbylamine reaction ($CHCl_3$ & alc. KOH)	Give foul smelling Carbylamine.	No reaction	No reaction

3	Acylation	Form amides	Form amides	No reaction
4	Hinsberg’s test	Give clear solution which on acidification gives insoluble material	Give insoluble substance which is not affected by acid	Does not react
5	Azo dye test	Give coloured dyes	No reaction	No reaction

II. DIAZONIUM SALTS: The general formula of Diazonium salts is $RN_2^+ X^-$ where R stands for an aryl group and X^- ion may be Cl^- , Br^- , HSO_4^- , BF_4^- , etc. and the group N_2^+ is called Diazonium group. These are obtained when aromatic primary amine react with nitrous acid.

NOMENCLATURE:

For example, $C_6H_5N_2^+Cl^-$ are named as Benzenediazonium chloride and $C_6H_5N_2^+HSO_4^-$ is known as Benzenediazonium hydrogensulphate.

Method of Preparation of Diazonium Salts

Benzenediazonium chloride is prepared by the reaction of aniline with nitrous acid at 273-278K. Nitrous acid is produced in the reaction mixture by the reaction of sodium nitrite with hydrochloric acid. The conversion of primary aromatic amines into Diazonium salts is known as diazotization.

$NaNO_2 + 2HCl \qquad HONO + NaCl$

$C_6H_5NH_2 + NaNO_2 + 2HCl \overset{273-278}{\quad} C_6H_5N_2^+Cl^- + NaCl + 2H_2O$

Physical Properties:

Benzenediazonium chloride is a colourless crystalline solid. It is readily soluble in water and is stable in cold but reacts with water when warmed. It decomposes easily in the dry state.

Chemical Reactions:

The reactions of Diazonium salts can be divided into two categories:

(A) Reactions involving displacement of nitrogen

(B) Reactions involving retention of diazo group.

(A) Reactions involving displacement of nitrogen:

Diazonium group being a very good leaving group is substituted by other groups such as Cl^-, Br^-, I^-, CN^- and OH^- which displace nitrogen from the aromatic ring. The nitrogen formed escapes from the reaction mixture as a gas.

1. Replacement by halide or cyanide ion:

The Cl^-, Br^- and CN^- nucleophiles can easily be introduced in the benzene ring in the presence of Cu (I) ion. This reaction is called Sandmeyer reaction.

Cu2Cl2/HCl $Ar\ Cl + N_2$

ArN_2^+X Cu2Br2/HBr $Ar\ Br + N_2$

CuCN/KCN $Ar\ CN + N_2$

Alternatively, chlorine or bromine can also be introduced in the benzene ring by treating the Diazonium salt solution with corresponding halogen acid in the presence of copper powder. This is referred as Gatterman reaction.

Cu/HCl $Ar\ Cl + N_2 + Cu\ X$

ArN_2^+X

Cu/HBr $Ar\ Br + N_2 + Cu\ X$

2. Replacement by iodide ion: When the Diazonium salt solution is treated with potassium iodide, Iodobenzene is formed.

$C_6H_5N_2^+Cl^- + KI \qquad C_6H_5\ I + KCl + N_2$

3. Replacement by fluoride ion: When Benzenediazonium chloride is treated with fluoroboric acid, Benzenediazonium fluoroborate is precipitated which on heating decomposes to yield fluorobenzene.

$C_6H_5N_2^+Cl^- + HBF_4 \qquad C_6H_5N_2^+BF_4^- \qquad C_6H_5\ F + BF_3 + N_2$

4. Replacement by H: Certain mild reducing agents like hypo phosphorous acid (phosphinic acid) or ethanol reduce Diazonium salts to benzene and they get oxidized to phosphorous acid and ethanal, respectively.

$C_6H_5N_2^+Cl^- + H_3PO_2 + H_2O \qquad C_6H_6 + H_3PO_3 + N_2 + HCl$

$C_6H_5N_2^+Cl^- + CH_3CH_2OH \qquad C_6H_6 + CH_3CHO + N_2 + HCl$

5. Replacement by hydroxyl group: When aqueous solution of Diazonium salt is boiled up to 283 K, it gives phenol. Therefore, Diazonium group replaced by hydroxyl group.

$C_6H_5N_2^+Cl^- + H_2O \qquad C_6H_5OH + N_2 + HCl$

6. Replacement by $–NO_2$ group: Nitrobenzene is prepared by heating Benzenediazonium fluoroborate with aqueous sodium nitrite solution in the presence of copper, the Diazonium group is replaced by $–NO_2$ group.

$C_6H_5N_2^+Cl^- + HBF_4 \qquad C_6H_5N_2^+BF_4^-$ NaNO2/Cu $C_6H_5\ NO_2 + NaBF_4 + N_2$

(B) Reactions involving retention of diazo group

Coupling reactions:

Benzenediazonium chloride reacts with phenol in which the phenol molecule at its para position is coupled with the Diazonium salt to form p-hydroxy azobenzene. This type of reaction is known as coupling reaction.

Similarly, the reaction of Benzenediazonium chloride with aniline yields p-amino azobenzene. This is an example of electrophilic substitution reaction.

$C_6H_5N_2^+Cl^- + C_6H_5\ OH \qquad\qquad C_6H_5N{=}N\text{- }C_6H_4\ OH + Cl^- + H_2O$

p-hydroxy azobenzene (Orange dye)

$C_6H_5N_2^+Cl^- + C_6H_5\ NH_2 \qquad\qquad C_6H_5N{=}N\text{- }C_6H_4\ NH_2 + Cl^- + H_2O$

p-amino azobenzene (Yellow dye)

ASSIGNMENTS:

Q1. What is the most basic aromatic amine’s common name?
(a) Benzenamine
(b) Benzylamine
(c) Aniline
(d) Aminobenzene
Ans. (c) The IUPAC designation for it is Benzenamine, although it’s also known as aminobenzene.
Q2. When acetamide is converted to methylamine, what is the name of the reaction?
(a) Friedel-Craft’s reaction
(b) Hofmann reaction
(c) Hoffmann bromamide degradation reaction
(d) Hinsberg reaction
Ans. (c) When bromine is added to an amide in an aqueous or ethanolic sodium hydroxide solution, the amide degrades, resulting in the creation of primary amine.
Q3. Which test can tell the difference between p-chloroaniline and anilinium hydrochloride?
(a) Sandmeyer reaction
(b) Carbylamine test
(c) $AgNO_3$
(d) $NaHCO_3$
Ans. (d) An acid salt, anilinium hydrochloride, liberates CO_2 from $NaHCO_3$. However, p-chloro aniline is basic rather than acidic, it does not release CO_2.
Q4. By reacting with which of the following, primary amines can be separated from secondary and tertiary amines?
(a) Chloroform alone
(b) Methyl iodide
(c) Chloroform and alcoholic KOH
(d) Zinc dust
Ans. (c) Secondary and tertiary amines do not react with $CHCl_3$ and alc. KOH generates isocyanide, whereas primary amine does.
Q5. Which of the following statements concerning methylamine is correct?
(a) Methylamine is stronger base than NH_3
(b) Methylamine is less basic than NH_3
(c) Methylamine is slightly acidic
(d) Methylamine forms salts with alkali

Ans. (a) Due to the +I effect, the presence of an alkyl group enhances the electron density of the nitrogen atom.

Q6. Write the names according to IUPAC and indicate primary, secondary and tertiary amines of different isomeric amines corresponding to the molecular formula, $C_4H_{11}N$.

Ans. Eight isomeric amines corresponding to the molecular formula, $C_4H_{11}N$:

i. Butanamine (primary)
ii. Butan-2-amine(primary)
iii. 2-methyl propanamine (primary)
iv. 2-methyl propan-2-amine (primary)
v. N-methyl propanamine (secondary)
vi. N-methyl propan-2-amine (secondary)
vii. N-ethyl Ethanamine (secondary)
viii. N, N-dimethyl Ethanamine (tertiary)

Q7. Write chemical equations for the following reactions:

(i) Reaction of ethanolic NH_3 with C_2H_5Cl.

(ii) Ammonolysis of benzyl chloride and reaction of amine so formed with two moles of CH_3Cl.

Ans. (i) Ethanamine, N-ethyl Ethanamine, N, N-diethyl Ethanamine is formed.

(ii)Benzyl amine, N, N-dimethyl phenyl methanamine is formed.

Q8. Write chemical equations for the following conversions:

(i) CH_3 –CH_2 –Cl into CH_3 –CH_2 –CH_2 –NH_2

(ii) C_6H_5 –CH_2 –Cl into C_6H_5 –CH_2 –CH_2 –NH_2

Ans. By treatment with KCN followed by treatment with Na, C_2H_5OH

(i)CH_3 –CH_2 -Cl + KCN CH_3 –CH_2 -CN + 4H CH_3 –CH_2 -CH_2 NH_2

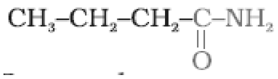
(ii) C_6H_5 –CH_2 -Cl + KCN C_6H_5 –CH_2 -CN + 4H C_6H_5 –CH_2 -CH_2 NH_2

Q9. Write structures and IUPAC names of

(i) the amide which gives propanamine by Hoffmann bromamide reaction.

(ii) the amine produced by the Hoffmann degradation of benzamide.

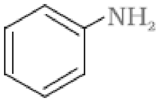
Ans. (i) Propanamine contains three carbons. Hence, the amide molecule must contain four carbon atoms. Structure and IUPAC name of the starting amide with four carbon atoms are given below:



$CH_3\text{–}CH_2\text{–}CH_2\text{–}\underset{\underset{O}{\|}}{C}\text{–}NH_2$

Butanamide

(ii) Benzamide is an aromatic amide containing seven carbon atoms. Hence, the amine formed from benzamide is aromatic primary amine containing six carbon atoms.



Aniline or benzenamine

Q10. Arrange the following in decreasing order of their basic strength:

$C_6H_5NH_2$, $C_2H_5NH_2$, $(C_2H_5)_2NH$, NH_3

Ans. The decreasing order of basic strength of the above amines and ammonia follows the following order:

$(C_2H_5)_2NH > C_2H_5NH_2 > NH_3 > C_6H_5NH_2$

Q11. Arrange the following in increasing order of their basic strength:

(i) $C_2H_5NH_2$, $C_6H_5NH_2$, NH_3, $C_6H_5CH_2NH_2$ and $(C_2H_5)_2NH$

(ii) $C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$, $C_6H_5NH_2$

(iii) CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$, $C_6H_5NH_2$, $C_6H_5CH_2NH_2$.

Ans. (i) $C_6H_5NH_2 < NH_3 < C_6H_5CH_2NH_2 < C_2H_5NH_2 < (C_2H_5)_2NH$

(ii) $C_6H_5NH_2 < C_2H_5NH_2 < (C_2H_5)_3N < (C_2H_5)_2NH$

(iii) $C_6H_5NH_2 < C_6H_5CH_2NH_2 < (CH_3)_3N < CH_3NH_2 < (CH_3)_2NH$

Q12. (a) Complete the following acid-base reactions and name the products:

(i) $CH_3CH_2CH_2NH_2 + HCl \rightarrow$

(ii) $(C_2H_5)_3N + HCl \rightarrow$

(b)Write chemical reaction of aniline with benzoyl chloride and write the name of the product obtained.

Ans. (a) (i) $CH_3CH_2CH_2NH_2 + HCl \rightarrow CH_3CH_2CH_2NH_3^+Cl^-$

(ii) $(C_2H_5)_3N + HCl \rightarrow (C_2H_5)_3NH^+Cl^-$

(b) N-Phenyl benzamide (Benzanilide)

Q13. Arrange the following:

(i) In decreasing order of the pKb values: $C_2H_5NH_2$, $C_6H_5NHCH_3$, $(C_2H_5)_2NH$ and $C_6H_5NH_2$

(ii) In decreasing order of basic strength: $C_6H_5NH_2$, $C_6H_5N(CH_3)_2$, $(C_2H_5)_2NH$ and CH_3NH_2

(iii) In increasing order of basic strength:

(a) Aniline, p-nitroaniline and p-toluidine

(b) $C_6H_5NH_2$, $C_6H_5NHCH_3$, $C_6H_5CH_2NH_2$.

Ans. (i) Stronger the base lesser the pKb values.

$C_6H_5NH_2 > C_6H_5NHCH_3 > C_2H_5NH_2 > (C_2H_5)_2NH$

(ii) $(C_2H_5)_2NH > CH_3NH_2 > C_6H_5N(CH_3)_2 > C_6H_5NH_2$

(iii)(a) p-nitro aniline < Aniline < p-toluidine

(b) $C_6H_5NH_2 < C_6H_5NHCH_3 < C_6H_5CH_2NH_2$.

Q14. An aromatic compound ‘A’ on treatment with aqueous ammonia and heating forms compound ‘B’ which on heating with Br_2 and KOH forms a compound ‘C’ of molecular formula C_6H_7N. Write the structures and IUPAC names of compounds A, B and C.

Ans. A = C_6H_5COOH, B = $C_6H_5CONH_2$, C = $C_6H_5NH_2$.

Q15. Give plausible explanation for each of the following:

(i) Why are amines less acidic than alcohols of comparable molecular masses?

(ii) Why do primary amines have higher boiling point than tertiary amines?

(iii) Why are aliphatic amines stronger bases than aromatic amines?

(iv) pKb of aniline is more than that of methylamine.

(v) Aniline does not undergo Friedel-Crafts reaction.

Ans. (i) Loss of proton from amines gives amide ion whereas loss of proton from alcohol gives alkoxide ion. O is more electronegative than N, therefore, alkoxide ion can accommodate the negative charge more easily than amide ion. Alkoxide ion is more stable than amide ion. Thus, alcohols are more acidic than amines.

(ii)Primary amines (RNH_2) form intermolecular hydrogen bonding But Tertiary amine (R_3N) do not have hydrogen and do not form hydrogen bond.

(iii)Aniline is less basic than ethyl amine by Kb value:

Ethyl amine Kb = 4.7 x 10 $^{-4}$

Aniline Kb = 4.2 x 10 $^{-10}$

Aniline is less basic character due to resonance.

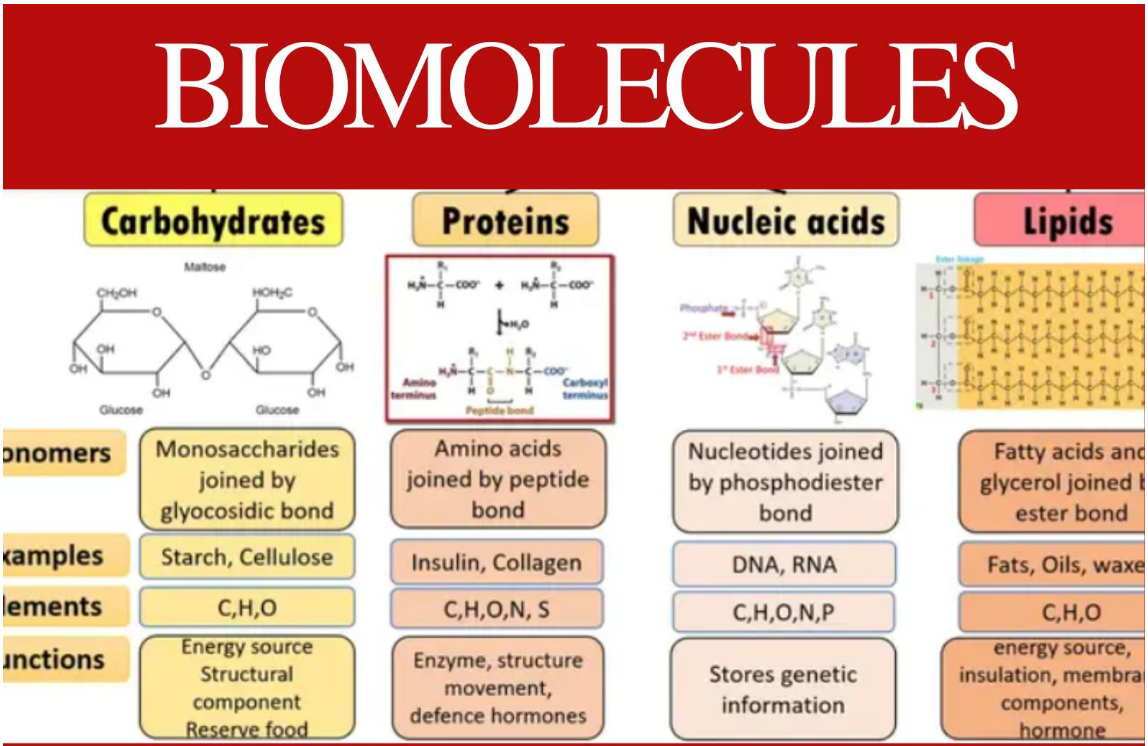
(iv) pKb of aniline is higher than that of methyl amine.

(v)Aniline being the Lewis base reacts with Lewis acid $AlCl_3$ to form salt.

$C_6H_5NH_2 + AlCl_3 \qquad C_6H_5NH_2^{+}AlCl_3^{-}$

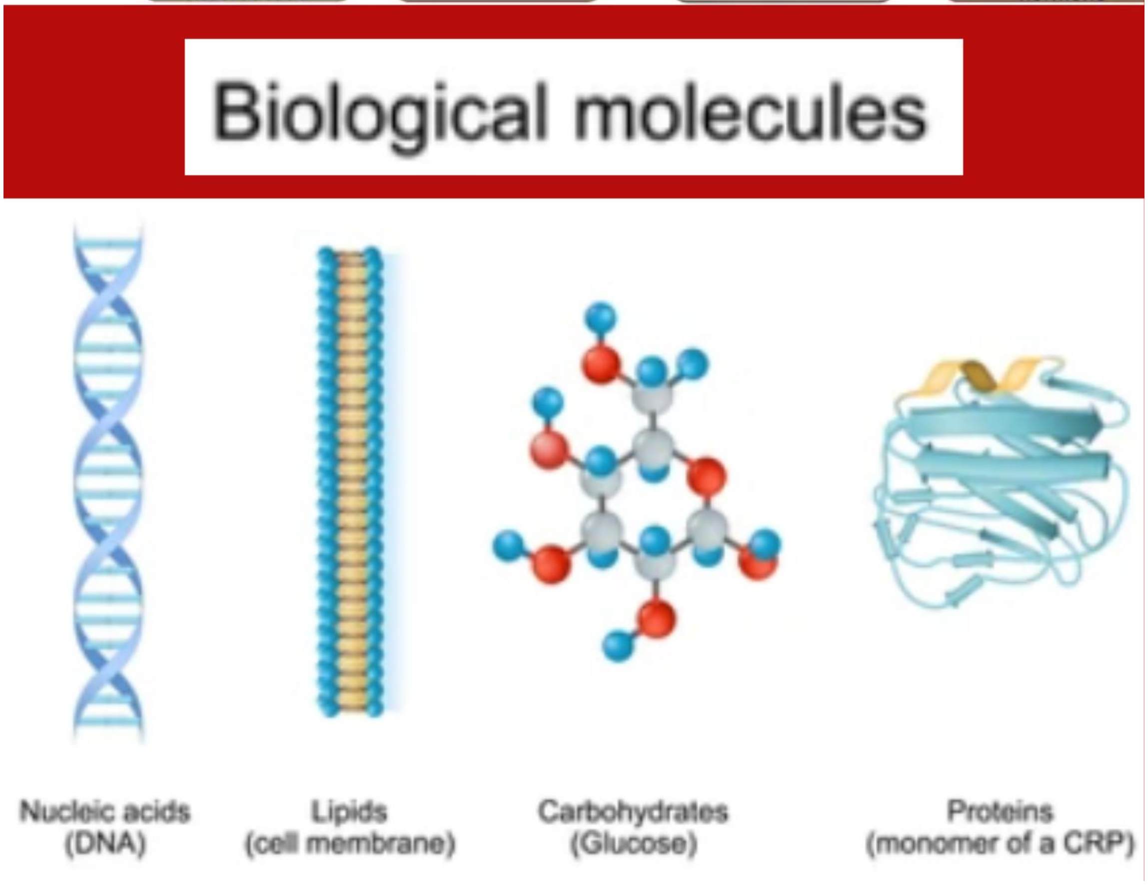
(Salt)

UNIT X BIOMOLECULES

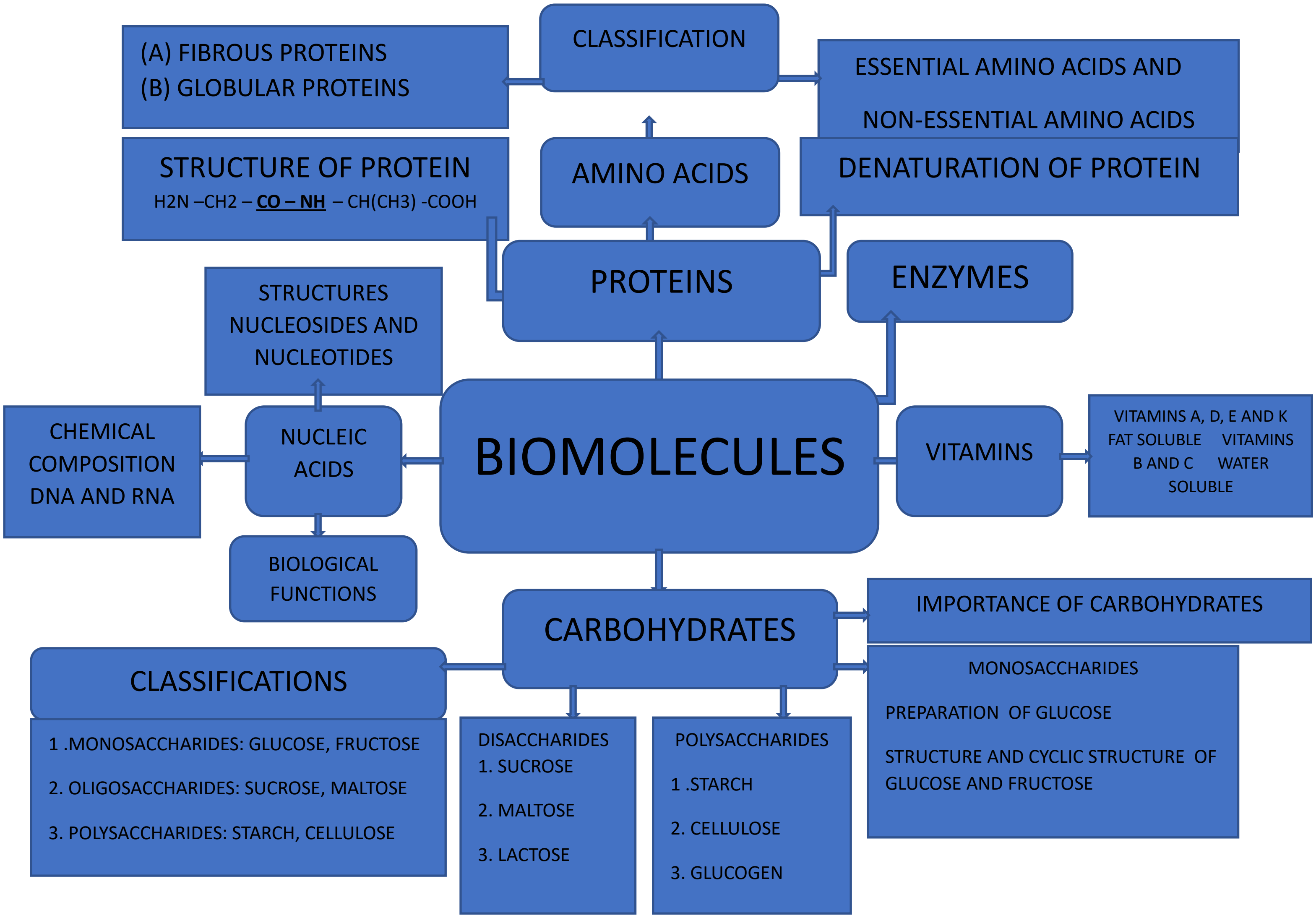


BIOMOLECULES

	Carbohydrates	Proteins	Nucleic acids	Lipids
onomers	Monosaccharides joined by glyocosidic bond	Amino acids joined by peptide bond	Nucleotides joined by phosphodiester bond	Fatty acids an glycerol joined ester bond
xamples	Starch, Cellulose	Insulin, Collagen	DNA, RNA	Fats, Oils, waxe
lements	C,H,O	C,H,O,N, S	C,H,O,N,P	C,H,O
unctions	Energy source Structural component Reserve food	Enzyme, structure movement, defence hormones	Stores genetic information	energy source, insulation, membra components, hormone



Biological molecules



(A) FIBROUS PROTEINS
(B) GLOBULAR PROTEINS

CLASSIFICATION

ESSENTIAL AMINO ACIDS AND
NON-ESSENTIAL AMINO ACIDS

STRUCTURE OF PROTEIN
H2N –CH2 – **CO – NH** – CH(CH3) -COOH

AMINO ACIDS

DENATURATION OF PROTEIN

PROTEINS

ENZYMES

STRUCTURES
NUCLEOSIDES AND
NUCLEOTIDES

CHEMICAL
COMPOSITION
DNA AND RNA

NUCLEIC
ACIDS

BIOMOLECULES

VITAMINS

VITAMINS A, D, E AND K
FAT SOLUBLE VITAMINS
B AND C WATER
SOLUBLE

BIOLOGICAL
FUNCTIONS

CARBOHYDRATES

IMPORTANCE OF CARBOHYDRATES

CLASSIFICATIONS

1 .MONOSACCHARIDES: GLUCOSE, FRUCTOSE

2. OLIGOSACCHARIDES: SUCROSE, MALTOSE

3. POLYSACCHARIDES: STARCH, CELLULOSE

DISACCHARIDES
1. SUCROSE

2. MALTOSE

3. LACTOSE

POLYSACCHARIDES

1 .STARCH

2. CELLULOSE

3. GLUCOGEN

MONOSACCHARIDES

PREPARATION OF GLUCOSE

STRUCTURE AND CYCLIC STRUCTURE OF GLUCOSE AND FRUCTOSE

Introduction: The complex organic substances like carbohydrates, proteins, nucleic acids and amino acids etc. which combine in a specific manner to produce living systems and maintain it are called biomolecules. The branch of chemistry that deals with the study of chemical reactions that occur in living organisms is called biomolecules.

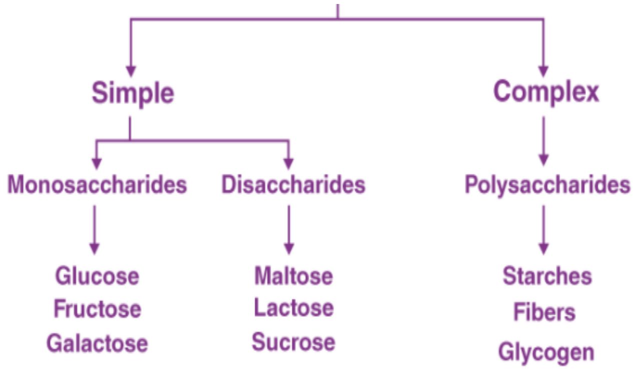
Carbohydrates: They are polyhydroxy-aldehydes or ketones or substances which give these substances on hydrolysis and contain at least one chiral atom.

They have general formula of $C_x(H_2O)_y$

Rhamnose ($C_6H_{12}O_5$), deoxyribose ($C_5H_{10}O_4$) are known which are carbohydrates by their chemical behaviour does not obey this formula.

Classification of Carbohydrates:

Carbohydrates



Monosaccharide: These are simplest carbohydrate which can’t be hydrolyzed further into smaller compounds. They are called as aldose or ketose depending upon whether they have aldehyde or ketone group. Depending upon the number of carbon atoms present they are called as triose, tetrose, pentoses, hexoses etc. Most of the monosaccharides are sweet smelling crystalline solids, water soluble and are also capable of diffusing through cell membranes.

For example: Glucose is aldohexose while fructose is a ketohexose. Both of them have 6 carbon atoms. The simplest monosaccharide is a triose (glyceraldehyde) $C_3H_6O_3$

Preparation of glucose:

1. From sucrose (Cane sugar): If sucrose is boiled with dilute HCl or H_2SO_4 in alcoholic solution, glucose and fructose are obtained in equal amounts.

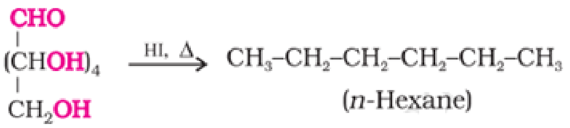
$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

2. From starch: Commercially glucose is obtained by hydrolysis of starch by boiling it with dilute H_2SO_4 at 393 K under pressure.

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

Structure of glucose: Glucose is an aldohexose and is also known as dextrose. It is the monomer of many of the larger carbohydrates, namely starch, cellulose.

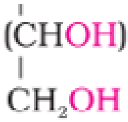
1. Its molecular formula was found to be $C_6H_{12}O_6$.
2. On prolonged heating with HI, it forms n-hexane, suggesting that all the six carbon atoms are linked in a straight chain.



$$\begin{array}{l} CHO \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array} \xrightarrow{HI,\ \Delta} \underset{(n\text{-Hexane})}{CH_3\text{–}CH_2\text{–}CH_2\text{–}CH_2\text{–}CH_2\text{–}CH_3}$$

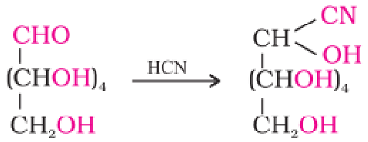
3. Glucose reacts with hydroxylamine to form a Glucose oxime.

Glucose + NH_4OH CH = N – OH



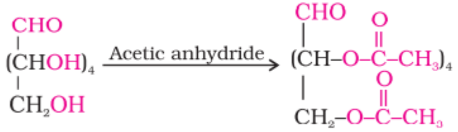
$$\begin{array}{l} | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array}$$

4. Glucose reacts with a molecule of hydrogen cyanide to give cyanohydrin.



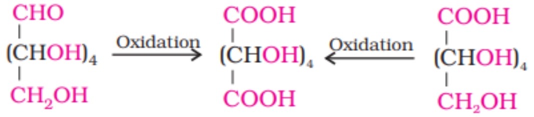
$$CHO-(CHOH)_4-CH_2OH \xrightarrow{HCN} CH(CN)(OH)-(CHOH)_4-CH_2OH$$

5. Acetylation of glucose with acetic anhydride gives glucose pentaacetate which confirms the presence of five –OH groups.



$$CHO-(CHOH)_4-CH_2OH \xrightarrow{\text{Acetic anhydride}} CHO-(CH-O-\overset{O}{\overset{\|}{C}}-CH_3)_4-CH_2-O-\overset{O}{\overset{\|}{C}}-CH_3$$

6. On oxidation with nitric acid, glucose as well as gluconic acid both yield a dicarboxylic acid, saccharic acid. This indicates the presence of a primary alcoholic (–OH) group in glucose.

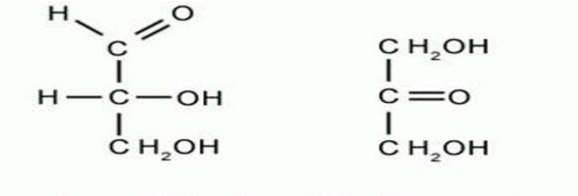


$$CHO-(CHOH)_4-CH_2OH \xrightarrow{\text{Oxidation}} COOH-(CHOH)_4-COOH \xleftarrow{\text{Oxidation}} COOH-(CHOH)_4-CH_2OH$$

Saccharic acid

Gluconic acid

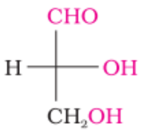
Glyceraldehyde and Dihydroxyacetone: They have one or more asymmetric carbon and are optically active. **Their structures are:**



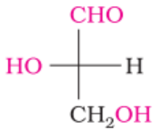
D-Glyceraldehyde Dihydroxyacetone

Configuration: All naturally occurring monosaccharides belong to D—series that is OH group at their penultimate C-atom.

Structures of (+) – Glyceraldehyde and (-) – Glyceraldehyde

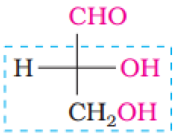


(+) – Glyceraldehyde

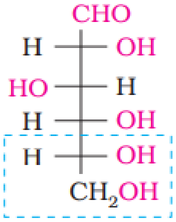


(–) – Glyceraldehyde

Structures of D-(+) – Glyceraldehyde and D-(+) - Glucose

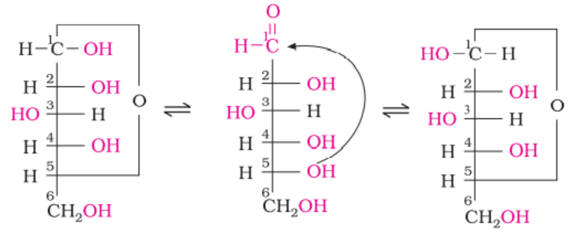


D– (+) – Glyceraldehyde



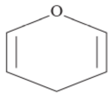
D–(+) – Glucose

Cyclic structure of glucose:

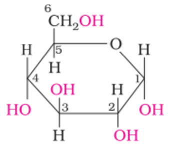


α – D – (+) – Glucose β – D– (+) – Glucose

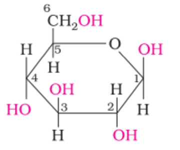
The two cyclic hemiacetal forms of glucose differ only in the configuration of the hydroxyl group at C1, called anomeric carbon. Such isomers, i.e., **α-form and β-form, are called anomers**. The six membered cyclic structure of glucose is called pyranose structure (α– or β–), in analogy with pyran. Pyran is a cyclic organic compound with one oxygen atom and five carbon atoms in the ring. The cyclic structure of glucose:



Pyran

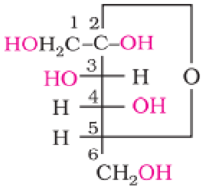


α – D – (+) – Glucopyranose

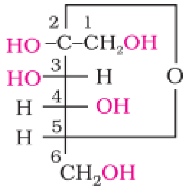


β – D – (+) – Glucopyranose

Fructose is a ketohexose and has the molecular formula $C_6H_{12}O_6$. The ring, thus formed is a five membered ring and is named as furanose with analogy to the compound furan. Furan is a five membered cyclic compound with one oxygen and four carbon atoms.

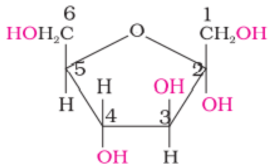


α – D – (–) – Fructofuranose

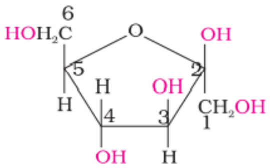


β – D – (–) – Fructofuranose

The cyclic structures of two anomers of fructose are represented by Haworth structures as given.

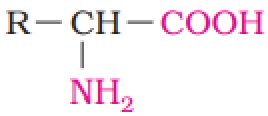


α – D – (–) – Fructofuranose



β – D – (–) – Fructofuranose

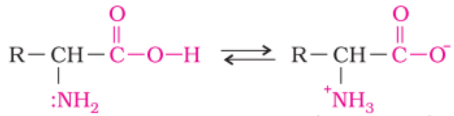
Amino acids: Amino acids contain amino ($–NH_2$) and carboxyl (–COOH) functional groups. A simple amino acid can be represented:



$$R-\underset{\substack{|\\ NH_2}}{CH}-COOH$$

α-amino acid
(R = side chain)

Due to transfer of proton from carboxy to amino group, alpha amino acid exists as dipolar ion or called **as Zwitter ion.**

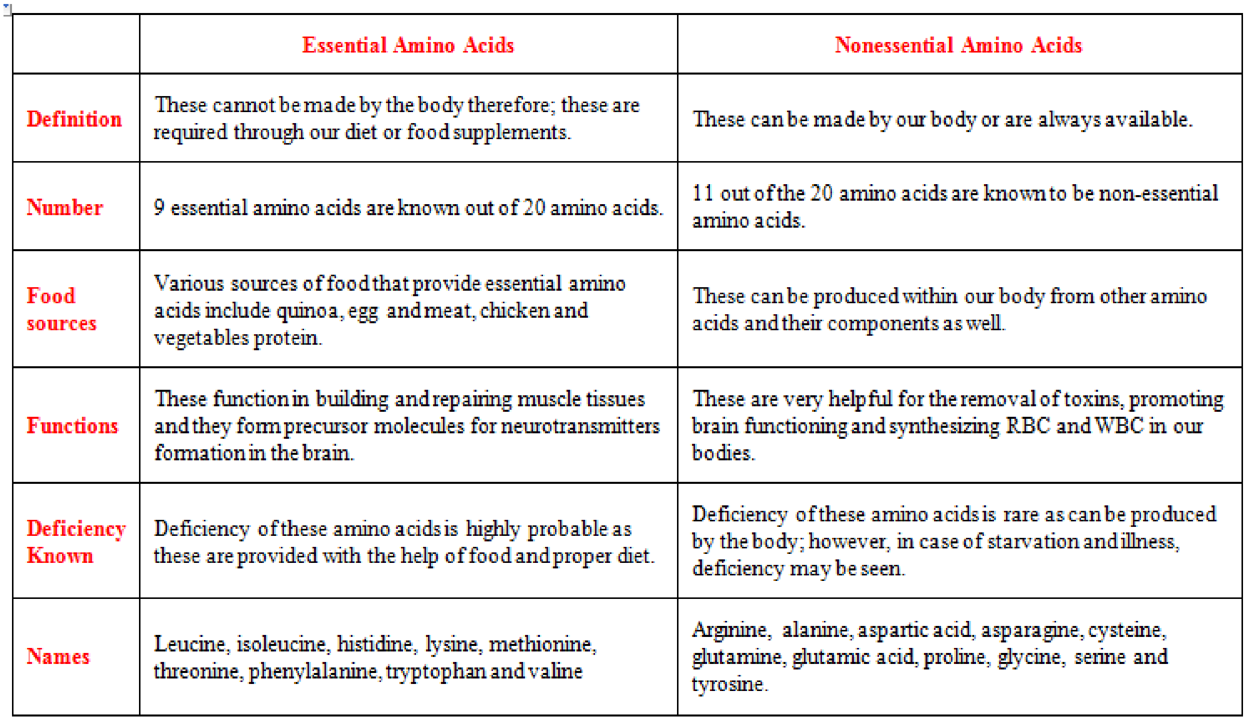


$$R-\underset{\substack{|\\ :NH_2}}{CH}-\overset{\substack{O\\ \|}}{C}-O-H \rightleftharpoons R-\underset{\substack{|\\ {}^{+}NH_3}}{CH}-\overset{\substack{O\\ \|}}{C}-O^{-}$$

(Zwitter ion)

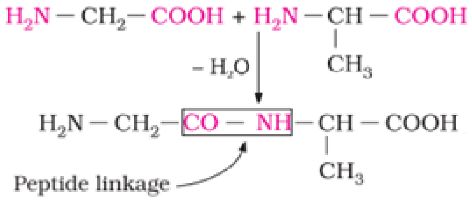
The isoelectric point(pl) of an amino acid is the pH of which it has no net charge. The pH of an amino acid that does not have an ionizable side chain such as alanine, is midway between its two pka values. If an amino acid has ionizable side chain.

Difference between Essential and Nonessential Amino Acids



	Essential Amino Acids	Nonessential Amino Acids
Definition	These cannot be made by the body therefore; these are required through our diet or food supplements.	These can be made by our body or are always available.
Number	9 essential amino acids are known out of 20 amino acids.	11 out of the 20 amino acids are known to be non-essential amino acids.
Food sources	Various sources of food that provide essential amino acids include quinoa, egg and meat, chicken and vegetables protein.	These can be produced within our body from other amino acids and their components as well.
Functions	These function in building and repairing muscle tissues and they form precursor molecules for neurotransmitters formation in the brain.	These are very helpful for the removal of toxins, promoting brain functioning and synthesizing RBC and WBC in our bodies.
Deficiency Known	Deficiency of these amino acids is highly probable as these are provided with the help of food and proper diet.	Deficiency of these amino acids is rare as can be produced by the body; however, in case of starvation and illness, deficiency may be seen.
Names	Leucine, isoleucine, histidine, lysine, methionine, threonine, phenylalanine, tryptophan and valine	Arginine, alanine, aspartic acid, asparagine, cysteine, glutamine, glutamic acid, proline, glycine, serine and tyrosine.

Proteins: Proteins are the polymers of α-amino acids and they are connected to each other by peptide bond or peptide linkage. Peptide linkage is an amide formed between –COOH group and $-NH_2$ group. The reaction between two molecules of similar or different amino acids, proceeds through the combination of the amino group of one molecule with the carboxyl group of the other. This results in the elimination of a water molecule and formation of a peptide bond –CO–NH–. The product of the reaction is called a dipeptide because it is made up of two amino acids. For example, when carboxyl group of glycine combines with the amino group of alanine we get a dipeptide, glycylalanine.



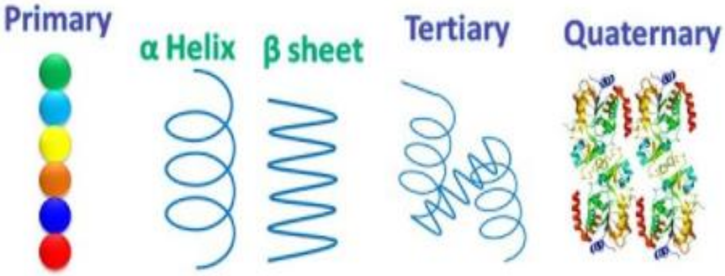
$$H_2N-CH_2-COOH + H_2N-\underset{\displaystyle CH_3}{CH}-COOH \xrightarrow{-H_2O} H_2N-CH_2-\boxed{CO-NH}-\underset{\displaystyle CH_3}{CH}-COOH$$

Glycylalanine (Gly-Ala)

Proteins are complex nitrogenous molecules which are essential for the growth and maintenance of life. **Structurally,** proteins are long polymers of amino acids linked by peptide (-CO—NH-) bond.

Structure of proteins: Proteins have three structures:

- Primary structure
- Secondary structure (Alpha helix and Beta pleated sheet)
- Tertiary structure (Fibrous proteins and Globular proteins)



Forces that stabilize protein structures: The forces that are present are as follows:

- **Hydrogen bonding**: These forces operate between a partially positive hydrogen and partially negative atom like O or N on the same or on another molecule.
- **Anionic bonding**: A bonding between cation and anion of side chains resulting in side linkage.
- **Hydrophobic bonding**: Some side chains in same amino acid are hydrophobic. In aqueous solutions proteins fold in such a way that these chains get clustered inside the folds. The polar side chains which are hydrophilic lie on the outside or surface of proteins.
- **Covalent bonding**: The bond occurs between S atoms of two residues between two adjacent chains.

Denaturation of proteins

- The globular proteins, which are soluble in water on heating or on treatment of mineral acids or bases, undergo coagulation or precipitation to give fibrous proteins which are insoluble in water.
- After coagulation, proteins lose their biological activity this is called denaturation.

- It can be reversible or irreversible.
- Coagulation of lactalbumin to form cheese and coagulation of albumins are examples of denaturation.

Classification of proteins on the basis of composition:

- **Simple proteins**: On hydrolysis they give only amino acids. Example: Globulins and albumin
- **Conjugated proteins**: They contain non protein group attached to the protein part. These non-protein groups are called prosthetic groups. Example: Nucleo-protein contains nucleic acid, phosphor-protein contains phosphoric acid, glycol-proteins contains carbohydrates etc.
- **Derived proteins**: These are the degradation products obtained by the hydrolysis of simple and conjugated proteins. Example: Peptides, peptones etc
- **Fibrous proteins**: They are long and thread like and tend to lie side by side to form fibers. In some cases, they are held together by hydrogen bonds at many points. These proteins serve as a chief structural material of animal tissues.
- **Globular proteins**: The molecules of these proteins are folded into compact units and form spheroid shapes. Intermolecular forces are weak. These proteins are soluble in water or aqueous solution of acids, bases or salts. Globular proteins make up all enzymes, hormones, fibrinogen etc.

- FIBROUS AND GLOBULAR PROTEINS:

PROPERTIES	**FIBROUS PROTEINS**	**GLOBULAR PROTEINS**
SHAPE	LONG & NARROW	ROUNDED/SPHERICAL
ROLE	STRUCTURAL (STRENGTH & SUPPORT)	FUNCTIONAL (CATALYSTS & TRANSPORT)
SOLUBILITY	INSOLUBLE IN WATER	SOLUBLE IN WATER
SEQUENCE	REPETITIVE AMINO ACIDS	IRREGULAR AMINO ACIDS
STABILITY	LESS SENSITIVE TO CHANGES IN HEAT & pH	LESS SENSITIVE TO CHANGES IN HEAT & pH
EXAMPLES	KERATIN, COLLAGEN	HEMOGLOBIN, INSULIN

Role of proteins

- They act as enzymes and transport agents.
- They are structural materials for nails, hair etc.
- Antibodies formed in body are globular proteins.
- They are metabolic regulators like insulin etc.

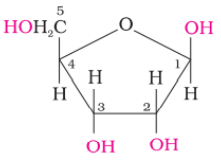
Hydrolysis of proteins

Proteins are hydrolysing when boiled with acids or alkalis or when treated with enzymes. Every protein has an isoelectric point at which their ionization is minimum. Proteins have charged groups i.e., NH_3^+ and COO^- at the ends of peptide chain. They are amphoteric in nature.

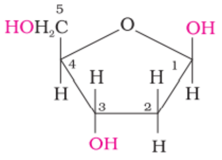
Protein accepts a proton in strong basic solution. The pH at which the protein molecule has no net charge is known as isoelectric point.

Nucleic acids: The particles in nucleus of the cell, responsible for heredity, are called chromosomes which are made up of proteins and another type of biomolecules called nucleic acids. These are mainly of two types, the deoxyribonucleic acid (DNA) and ribonucleic acid (RNA).

Structure of nucleic acids: In DNA molecules, the sugar moiety is β-D-2-deoxyribose whereas in RNA molecule, it is β-D-ribose.



β–D–ribose

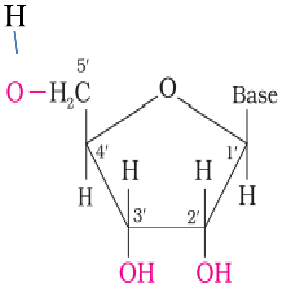


β–D–2–deoxyribose

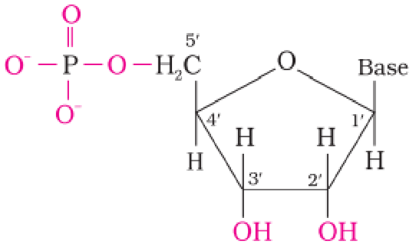
The nitrogenous base and a pentose sugar are called as nucleosides.
The nitrogenous base, a pentose sugar and a phosphate group are called as nucleotides.

Each nucleotide consists of 3 parts:

- A pentose sugars
- A nitrogenous base
- A phosphate groups



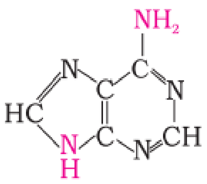
Nucleoside

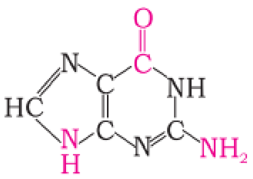


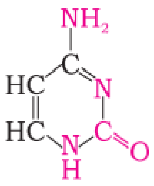
Nucleotide

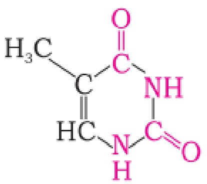
Nitrogenous bases are of two types: Purines and Pyrimidines
Purines: adenine and guanine
Pyrimidines: cytosine, thiamine and uracil

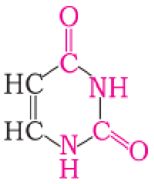
DNA contains four bases viz. adenine (A), guanine (G), cytosine (C) and thymine (T).
RNA also contains four bases; the first three bases are same as in DNA but the fourth one is uracil (U).


Adenine (A)


Guanine (G)


Cytosine (C)


Thymine (T)


Uracil (U)

Types of nucleic acids: Deoxyribonucleic acid (DNA) & Ribonucleic acid (RNA)
Main point of differences between DNA and RNA:

DNA (Deoxyribonucleic acid)	**RNA (Ribonucleic acid)**
1.It occurs mainly in the nucleus of the cell.	1.It occurs in the cytoplasm of the cell.
2.It has double stranded α-helix structure in which two strands are coiled spirally in opposite directions.	2.It has single stranded α-helix structure
3.The sugar molecule is 2-deoxyribose.	3.The sugar molecule is ribose.
4.Nitrogenous base uracil is not present.	4.Nitrogenous base thymine is not present.
5.DNA has unique property of replication.	5.RNA usually does not replicate.
6.It is responsible for the transmission for heredity character.	6.Helps in protein biosynthesis
7.DNA molecules are very large; their molecular masses may vary from $6 \times 10^6 – 16 \times 10^6$ u.	7.RNA molecules are much smaller with molecular mass ranging from $2 \times 10^4 – 4 \times 10^4$ u.

ASSIGNMENTS:

Q1. Sucrose is a _____ chemical, and the hydrolysis product combination is ______in nature.

(a) dextrorotatory; dextrorotatory

(b) laevorotatory; laevorotatory

(c) laevorotatory; dextrorotatory

(d) dextrorotatory; laevorotatory

Ans. (d) Sucrose is a dextrorotatory sugar that produces a combination of dextrorotatory glucose and laevorotatory fructose when hydrolyzed.

Q2. Which of the following statements about maltose is incorrect?

(a) It consists of two glucopyranose units

(b) It is a disaccharide

(c) Glycosidic bond between C1 of one unit and C4 of the other unit

(d) It is a non-reducing sugar

Ans. (d)

Q3. Which of the following statements about starch is incorrect?

(a) It gives blue colour with iodine

(b) It is a polymer of α-D-glucose

(c) It is a reducing carbohydrate

(d) It consists of branched chains

Ans. (c) Because it does not decrease Fehling's solution or Tollen's reagent, starch is a non-reducing saccharide.

Q4. RNA lacks the nitrogen base of _______

(a) Thymine

(b) Cytosine

(c) Uracil

(d) Adenine

Ans. (a) RNA contains the pyrimidine Uracil, whereas DNA contains Thymine.

Q5. When converting a disaccharide to monosaccharides, which bond is hydrolyzed?

(a) Disulfide bond

(b) Glycosidic bond

(c) Phosphodiester bond

(d) Hydrogen bond

Ans. (b)

Q6. Classify the following into monosaccharides and disaccharides.

Ribose, 2-deoxyribose, maltose, galactose, fructose and lactose.

Ans. Ribose, 2-deoxyribose, galactose, fructose - monosaccharides

Maltose and lactose - disaccharides.

Q7. Where does the water present in the egg go after boiling the egg?

Ans. When an egg is boiled in water, the water present in egg is used in denaturation of protein probably through H-bonding.

Q8 Why cannot vitamin C be stored in our body?

Ans. Because it is soluble in water and readily excreted in urine and cannot be stored in our body.

Q9. Enumerate the reactions of D-glucose which cannot be explained by its open chain structure.

Ans. (i) Despite having aldehyde group, glucose does not give Schiff test and 2,4-DNP test.

(ii)Glucose does not react with sodium hydrogen bisulphite to form addition product.

(iii)The pentaacetate of glucose does not react with hydroxyl amine showing the absence of free -CHO group.

Q10. What are essential and non-essential amino acids? Give two examples of each type.

Ans. The amino acids which can be made by our bodies and are not required in our diet are called non-essential amino acids. For example, glycine and alanine

The amino acids which cannot be made by our bodies and must be supplied in our diet are called essential amino acids. For example, valine and leucine.

Q11. What happens when D-glucose is treated with the following reagents?

(i) HI (ii) Bromine water (iii) HNO_3

Ans. (i) when glucose is treated with HI, it forms n-hexane.

(ii) when glucose is treated with Bromine water, gluconic acid is formed.

(iii) when glucose is treated with nitric acid, Saccharic acid is formed.

Q12. Define the following as related to proteins

(i)Peptide linkage (ii) Primary structure (iii) Denaturation.

Ans. (i)Peptide linkage- Peptide bond is formed by the condensation of two or more, same or different α-amino acids. -CO -NH- linkage is called peptide linkage.

(ii) Primary structure- Primary structure of proteins give the sequence in which amino acids are linked in one or more polypeptide chains of proteins.

(iii) Denaturation- A process that changes the physical and biological properties without affecting the chemical composition of a protein is called denaturation. The denaturation is caused by certain physical or chemical treatments such as in pH, temperature, presence of some salts or certain chemical agents.

Q13. (a) How do you explain the amphoteric behaviour of amino acids?

(b)The melting points and solubility in water of amino acids are generally higher than that of the corresponding halo acids. Explain.

Ans. (a) Due to dipolar or Zwitter ion structure, amino acids are amphoteric in nature. The acidic character of the amino acids due to the $-NH_3^+$ group and the basic character is due to the $-COO^-$ group.

(b)Amino acids have strong electrostatic attraction and hence have high melting points and highly soluble in water.

Q14. Differentiate the following

(i) Globular and fibrous proteins.
(ii) Nucleoside and a nucleotide.

Ans. (i) Fibrous proteins: They are long and thread like and tend to lie side by side to form fibers. In some cases, they are held together by hydrogen bonds at many points. These proteins serve as a chief structural material of animal tissues. Examples, keratin, collagen

Globular proteins: The molecules of these proteins are folded into compact units and form spheroid shapes. Intermolecular forces are weak. These proteins are soluble in water or aqueous solution of acids, bases or salts. Globular proteins make up all enzymes, hormones, fibrinogen etc. Examples, hemoglobin, insulin

(ii) The nitrogenous base and a pentose sugar are called as nucleosides.
The nitrogenous base, a pentose sugar and a phosphate group are called as nucleotides.

Q15. (a) Name the vitamins in each case whose deficiency causes

(i) Night blindness
(ii) Rickets
(iii) Poor coagulation of blood
(iv) Scurvy

(b)What is isoelectric point?

(c)Which amino acid is not optically active?

Ans. (a) (i) Vitamin A (ii) Vitamin D (iii) Vitamin K (iv) Vitamin C

(b)The pH at which no net migration of amino acid takes place under the influence of an applied electric field is called isoelectric point. For example, isoelectric point of glycine is 6.1.

(c)Glycine, NH_2CH_2COOH