

SOLUTION (GIST POINTS)

Concentration of Solutions:-

w/w% Composition: Mass of solute present per 100 g. of solution

$$w/w\% \text{ Composition} = \frac{w \text{ Solute}}{w \text{ Solution}} \times 100$$

Molarity [M]: No. of moles of solute present per liter of solution is called 'molarity of solution'. It is temperature dependent. $M = \text{No. of Moles of solute} / \text{Volume of solution in litre}$

Molality [m]: No. of moles of solute present per kg. of solvent is called molality. It is temperature independent. $m = \text{No. of Moles of solute} / \text{Mass of Solvent in Kg}$

Normality[N]: No. of gram equivalent of solute present per liter of solution is called normality of solution.

$$N = \text{No. of gm equivalent of solute} / \text{Volume of solution in litre}$$

Parts Per Million [ppm]: It is used for very dilute solutions, Parts of solute in per million parts of solution are called ppm. $\text{Ppm} = \text{Part of solute} \times 10^6 / \text{Part of solution}$

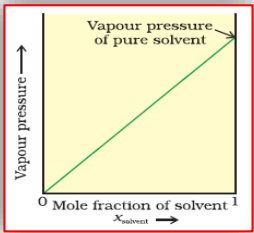
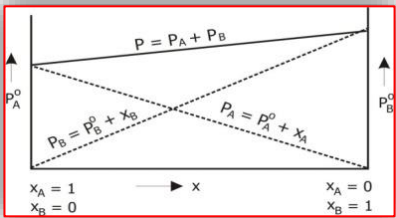
Mole Fraction: Ratio of moles of components to total no. of moles of all the components of solution is called mole fraction (x) of the component.

Henry's law :- "The partial pressure of the gas in vapour phase p is proportional to the mole fraction of the gas x in the solution." $P = K_H x$

Applications of Henry Law (1) In Packing of soda/ Soft drinks (2) In Deep sea diving (He = 11.7 % , N₂ = 56.2 % and O₂ = 32.1%) (3) Functions of lungs (4) At high altitudes pressure is low there for breathing problems lead to ANOXIA (unable to think and weak)

Vapour Pressure: The pressure exerted by vapours over the liquid surface at equilibrium is called **vapour pressure** of the liquid.

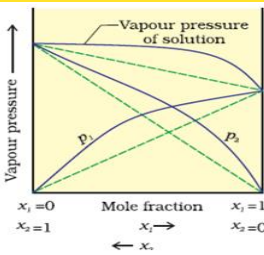
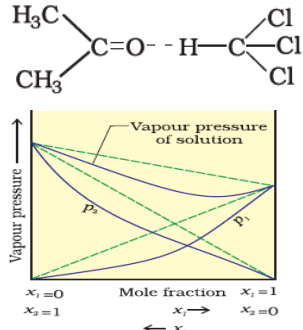
Raoult's Law: "The V.P. of any volatile component in the solution is directly proportional to its mole fraction".

Raoult's Law for Solutions Containing Non-Volatile Solute	Raoult's Law for Solution Containing Volatile Solute
	

Ideal and Non-Ideal Solutions:

Ideal Solution	Non Ideal Solution
Follows Raoult's law at all temperature and concentrations. $P = P_A + P_B$	Does not follow Raoult's law at all temperature and pressure. $P \neq P_A + P_B$
Intermolecular forces in resulting solution are same as in pure components. $A - B = A - A = B - B$	Intermolecular forces in resulting solution are different from the inter molecular force of pure components. $A - B \neq A - A, B - B$
No change in volume while mixing components. $\Delta V_{\text{mix}} = 0$	Change in volume while mixing components. $\Delta V_{\text{mix}} \neq 0$
No heat change take place while mixing the components. $\Delta H_{\text{mix}} = 0$	Heat changes take place while mixing the components. $\Delta H_{\text{mix}} \neq 0$
Eg: n - hexane + n - heptanes & benzene + toluene	Eg: Acetone + Water & Acetone + CHCl ₃

Non Ideal Solution

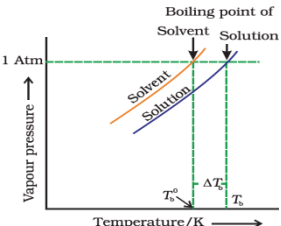
Showing Positive elevation from Raoult's Law	Showing Negative Deviation from Raoult's Law
Vapour pressure of resulting solution is greater than sum of partial pressure of components. $P > P_A + P_B$	Vapour pressure of resulting solution is less than sum of the partial pressure of pure components. $P < P_A + P_B$
Resulting intermolecular force is weaker than pure components.	Resulting intermolecular force is stronger than pure components.
$\Delta V_{mix} = +ve$	$\Delta V_{mix} = -ve$
Volume of solution > Sum of volume of pure components	Volume of solution < Sum of volume of pure components
$\Delta H_{mix} = +ve$ Endothermic mixing process	$\Delta H_{mix} = -ve$ Exothermic process
Acetone + Water Alcohol + Water Carboxylic Acid + Water 	Acetone + $CHCl_3$, HNO_3 + H_2O 

Azeotrope: (Constant Boiling Mixture) :- Solution in which components are present in a fixed proportion, boils at a constant temperature irrespective of boiling point of pure components

• **Minimum Boiling Azeotrope:** Boils at a temperature lower than b.p.s. of pure components. [95% Alcohol]

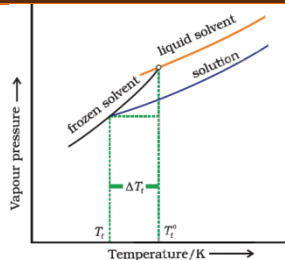
• **Maximum Boiling Azeotrope:** Boils at a temperature higher than b.p.s. of pure components. [68% HNO_3]

Colligative Properties:- The properties of dilute solutions which depend only on number particles of solute present in the solution and not on their identity are called *colligative properties*

1-Relative Lowering of Vapour Pressure $\frac{p_1^0 - p_1}{p_1^0} = \frac{w_2 \times M_1}{M_2 \times w_1}$	The relative lowering of vapour pressure of a solution containing a non-volatile solute is equal to the mole fraction of the solute present in the solution.	
2-Osmosis and Osmotic Pressure Diffusion:- Movement of solute particles from higher concentration to lower concentration. E.g. Incense stick Osmotic Pressure: Excess pressure which must be applied to a solution in order to prevent flow of solvent into the solution through the semi-permeable membrane. $\pi V = nRT$ π = Osmotic pressure R = Gas constant	Osmosis:- The phenomenon of the passage of pure solvent from a region of lower concentration (of the solution) to a region of its higher concentration through a semi-permeable membrane. Reverse Osmosis: If pressure greater than osmotic pressure is applied then, flow of solvent molecules is reversed, i.e. from a higher concentration solution to lower concentrated solution. This phenomenon is called "Reverse Osmosis". It is used in water purification and desalination of water.	
3- Elevation of Boiling Point : Difference between boiling of solution containing non volatile solute and B.P. of pure solvent is called elevation of B.P. $\Delta T_b = T_b - T_b^0$		$\Delta T_b \propto m$ [molality] $\Delta T_b = K_b m$ K_b = Molal Elevation Constant $\Delta T_b = K_b \frac{W_{solute} \times 1000}{M_{solute} \times W_{solvent}}$
4-Depression of Freezing Point Difference in freezing point of pure		$\Delta T_f \propto m$ [molality] $\Delta T_f = K_f m$

solvent and freezing point of solution is called 'Depression in Freezing Point'.

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



K_f = Molal Depression Constant

$$\Delta T_f = K_f \frac{W_{\text{solute}} \times 1000}{M_{\text{solute}} \times W_{\text{solvent}}}$$

Van't Hoff Factor:

$$i = \frac{\text{Observed colligative property (actual)}}{\text{Theoretical colligative property (expected)}}$$

$$= \frac{\text{No. of molecules actually present}}{\text{No. of molecules expected to be present}}$$

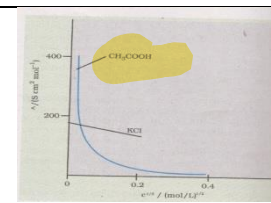
$$i = \frac{\text{No. of mole After dissociation/Association}}{\text{No. of mole Before dissociation/Association}}$$

$$i = \frac{\left[\frac{p^0 - p^s}{p^0}, \Delta T_f, \Delta T_b, \pi \right]_{\text{Observed}}}{\left[\frac{p^0 - p^s}{p^0}, \Delta T_f, \Delta T_b, \pi \right]_{\text{Theoretical}}}$$

Association	Dimerisation	Trimerisation	Tetramerisation	pentamerisation
$i =$	1/2	1/3	1/4	1/5
dissociation	NaCl	MgCl ₂	AlCl ₃	K ₄ [Fe(CN) ₆]
$i =$	2	3	4	5

UNIT-3 ELECTROCHEMISTRY

SNO.	Terminology
1.	Conductance : Reciprocal of the resistance $G = \frac{1}{R}$ Unit is Ω^{-1}
2	Specific Resistance/Resistivity : $\rho = R A / l$ Unit is ohm-cm
3	Specific Conductance or Conductivity : $k = 1/\rho = l/RA$ $k = GG^*$ Conductivity of any conductor is the reciprocal of specific resistance and is denoted by κ (Greek work Kappa) unit Scm^{-1}
4	Molar Conductivity : It is defined as the conducting power of all the ions produced by one gram mol of an electrolyte in a solution. It is denoted by Λ_m unit $\text{Scm}^2\text{mol}^{-1}$. $\Lambda_m = \frac{\kappa \times 1000}{\text{Molarity}}$
5	Variation of molar conductivity with concentration For strong electrolytes λ decreases slightly with increase in concentration due to increase in number of ions per unit volume.e.g KCl For weak electrolytes it increases sharply with decrease in concentration as ionization of weak electrolytes increases on dilution e.g CH_3COOH
6	Kohlrausch's Law : According to this law, molar conductivity of an electrolyte, at infinite dilution can be expressed as the sum of contributions from its individual ions e.g. $\lambda^\circ \text{CaCl}_2 = \lambda^\circ (\text{Ca}^{2+}) + 2\lambda^\circ (\text{Cl}^-)$ $\lambda^\circ_{\text{Al}_2(\text{SO}_4)_3} = 2\lambda^\circ_{\text{Al}^{+3}} + 3\lambda^\circ_{\text{SO}_4^{-2}}$ Application of Kohlrausch's Law 1. For calculation of limiting molar conductivity $\lambda^\circ = \lambda^c / \lambda_m$ 2. For calculation of degree of dissociation $\alpha = \frac{\Lambda}{\Lambda^\circ}$ 3. For calculation of dissociation constant. $K_a = \frac{c\alpha^2}{(1-\alpha)} = \frac{c\Lambda^2}{\Lambda^\circ(\Lambda^\circ - \Lambda)}$
7	Faraday – First law of electrolysis : The amount of substance deposited during electrolysis is directly proportional to quantity of electricity passed. Faraday – Second Law : The amount of different substances liberated by the same quantity of electricity passing through the electrolytic solution is proportional to their chemical equivalent



	$W = zit$ and $z = \frac{m}{nF}$ therefore $w = \frac{m \times i \times t}{nF}$	weights $\frac{w_1}{w_2} = \frac{E_1}{E_2}$
8	Nernst equation $E_{cell} = E^{\circ}_{cell} - \frac{0.059}{n} \log \frac{[product]}{[react.]}$	Equilibrium constant K_c At equilibrium $Q = K_c$ and $E_{cell} = 0$ $E^{\circ}_{cell} = \frac{0.059}{n} \log K_c$
9.	Electrochemical Cell and Gibbs energy of the reaction $\Delta_r G = -nFE$ $\Delta_r G^{\circ} = -nFE^{\circ}$ $\Delta_r G^{\circ} = -2.303RT \log K_c$	Concentration Cell : A cell in which both electrodes are of the same type but the solution of electrolyte in which they dip have different concentration is concentration cell. $Cu / Cu^{2+}(C_1) // Cu^{2+}(C_2) / Cu$ $E_{cell} = \frac{2.303RT}{2F} \log \frac{C_2}{C_1}$

Products of electrolysis

NaCl (molten)	Cathode : $Na^{+}(l) + e^{-} \rightarrow Na(s)$	Anode : $Cl^{-} \rightarrow \frac{1}{2}Cl_2 + e^{-}$
NaCl (aq)	Cathode : $H_2O(l) + e^{-} \rightarrow \frac{1}{2}H_2(g) + OH^{-}$	Anode : $Cl^{-} \rightarrow \frac{1}{2}Cl_2 + e^{-}$
H_2SO_4 (dil)	Cathode : $H^{+} + e^{-} \rightarrow \frac{1}{2}H_2$	Anode: $2H_2O(l) \rightarrow O_2(g) + 4H^{+}(aq) + 4e^{-}$
H_2SO_4 (conc)	Cathode : $H^{+} + e^{-} \rightarrow \frac{1}{2}H_2$	Anode: $2SO_4^{2-}(aq) \rightarrow S_2O_8^{2-}(aq) + 2e^{-}$
$AgNO_3$ (aq)-Ag electrodes	Cathode : $Ag^{+}(aq) + e^{-} \rightarrow Ag(s)$	Anode: $Ag(s) \rightarrow Ag^{+}(aq) + e^{-}$
$AgNO_3$ (aq)- Pt electrodes	Cathode : $Ag^{+}(aq) + e^{-} \rightarrow Ag(s)$	Anode: $2H_2O(l) \rightarrow O_2(g) + 4H^{+}(aq) + 4e^{-}$
$CuCl$ (aq)- Pt electrodes	Cathode : $Cu^{+}(aq) + e^{-} \rightarrow Cu(s)$	Anode: $2H_2O(l) \rightarrow O_2(g) + 4H^{+}(aq) + 4e^{-}$

Electrochemical Cell			Electrolytic Cell	
1. It is device to convert chemical energy to electrical energy 2. It is based upon redox reaction which is spontaneous.			1. It is device to convert electrical energy into chemical energy 2. The redox reaction is non-spontaneous and takes place only when electrical energy is supplied.	
SN O.	Name of cell	Electrolyte	Chemical Reaction	Remark
1	Mercury Cell	Paste of KOH & $Zn(OH)_2$	Anode:- zinc-mercury amalgam $Zn(Hg) + 2OH^{-} \rightarrow ZnO(s) + H_2O + 2e^{-}$ Cathode:- HgO and carbon $HgO + H_2O + 2e^{-} \rightarrow Hg(l) + 2OH^{-}$ Overall reaction:- $Zn(Hg) + HgO \rightarrow ZnO + H_2$	Provide constant voltage and does not corroded due to absence of ion in overall reaction. Voltage 1.35V
2	Dry Cell :	$ZnCl_2$ and NH_4Cl	Anode :- Zinc rod $Zn(s) \rightarrow Zn^{2+} + 2e^{-}$ Cathode:-Carbon rod surrounded by MnO_2 $2MnO_2 + 2NH_4^{+} + 2e^{-} \rightarrow Mn_2O_3 + 2NH_3$ Overall Reaction:- $Zn + 2MnO_2 + 2NH_4^{+} \rightarrow Zn^{2+} + Mn_2O_3 + 2NH_3$	Corroded due to the presence of ion in overall reaction. $ZnCl_2$ is used to make a complex $[Zn(NH_3)_2Cl_2]$ it saves the bursting of cell, Voltage 1.5V
3	Lead Storage (Secondary Batteries) :	38% H_2SO_4	Anode:- Pb grid $PbSO_4(s) + 2e^{-} \rightarrow Pb(s) + SO_4^{2-}(aq)$ Cathode:-Pb grid filled with PbO_2 $PbO_2(s) + SO_4^{2-} + 4H^{+}(aq) + 2e^{-} \rightarrow PbSO_4(s) + 2H_2O(l)$ Overall Cell Reaction:- $Pb(s) + PbO_2(s) + 2H_2SO_4 \rightarrow 2PbSO_4(s) + 2H_2O(l)$	Can be Recharged by reversing the electrodes Reactant become products and products become reactants
4	Fuel Cell :	KOH solution	Anode :- $2H_2 + 4OH^{-} \rightarrow 4H_2O + 4e^{-}$ Cathode :- $O_2(g) + 2H_2O(l) + 4e^{-} \rightarrow 4OH^{-}(aq)$ Overall Reaction:- $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$	Eco friendly, Efficiency 60-70%
5.	Corrosion	H_2CO_3	Anode (oxidation) :- $Fe(s) + Fe^{2+}(aq) + 2e^{-}$ Cathode (Reduction) :- $O_2(g) + 4H^{+}(aq) + 4e^{-} \rightarrow 2H_2O(l)$	Formula of rust $Fe_2O_3 \cdot xH_2O$

			Atmospheric Oxidation:- $2\text{Fe}^{2+}_{(\text{aq})} + 2\text{H}_2\text{O}_{(\text{l})} + 1/2\text{O}_2 \rightarrow \text{Fe}_2\text{O}_{3(\text{s})} + 4\text{H}^{+}_{(\text{aq})}$	
Prevention of Corrosion		By covering the surface with paint or by some chemicals (e.g. bisphenol). / Cover the surface by other metals (Sn, Zn, etc.) that are inert or react to save the object. An electrochemical method (sacrificial electrode like Mg, Zn, etc.) which corrodes itself but saves the object.		

CHAPTER-4 CHEMICAL KINETICS

RATE OF REACTION	The change in concentration of either reactant or product per unit time. Example : $N_2 + 3H_2 \rightarrow 2NH_3$ $\text{Rate of reaction} = + \frac{1}{2} \frac{d[NH_3]}{dt} = - \frac{d[N_2]}{dt} = - \frac{1}{3} \frac{d[H_2]}{dt}$																		
Unit of rate	$\text{Mol L}^{-1}\text{time}^{-1}$ or $\text{mol L}^{-1} \text{S}^{-1}$																		
Rate Law	The expression of rate of reaction in term of concentration of reactant $aA + bB \rightarrow \text{Product}$ $\text{Rate} = K[A]^x[B]^y$																		
Rate Constant	Specific Rate of reaction :-Rate of reaction when concentration are taken as unity $\text{Rate} = K[A]^x[B]^y$ $[A]=1$ $[B]=1$ $\text{Rate}=K$																		
Unit of rate constatnt	$\text{Unit of } k = \left[\frac{\text{mol}}{\text{L}} \right]^{1-n} \times \text{time}^{-1}$ For gaseous reaction unit of k may be = $(\text{atm})^{1-n} \times \text{time}^{-1}$ N - Order of reaction																		
Order of reaction	The sum of powerof concentration of reactant in rate law expression $aA + bB \rightarrow \text{Product}$ $\text{Rate} = K[A]^x[B]^y$ Order of reaction = $x+y$ It may be Zero,Positive or Negative or fraction.It is experimental quantity.																		
Mechanism of Reaction	Elementary reaction:- Chemical reaction complete in single step and have exponant in rate law expression equal to their stoichiometric coefficient.Zero order reaction can not be an elementry reaction. Complex Reaction:- For the complex reaction,The overall reaction is controlled by the slowest step. In the rate law expression,rate of reaction depends on concentration of reactant of slowest step which must be free from intermediate. <table><tr><td>(i)Thermal decomposition of N_2O_5 $2N_2O_5 \rightarrow 4 NO_2 + O_2$</td><td>(ii) Reaction of NO_2 and F_2 $2NO_2 + F_2 \rightarrow 2NO_2F$</td></tr><tr><td>Step(i) $N_2O_5 \xrightarrow{\text{slow}} NO_2 + NO_3$ Step(ii) $N_2O_5 + NO_3 \xrightarrow{\text{fast}} 3NO_2 + O_2$</td><td>Step(i) $NO_2 + F_2 \xrightarrow{\text{slow}} NO_2F + F$ Step(ii) $NO_2 + F \xrightarrow{\text{fast}} NO_2F$</td></tr></table>			(i)Thermal decomposition of N_2O_5 $2N_2O_5 \rightarrow 4 NO_2 + O_2$	(ii) Reaction of NO_2 and F_2 $2NO_2 + F_2 \rightarrow 2NO_2F$	Step(i) $N_2O_5 \xrightarrow{\text{slow}} NO_2 + NO_3$ Step(ii) $N_2O_5 + NO_3 \xrightarrow{\text{fast}} 3NO_2 + O_2$	Step(i) $NO_2 + F_2 \xrightarrow{\text{slow}} NO_2F + F$ Step(ii) $NO_2 + F \xrightarrow{\text{fast}} NO_2F$												
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Difference between Order of Reaction and Molecularity	<table><tr><th>Order of Reaction</th><th>Molecularity</th></tr><tr><td>➤ 1.The sum of the exponents (powers) by which the concentration terms are raised in rate law.</td><td>➤ 1.The no. atoms , ions or molecule that must collide with one another simultaneously so that chemical reaction take place</td></tr><tr><td>➤ 2.Determined Experimently by rate law</td><td>➤ 2.Theoretical concept ,determined by slowest step</td></tr><tr><td>➤ 3.May be Zero and negetive</td><td>➤ 3.Never be Zero and negetive</td></tr><tr><td>➤ 4.May be Fraction</td><td>➤ 4.Neverbe Fraction</td></tr></table>	Order of Reaction	Molecularity	➤ 1.The sum of the exponents (powers) by which the concentration terms are raised in rate law.	➤ 1.The no. atoms , ions or molecule that must collide with one another simultaneously so that chemical reaction take place	➤ 2.Determined Experimently by rate law	➤ 2.Theoretical concept ,determined by slowest step	➤ 3.May be Zero and negetive	➤ 3.Never be Zero and negetive	➤ 4.May be Fraction	➤ 4.Neverbe Fraction								
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Pseudo first order reaction	A chemical reaction which seems to be higher order but actually they are of first order ➤ For these reaction,Order of reaction is one but molecularity is more than one Example :- <u>Hydrolysis of ester in acedic medium</u> , $CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$ Rate = $K[CH_3COOC_2H_5][H_2O]$ When water is in excess then $K'[CH_3COOC_2H_5]$ <u>Inversion of cane sugar in acidic medium</u> $C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6$ Rate = $K[C_{12}H_{22}O_{11}][H_2O]$ When water is in excess then $K'[C_{12}H_{22}O_{11}]$																		
METHOD OF DETERMINING ORDER OF REACTION	Initial Rate Method: The data's are given in term of different rates at different concentrations, thus we calculate the rate expression and then find the order of reaction. Example: Reaction $A + B \rightarrow \text{Product}$ <table><tr><th>S.No.</th><th>Conc. of A</th><th>Conc. of B</th><th>Rate</th></tr><tr><td>1.</td><td>x_1</td><td>y_1</td><td>r_1</td></tr><tr><td>2.</td><td>x_2</td><td>y_2</td><td>r_2</td></tr><tr><td>3.</td><td>x_3</td><td>y_3</td><td>r_3</td></tr></table> <div><p>According to rate law</p>$\text{Rate}_1 = k(x_1)^m(y_1)^n \dots\dots\dots(i)$$\text{Rate}_2 = k(x_2)^m(y_2)^n \dots\dots\dots(ii)$$\text{Rate}_3 = k(x_3)^m(y_3)^n \dots\dots\dots(iii)$<p>Here we have three unknown quantities k, m, n and we have three equations thus the solution is possible and k, m, n have unique value, Thus order of reaction = $m + n$</p></div> Example: Consider the following data for the reaction $A + B = \text{Products}$ and Determine the order of the reaction with respect to A and w.r.t. B and the overall order of the reaction.			S.No.	Conc. of A	Conc. of B	Rate	1.	x_1	y_1	r_1	2.	x_2	y_2	r_2	3.	x_3	y_3	r_3
S.No.	Conc. of A	Conc. of B	Rate																
1.	x_1	y_1	r_1																
2.	x_2	y_2	r_2																
3.	x_3	y_3	r_3																

Also calculate rate constant.

Exp.	Initial conc. (A)	Initial conc. (B)	Initial rate (mol L ⁻¹ s ⁻¹)
1	0.10 M	1.00 M	2.1 × 10 ⁻³
2	0.20 M	1.00 M	8.4 × 10 ⁻³
3	0.20 M	2.00 M	8.4 × 10 ⁻³

ANSWER:

Exp.	Rate = K [A] ^x [B] ^y	Eq. (i)/(ii) Then (1/2) ^x = (1/4) Therefore x = 2
1	Rate = K [0.10] ^x [1.00] ^y = 2.1 × 10 ⁻³(i)	
2	Rate = K [0.20] ^x [1.00] ^y = 8.4 × 10 ⁻³(ii)	Eq.(ii)/(iii) Then (1/2) ^y = (1)
3	Rate = K [0.20] ^x [2.00] ^y = 8.4 × 10 ⁻³(iii)	Therefore y = 0

Rate law = K[A]²[B]⁰ K = 2.1 × 10⁻³ / [0.1]²[1.00]⁰

Differential and Integrated Rate Laws:

Reaction in which the rate of reaction is directly proportional to one power of concentration of reactant

Zero Order Reactions:

Rate of reaction = K[reactant]⁰

A → Products

$$-d[A]/dt = K_0 [A]^0$$

$$-d[A] = K_0 dt$$

On integrating both side

$$\int -d[A] = \int K_0 dt$$

$$-[A] = K_0 t + C \text{ --(i)}$$

(Where C = integrating constant)

At t = 0 [A] = [A₀] then C = - [A₀]

Putting the value of C in equation (i)

$$[A] = K_0 t - [A_0]$$

$$\text{Or } K_0 t = [A_0] - [A]$$

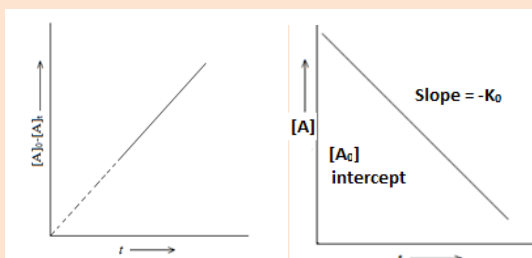
$$[A] = -K_0 t + [A_0] \text{ that is } Y = -mx + C$$

$$[A]_0 - [A]_t = K_0 t$$

Where, [A]₀ = Initial concentration of A

[A] = Concentration of A at time t.

K₀ = Rate constant for zero order reaction.



Unit of rate constant = mol litre⁻¹s⁻¹

Examples:

- Enzyme catalyzed reactions
- Decomposition of gases on the surface of metallic catalysts like decomposition of HI on gold surface.

First Order Reactions:

Rate of reaction = K[reactant]¹

A → Products

$$-d[A]/dt = K_1 [A]^1$$

$$-d[A]/[A] = K_1 dt$$

On integrating both side

$$\int -d[A]/[A] = \int K_1 dt$$

$$-\ln[A] = K_1 t + C \text{ --(i)}$$

(Where C = integrating constant)

At t = 0 [A] = [A₀] then C = - ln[A₀]

Putting the value of C in equation (i)

$$\ln[A] = K_1 t - \ln[A_0]$$

$$\text{Or } K_1 t = \ln[A_0] - \ln[A]$$

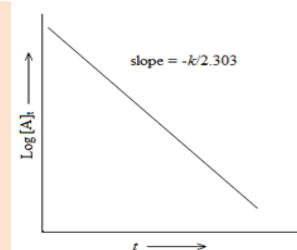
$$\ln[A] = -K_1 t + \ln[A_0] \text{ that is } Y = -mx + C$$

$$\text{or } k_1 = (2.303/t) \log ([A]_0 / [A])$$

Where, [A]₀ = Initial concentration of A

[A] = Concentration of A at time t.

K₁ = Rate constant for First order reaction.



Units of k₁ = s⁻¹ **EXAMPLES**

- $\text{H}_2\text{O}_2 \longrightarrow \text{H}_2\text{O} + \frac{1}{2}\text{O}_2$
- $\text{CH}_3\text{COOCH}_3 + \text{H}_2\text{O} \xrightarrow{\text{acid}} \text{CH}_3\text{COOH} + \text{CH}_3\text{OH}$
- $\text{C}_{12}\text{H}_{22}\text{O}_{11} + \text{H}_2\text{O} \xrightarrow{\text{acid}} \text{C}_6\text{H}_{12}\text{O}_6 + \text{C}_6\text{H}_{12}\text{O}_6$
- $\text{NH}_4\text{NO}_2 \longrightarrow \text{N}_2 + 2\text{H}_2\text{O}$
- $\text{C}_6\text{H}_5\text{N} = \text{Cl} + \text{H}_2\text{O} \longrightarrow \text{C}_6\text{H}_5\text{OH} + \text{N}_2 + \text{HCl}$
- $\text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O} \xrightarrow{\text{H}^+} \text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH}$
- $2\text{PH}_3(\text{g}) \longrightarrow 2\text{P}(\text{s}) + 3\text{H}_2(\text{g})$
- $\text{N}_2\text{O}_5 \longrightarrow 2\text{NO}_2 + 1/2\text{O}_2$

Half Life

Half Life: Time required to consume the half of initial concentration of reactant is called half life period.

$$\text{At } t = t_{1/2} [A] = [A_0]/2$$

$$K_0 t_{1/2} = [A]_0 - [A_0]/2$$

$$t_{1/2} = [A]_0 / 2k$$

Half Life: Time required to consume the half of initial concentration of reactant is called half life period. **At** $t = t_{1/2} [A] = [A_0]/2$

$$k_1 = (2.303/t_{1/2}) \log ([A]_0 / [A_0]/2)$$

$$t_{1/2} = 0.693/k_1$$

Half-life is independent of the initial

Half life is directly proportion of the initial concentration of the reactant for a zero order reaction.	concentration of the reactant for a first order reaction
--	--

Factor Affecting rate of reaction

- **1. Nature of reactant:-**
Chemical Nature of Reactant:-Reaction having less value of activation energy will takes place faster
- **2. Concentration of Reactant:-** Rate of reaction \propto Conc. of Reactant
- **3. Temperature:-**On increasing temperature, rate of reaction increases whether the reaction is exothermic or endothermic because KE of molecule increase on increases temperature which led to increasing activated molecule.
- **Relation between rate constant and temperature**
(a)Generally it is found that for every 10 °C rise in temperature rate of reaction become 2 to 3 times
Temperature Coefficient:-It is defined as ratio of rate of a reaction at two different temperature which will differ by 10 °C

$$\mu = \frac{K_{T+10}}{K_T} = 2 \text{ to } 3 ; \quad \frac{r_2}{r_1} = \frac{K_2}{K_1} = \mu^{\Delta T/10}$$
- 5. Presence of catalyst:-In the presence of catalyst, E_a (Activation energy) decreases therefore rate of reaction increases
- 6. Exposure of radiation:-Rate of some reaction increases on exposure of radiation. These reaction are called photochemical reaction For Example:-

$$H_2 + Cl_2 \longrightarrow 2HCl \text{ (very slow reaction)} \quad H_2 + Cl_2 \xrightarrow{h\nu} 2HCl \text{ (explosive)}$$

The following data were obtained during the first order thermal decomposition of SO_2Cl_2 at a constant volume. $SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$. Calculate the rate constant.

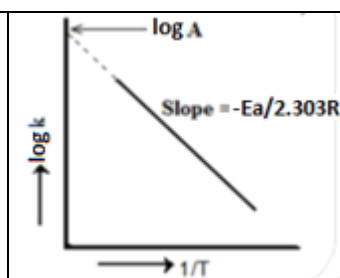
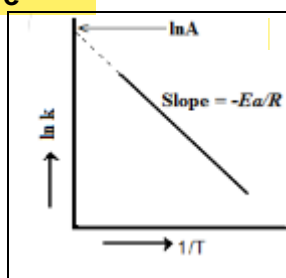
Exp	Time/s ⁻¹	Total pressure/atm
1	0	0.5
2	100	0.6

Ans: Given $p_0 = 0.5 \text{ atm}$ $P_t = 0.6 \text{ atm}$ $t = 100 \text{ sec}$ $n = 2/1 = 2$
 $k_1 = (2.303/t) \log (n-1)P_0 / nP_0 - P_t$
 OR $k_1 = (2.303/100) \log(0.5) / 2(0.5) - 0.6$ Or $K_1 = 2.231 \times 10^{-3} \text{ sec}^{-1}$

Arrhenius Equation

It shows the relationship between activation energy and rate constant and effect of temp on rate constant.

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



$$\log K_2/K_1 = E_a/2.303R [1/T_1 - 1/T_2]$$

THRESHOLD ENERGY

The Minimum extra amt of energy which the reactants molecules must have so that reactant molecule reacts and overcome the energy barriers and converts into products.

ACTIVATION ENERGY

The Minimum extra amt of energy absorbed by the reactant molecule so that their energy becomes equal to threshold energy.

Applications of Activation Energy:-

- Rate of reaction $\propto 1/\text{Activation Energy}$
- To find the nature of reaction (Exothermic/Endothermic reaction)
 - Activation Energy of Products - Activation Energy of Reactants = +ive Exothermic
 - Activation Energy of Products - Activation Energy of Reactants = -ive Endothermic.

Collision Theory of Reaction Rate

- **Collision frequency (Z):**-The number of collisions taking place per second per unit volume of the reaction mixture is known as collision frequency (Z).
- **Rate = $Z_{AB} e^{-E_a/RT}$** **Where Z=collision frequency and $-E_a/RT$ =Fraction of molecule having equal or more then activation energy.**
- For a collision to be effective, the following two barriers are to be cleared.
 1. Energy Barrier 2.Orientation Barrier
- To account for the orientation factor for the collision to be effective , Probability or Orientation or Steric factor(P) has been introduced
- **Rate = $PZ_{AB} e^{-E_a/RT}$**

UNIT-4 - d and f- BLOCK ELEMENTS

1	d-block elements are called transition elements	as they have incomplete d-orbitals in neutral or most stable oxidation state.
2	Zn, Hg, Cd, are not included as transition elements and why?	as they have filled d-orbitals in neutral and most stable +2 oxidation state.
3	Sc ³⁺ has d ⁰ configuration but it is transition metal	Because of partially filled d ¹ configuration of Sc
4	First series transition elements shows irregular trend of atomic radii	Due to shielding effect of inner 3d electrons which overcome ENC.
5	Atomic radii of Zr to Hf are almost same.	due to Lanthenoid Contraction.
6	First series transition elements shows irregular trend of IE	It is because of mutual exchange of energy between d and f orbitals after removal of one electron.
7	Transition metals have strong metallic bond, have high enthalpy of atomization and melting point.	due to presence of unpaired electrons.
8	Zn, Cd, Hg are not very hard and have low M.P. and B.P.	Due to presence of all paired electrons they have least enthalpy of atomization, very weak metallic bond & are not very hard with low M.P. and B.P.
9	d-block elements shows a large no. of oxidation state	due to presence of unpaired electrons or partially filled d-orbitals.
10	Which first series transition metal shows highest number of oxidation states and why?	Mn shows highest number of oxidation state due presence of highest number of unpaired electrons.
11	Which first series transition metal do not show variable oxidation states and why?	Sc , due to achieving noble gas configuration in +3 O.S
12	Cr ³⁺ is more stable as compared to Cr ²⁺	due to stable half filled t_{2g}³ configuration.
13	Cu ²⁺ is more stable in solution than Cu ⁺	due to high hydration enthalpy of Cu ²⁺ ion in solution.
14	Which first series transition metal shows +1 oxidation states and why?	Cu shows +1 oxidation state in gaseous form due to stable full filled 3d ¹⁰ configuration.
15	Higher oxidation states of transition metals found in their oxides and fluorides	because higher oxidation states stabilized by highly electronegative elements such as O and F

16	higher oxidation states are more common in oxides rather than fluorides of transition metals.	due to formation of $d\pi-p\pi$ bond between metal and oxygen.
17	+2 O.S becomes more stable in first series transition elements moving from left to right	as number of unpaired electrons decreases.
18	Write oxoanions of first series transition metals in which group number and O.N. of transition metal are same-	MnO_4^- , $Cr_2O_7^{2-}$, VO_3^- , CrO_4^{2-}
19	Moving from left to right E^0 for M^{2+}/M becomes less negative but it shows irregular trend	trends due to irregular variation of $IE_1 + IE_2$.
20	For copper $E^0 Cu^{2+}/Cu$ is +ve (+0.34 V)	it is due to low hydration enthalpy of Cu^{2+} which cannot compensate $\Delta_{sub}H^0 + IE_1 + IE_2$.
21	For Mn, $E^0 Mn^{3+}/Mn^{2+}$ is +ve	because by converting into Mn^{2+} it achieves half filled configuration.
22	For Cr, $E^0 Cr^{3+}/Cr^{2+}$ is -ve	because Cr^{3+} is more stable due to half filled t_{2g} configuration.
23	Most of the compounds of transition metal are coloured in solid state as well as in their solution form.	It is due to d-d transition
24	(Sc^{3+}, Ti^{4+}) does not exhibit any colour	Ions with vacant d-orbitals (d^0) as d-d transition is not possible in this type of ions.
25	(Zn^{2+}, Cu^+) does not exhibit any colour	full filled d-orbitals (d^{10}) as d-d transition is not possible in this type of ions.
26	Transition metals or ions are paramagnetic in nature	Due to presence of unpaired electrons (d^{1-9})
27	Transition metal form large number of coordination complexes	High charge by mass ratio, availability of vacant d-orbital & Variable oxidation state
28	What are Interstitial compounds?	Compounds in which small elements like H, B, C, N trapped in the interstitial space of metal lattice.
29	Transition metals form Interstitial compounds.	due to availability of interstitial space in metal lattice.
30	Why interstitial compounds are found to be more useful than pure metal?	These compounds have high M.P as compared to pure metals. These are very hard. Retain metallic conductivity and are Chemically inert.
31	Transition metals and their compounds are widely used as catalyst	Due to large surface area , variable oxidation state & Availability of vacant d-orbitals
32	transition metals form alloy.	Due to comparable metallic radii
33	Why oxides of Higher oxidation states of transition metals are acidic in nature whereas lower O.S. are basic in nature?	Higher oxidation states are more polarizing in nature . hence are acidic in nature whereas lower O.S. are less polarizing hence are basic in nature.
34	Actinoids shows greater number of oxidation states then lanthanoids	Due to comparable energy of 5f, 6d, and 7s orbitals.

35	It is difficult to study chemistry of actinoids.	Due to radio active nature and small half life																				
36	Ce(IV) is a good oxidizing agent in aq. sol ⁿ	because in aq. solution its E ⁰ _{Ce⁴⁺/Ce³⁺} is +1.74 V																				
37	Actinoid contraction is greater from element to element as compared to lanthanoids .	because of poor shielding by 5f orbitals due to its superficial position.																				
<div>Potassium Dichromate [K₂Cr₂O₇]</div> <div>Preparation:</div> <div>It is prepared from chromite ore : FeCr₂O₄ / FeO Cr₂O₃</div> <div>Step 1:</div> <div>4FeCr₂O₄ + 8Na₂CO₃ + 7O₂ → 8Na₂CrO₄ + 2Fe₂O₃ + 8CO₂</div> <div>Step 2:</div> <div>2Na₂CrO₄ (Yellow) + H₂SO₄ → Na₂Cr₂O₇(Orange) + Na₂SO₄ + H₂O</div> <div>Step 3:</div> <div>Na₂Cr₂O₇ + 2KCl → K₂Cr₂O₇ + 2NaCl</div> <div>Orange Orange</div> <div>Effect of pH:</div> <div>Cr₂O₇²⁻ (Orange) + 2OH⁻ → 2CrO₄²⁻ (Yellow) + H₂O</div> <div>2CrO₄²⁻ (Yellow) + 2H⁺ → Cr₂O₇²⁻ (Orange) + H₂O</div> <div>Oxidizing Character:</div> <div>Dichromate ion acts as strong oxidizing agent in acidic medium.</div> <div>Cr₂O₇²⁻ + 14H⁺ + 6e⁻ → 2Cr³⁺ + 7H₂O</div> <div>Cr₂O₇²⁻ + 14H⁺ + 6I⁻ → 2Cr³⁺ + 7H₂O + 3I₂</div> <div>Cr₂O₇²⁻ + 14H⁺ + 6Fe²⁺ → 2Cr³⁺ + 7H₂O + 6Fe³⁺</div> <div>Cr₂O₇²⁻ + 14H⁺ + 3Sn²⁺ → 2Cr³⁺ + 7H₂O + 3Sn⁴⁺</div> <div>Cr₂O₇²⁻ + 8H⁺ + 3H₂S → 2Cr³⁺ + 7H₂O + 3S</div>		<div>Potassium Permanganate [KMnO₄]</div> <div>Preparation:</div> <div>from pyrolucite ore [MnO₂]</div> <div>Step 1:</div> <div>2MnO₂ (Black) + 4KOH + O₂ → 2K₂MnO₄ (Green) + 2H₂O</div> <div>Step 2:</div> <div>3MnO₄²⁻ (Green) + 4H⁺ → 2MnO₄⁻ (Purple) + MnO₂ + 2H₂O</div> <div>Oxidizing Character: (Oxidation in acidic medium)</div> <div>MnO₄⁻ + 8H⁺ + 5e⁻ → Mn²⁺ + 4H₂O</div> <div>Eq. mass of KMnO₄ = 158/5 = 31.6</div> <div>MnO₄⁻ + 5Fe²⁺ + 8H⁺ → Mn²⁺ + 5Fe³⁺ + 4H₂O</div> <div>2MnO₄⁻ + 10Cl⁻ + 16H⁺ → 2Mn²⁺ + 8H₂O + 5Cl₂</div> <div>2MnO₄⁻ + 5C₂O₄²⁻ + 16H⁺ → 2Mn²⁺ + 10CO₂ + 8H₂O</div> <div>2MnO₄⁻ + 5SO₃²⁻ + 6H⁺ → 2Mn²⁺ + 5SO₄²⁻ + 3H₂O</div> <div>2MnO₄⁻ + 5NO₂⁻ + 6H⁺ → 2Mn²⁺ + 5NO₃⁻ + 3H₂O</div> <div>2MnO₄⁻ + 5S²⁻ + 16H⁺ → 2Mn²⁺ + 5S + 8H₂O</div> <div>2MnO₄⁻ + 3H₂O + I⁻ → 2MnO₂ + IO₃⁻ + 2OH⁻</div> <div>8MnO₄⁻ + 3S₂O₃²⁻ + H₂O → 8MnO₂ + 6SO₄²⁻ + 2OH⁻</div> <div>2MnO₄⁻ + 3 Mn²⁺ + 2 H₂O → 5MnO₂ + 4H⁺</div>																				
<div>f-Block Elements</div> <div>General configuration (n - 2) f¹⁻¹⁴ (n - 1)d⁰⁻¹ ns²</div> <table><tr><td>57La</td><td>[Xe] 5d¹ 6s²</td><td>89Ac</td><td>[Rn] 6d¹ 7s² -</td></tr><tr><td>58Ce</td><td>[Xe] 4f¹ 5d¹ 6s²</td><td>91Pa</td><td>[Rn] 5f² 6d¹ 7s²</td></tr><tr><td>63Eu</td><td>[Xe] 4f⁷ 5d⁰ 6s²</td><td>92U</td><td>[Rn] 5f³ 6d¹ 7s²</td></tr><tr><td>64Gd</td><td>[Xe] 4f⁷ 5d¹ 6s²</td><td>94Pu</td><td>[Rn] 5f⁶ 6d⁰ 7s²</td></tr><tr><td>70Yb</td><td>[Xe] 4f¹⁴ 5d⁰ 6s²</td><td></td><td></td></tr></table> <div>Lanthanoid Contraction-</div> <div>Regular decrease in atomic or ionic radii of Lanthenoid with increase in atomic number is called Lanthenoid contraction.</div> <div>Cause:</div> <div>It is due to imperfect shielding of one 4f orbital by another 4f orbital due to which ENC regularly increases with increase in atomic number.</div>		57La	[Xe] 5d ¹ 6s ²	89Ac	[Rn] 6d ¹ 7s ² -	58Ce	[Xe] 4f ¹ 5d ¹ 6s ²	91Pa	[Rn] 5f ² 6d ¹ 7s ²	63Eu	[Xe] 4f ⁷ 5d ⁰ 6s ²	92U	[Rn] 5f ³ 6d ¹ 7s ²	64Gd	[Xe] 4f ⁷ 5d ¹ 6s ²	94Pu	[Rn] 5f ⁶ 6d ⁰ 7s ²	70Yb	[Xe] 4f ¹⁴ 5d ⁰ 6s ²			<div>Consequences:</div> <div>1. Resemblance in the properties of second and third transition series from Zr & Hf) atomic size of 2nd and 3rd transition series become same.</div> <div>2. Similarity in the properties of Lanthanoids:- The decrease in atomic radii from Lanthenoid to Lanthenoid is very less hence it is very difficult to separate these elements in pure state.</div> <div>3. Basic strength of hydroxides of Lanthanoids decreases from Lanthenium (La) to Lutesium (Lu).</div> <div>Misch Metal</div> <div>– It is alloy of Lanthanoids(95%) with iron (5%)and Trace of S, C, Al ,Ca</div> <div>Lanthenoid – 95% Metal + Trace of S, C, Al ,Ca + Iron – 5%</div> <div>Uses-</div> <div>making bullet shells and flinter of lighters.</div>
57La	[Xe] 5d ¹ 6s ²	89Ac	[Rn] 6d ¹ 7s ² -																			
58Ce	[Xe] 4f ¹ 5d ¹ 6s ²	91Pa	[Rn] 5f ² 6d ¹ 7s ²																			
63Eu	[Xe] 4f ⁷ 5d ⁰ 6s ²	92U	[Rn] 5f ³ 6d ¹ 7s ²																			
64Gd	[Xe] 4f ⁷ 5d ¹ 6s ²	94Pu	[Rn] 5f ⁶ 6d ⁰ 7s ²																			
70Yb	[Xe] 4f ¹⁴ 5d ⁰ 6s ²																					
Lanthanoids		Actinoids																				
Last electron enters in 4f orbital		Last electron enters in 5f orbital																				
Are natural elements and non radioactive in nature		Are radioactive in nature and after Np they are synthetic elements																				
Shows less number of oxidation states [+2,+3,+4]		Shows greater number of oxidation states [+3,+4,+5,+6,+7]																				
Element to element lanthanoid contraction is less		Element to element actinoid contraction is more																				

LESSON: COORDINATION COMPOUNDS

Simple Salt	Double Salt	Complex Salt
Contain one type of cation and one type of anion. E.g. NaCl.	Contain two types of cations. E.g. Mohr's salt $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$, Potash Alum- $\text{Al}_2(\text{SO}_4)_3 \cdot \text{K}_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$	Contain complex ion. Eg. $\text{K}_4\text{Fe}(\text{CN})_6 \rightarrow 4\text{K}^+ + [\text{Fe}(\text{CN})_6]^{4-}$

Transition metal have great tendency to form coordination compounds because: Small size and high charge, Availability of vacant d-orbitals & Tendency to show variable oxidation states.

Basic Terms

<p>1. Coordination Sphere: Central metal atom and ligands bonded to CMA called coordination sphere → represented in a square bracket.</p> <p>2. Central Metal Atom: Accept electrons for the formation of coordinate bond is called central metal atom. (Lewis acid)</p> <p>3. Ligand: Provide pair of electron for formation of coordinate bond to central metal atom is called ligand. (Lewis Base) F⁻ -Fluorido, Cl⁻ - Chlorido, Br⁻ -Bromido I⁻ - Iodido, H⁻ -Hydrido, OH⁻ - Hydroxido CN⁻ -Cyanido, SCN⁻ - Thiocyanato NCS⁻ - Isothiocyanato, CH₃COO⁻ -Acetato SO₄²⁻ - Sulphato, CO₃²⁻ - Carbonato (COO⁻)₂ or C₂O₄²⁻ - Oxalato (ox), NO₃⁻ - Nitrato NO₂⁻ - Nitrito(N), PO₄³⁻ - Phosphato</p> <p>Neutral ligands- H₂O- Aqua , NH₃ - Ammine R NH₂ -Alkanamine, CO –Carbonyl, H₂NCH₂CH₂NH₂ - ethane-1,2–diamine Ethylenediaminetetraacetate ion (EDTA⁴⁻) Ligand which has two different donor atoms and either of the two ligetes in the complex is called ambidentate ligand. Examples NO₂⁻ and SCN⁻</p>	<p>4.Coordination Number: Number of coordinate bonds formed by ligands with central metal atom in the complex is called coordination number of complex. eg. - [Mg(EDTA)]²⁻ [Fe(CN)₆]⁴⁻ [Co(en)₃]³⁺ ↓ ↓ ↓ C.N. 6 6 6</p> <p>5) Homoleptic and Hetroleptic Complexes: A complex with same type of ligands surrounding central metal atom is called homoleptic complex. E.g.- [Cu(NH₃)₄]²⁺, [Pt(NH₃)₄]²⁺ A complex with different types of ligands surrounding central metal atom is called hetroleptic complex. E.g. [Pt(NH₃)₂Cl₂]</p> <p>6. Coordination Polyhedron: Spatial arrangement of ligands around central metal atom or ion is called coordination polyhedron.</p> <p>Writing Formula of Coordination Complex: 1. Cation is written first followed by anion. 2. In coordination sphere central metal atom is written first followed by ligands. 3. If more than one type of ligands are present then alphabet is followed. <div style="text-align: center;">$\text{Na}_2[\text{Fe}(\text{H}_2\text{O})_4(\text{NO}) \text{Br}]$</div></p>
<p><u>Nomenclature of Coordination Compounds:</u></p> <ol style="list-style-type: none"> Cation is written first followed by anion. While writing name of coordination sphere ligands are named first followed by central metal atom. To indicate number of ligands prefix di, tri, tetra, penta, hexa, hepta etc are used. If ligands itself involve such prefixes in its name then prefix bis, tris, tetrakis, and so on are used to indicate number of ligands. While writing name of central metal atom: - <ol style="list-style-type: none"> If coordination sphere is cation name of metal atoms written as such: Fe – Iron, Au – Gold, Cu – Copper, Cr – Chromium, Ag – Silver. If, coordination sphere is anion suffix ‘ate’ is used to write name of central metal atom. Such as: Fe – Ferrate, Hg – Mercurate, Cu – Cuperate, Ag – Argentate, Au – Aurate, Pd – Peladate, Cr - Chromate After writing name of central metal atom its 	<p>oxidation number is indicated in perantheses ‘()’.</p> <ol style="list-style-type: none"> $\text{Na}_2 [\text{Fe} (\text{H}_2\text{O}) \text{Br}_4 (\text{NO})]$ Sodium tetrabromidonitrosylferrate (II) $[\text{Fe} (\text{H}_2\text{O})_4 \text{Br} (\text{NO})] \text{SO}_4$ Tetraquabromidonitrosyliron (III) sulphate $\text{K}_4 [\text{Fe} (\text{CN})_6]$ Potassium hexacyanoferrate (II) $[\text{Cr} (\text{NH}_3)_3 (\text{H}_2\text{O})_3] \text{Cl}_3$ Triamminetriaquachromium (III) Chloride $[\text{Pt} (\text{NH}_3)_2 \text{Cl} (\text{NO}_2)]$ Diamminechloridonitritoplatinum (II) $[\text{Ni} (\text{CO})_4]$ Tetracarbonyl Nickel (0) $\text{CO} (\text{NH}_3)_5 \text{CO}_3] \text{Cl}$ Pentamminecarbonato cobalt (III) chloride $\text{K}_3 [\text{Cr} (\text{C}_2\text{O}_4)_3]$ Potassium trioxalate chromate (III) $\text{Hg} [\text{Co} (\text{SCN})_4]$

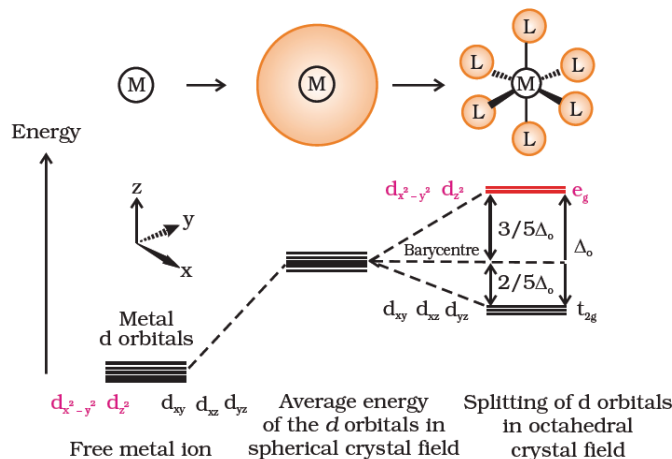
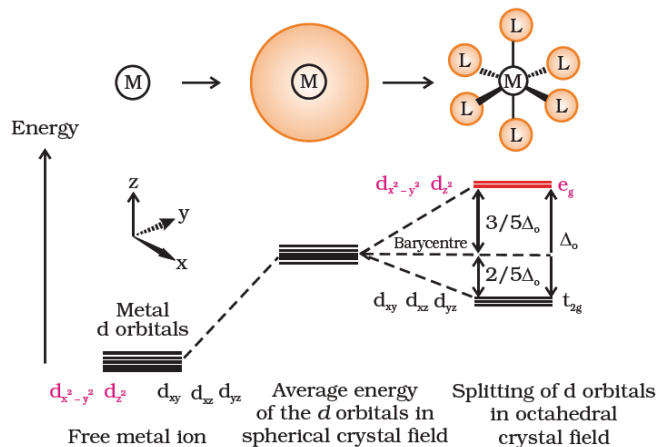
	Mercury tetrathiocyanato cobaltate (III)
<u>Isomerism in Coordination Compounds</u> (a) Structural isomerism (i) Linkage isomerism- Arises in a coordination compound containing ambidentate ligand. M–SCN, M–NCS & (–NO ₂), (–ONO) (ii) Coordination isomerism- Arises from the interchange of ligands between cationic and anionic entities of different metal ions present in a complex. [Co(NH ₃) ₆][Cr(CN) ₆] & [Cr(NH ₃) ₆][Co(CN) ₆] (iii) Ionisation isomerism- Arises when the counter ion in a complex salt is itself a potential ligand and can displace a ligand which can then become the counter ion. [Co(NH ₃) ₅ (SO ₄)]Br & [Co(NH ₃) ₅ Br]SO ₄ . (iv) Solvate isomerism- Arises due to exchange of H ₂ O as ligand and counter anion in the complex. [Cr(H ₂ O) ₆]Cl ₃ & [Cr(H ₂ O) ₅ Cl]Cl ₂ .H ₂ O	(b) Stereoisomerism (i) Geometrical isomerism- Arises in heteroleptic complexes due to different possible geometric arrangements of the ligands. If same ligands are on same side – Cis isomer. If same ligands are on opposite side – trans isomer. Tetrahedral complexes does not exhibit geometrical isomerism due to some relative position of ligands around central metal atom. Square planner complexes with formula MA ₂ B ₂ - two geometrical isomers, MABCD- Three isomers Octahedral complexes- MA ₄ B ₂ , M(aa) ₂ A ₂ – Cis & trans MA ₃ B ₃ - Fac & mer isomers (ii) Optical isomerism- Optical isomers are mirror images that cannot be superimposed on one another. These are called as enantiomers. [PtCl ₂ (en) ₂] ²⁺
<u>Bonding in coordination compounds-</u> (I) <u>Werner's Coordination Theory-</u> Primary valence is ionizable and refers charge present on complex ion. Secondary valence is non-ionizable and refers coordination number of complex. The ions/groups bound by the secondary linkages to the metal have characteristic spatial arrangements corresponding to different coordination numbers.	

2) Valence Bond Theory or VBT

Complex	Oxidation state of CMA	Hybridization	Geometry	Magnetic nature	Number of unpaired electrons	Outer sphere / Inner sphere
[Co(NH ₃) ₆] ³⁺	+3	d ² sp ³	Octahedral	Diamagnetic	0	Inner sphere
[CoF ₆] ³⁻	+3	sp ³ d ²	Octahedral	Paramagnetic	0	Outer sphere
[Co(C ₂ O ₄) ₃] ³⁻	+3	d ² sp ³	Octahedral	Diamagnetic	0	Inner sphere
[Mn(CN) ₆] ²⁻	+2	d ² sp ³	Octahedral	Paramagnetic	1	Inner sphere
[Fe(CN) ₆] ³⁻	+2	d ² sp ³	Octahedral	Paramagnetic	1	Inner sphere
[Fe(H ₂ O) ₆] ³⁺	+2	sp ³ d ²	Octahedral	Paramagnetic	5	Outer sphere
[Ni(NH ₃) ₆] ²⁺	+2	sp ³ d ²	Octahedral	Paramagnetic	2	Outer sphere
[NiCl ₄] ²⁻	+2	sp ³	Tetrahedral	Paramagnetic	2	-----
[Ni(CO) ₄]	0	sp ³	Tetrahedral	Diamagnetic	0	-----
[Ni(CN) ₄] ²⁻	+2	dsp ²	Square planner	Diamagnetic	0	-----

3) Crystal Field Theory [CFT]

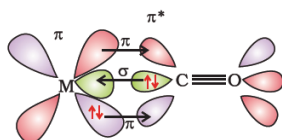
<u>Splitting of d-orbitals in octahedral field:</u>	<u>Splitting of d-orbitals in tetrahedral field:</u>
--	---



Metal Carbonyls: Homoleptic complex of transition metal with carbonyl ligand are called metal carbonyls. E.g. $[\text{Ni}(\text{CO})_4]$, $[\text{Fe}(\text{CO})_5]$, $[\text{Cr}(\text{CO})_6]$, $[\text{Co}_2(\text{CO})_8]$, $[\text{Co}_3(\text{CO})_{12}]$, $[\text{Mn}_2(\text{CO})_{10}]$

The metal-carbon bond in metal carbonyls possess both σ and π character. The M-C σ bond is formed by the donation of lone pair of electrons on the carbonyl carbon into a vacant orbital of the metal. The M-C π bond is formed by the donation of a pair of electrons from a filled d orbital of metal into the vacant antibonding π^* orbital of carbon monoxide. The metal to ligand bonding creates a synergic effect which strengthens the bond between CO and the metal.

$d\pi-p\pi$ Back Bond



Application of Coordination Complexes:

a) Biological System: Chlorophyll – complex of Mg

Haemoglobin – complex of Fe, Vit. B-12 – complex of Co

b) Metallurgy:

Extraction of Au, Ag, by cyanide process.

Refining of Ni by Mond's process

Refining of Zr by Van Arkel process.

c) Quantitative Analysis: Estimation of hardness of water Ca^{2+} and Mg^{2+} are estimated by complexometric titration using EDTA.

d) Qualitative Analysis: Cu^{2+} , Fe^{2+} , Zn^{2+} , Ni^{2+} , NO_3^- , etc ions are confirmed by reactions involving complex formation.

e) Industrial Catalyst: $[(\text{Ph}_3\text{P})_3\text{RhCl}]$, a Wilkinson catalyst, is used for the hydrogenation of alkenes

f) Black & White Photography:

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, $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$.

g) As medicines:

Cisplatin [Cancer Treatment],

EDTA [Used to remove heavy metal poison using chelate therapy.

ORGANIC CHEMISTRY

1. IUPAC NOMENCLATURE : SOME BASIC RULES

1. The four components of IUPAC name are:

Prefix(subst)→ Word root(meth, eth, etc)→ Pri. Suffix (ane/ene/yne)→ Sec Suffix(main group)

Note : if the name of sec. suffix starts with a vowel then pri suffix will be :an / en / yn]

2. locate the longest carbon chain by giving the preference as :

functional group > double bond > triple bond > substituent / side chain

3. follow lowest SUM rule also

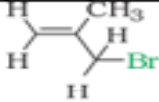
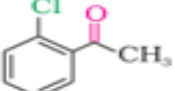
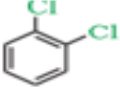
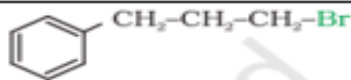
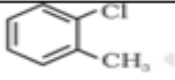
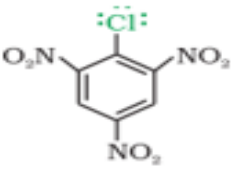
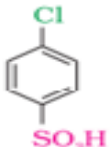
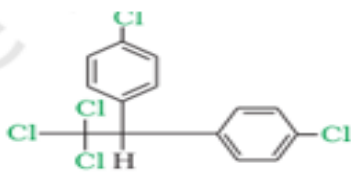
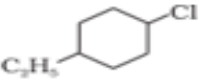
4. In a molecule the main group will be named as suffix. All the other groups will be written alphabetically as prefixes

5. Prefix and suffix names of the functional groups with decreasing Priority

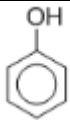
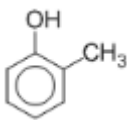
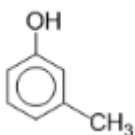
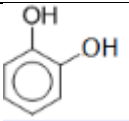

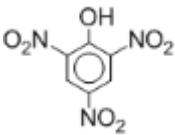
Sl No	Class of Compound	Functional Group	Prefix	Suffix
1	Sulphonic Acid	- SO ₃ H		sulphonic acid
2	Carboxylic Acid	- COOH	carboxy	oic acid
3	Acid Anhydride	- CO.O.CO-		oic anhydride
4	Ester	- COOR	alkoxy carbonyl	oate
5	Acid Halides	- COX	haloformyl	oyl halide
6	Amides	-CONH ₂	carbamoyl	amide
7	Nitriles(Cyanides)	- CN	cyano	Nitrile
8	Isonitrile(Isonitrile)	-NC	isocyano	isonitrile
9	Aldehyde	- CHO	formyl	al
10	Ketone	>C=O	oxo / keto	one
11	Alcohol	- OH	hydroxy	ol
12	Thiol	-SH	mercepto	thiol
13	Amines	- NH ₂	amino	amine
14	Ether	-O-	alkoxy	Oxy alkane

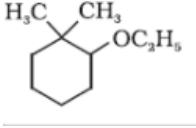
Group	Name(Prefix)		Group	Name(Prefix)
- Br	Bromo		- OCH ₃	Methoxy
- Cl	Chloro		- NO ₂	Nitro
- OCH ₂ CH ₃	Ethoxy		- NO	Nitroso
- F	Fluoro		-C ₆ H ₅	Phenyl
- I	Iodo			

10. HALOALKANES AND HALOARENES

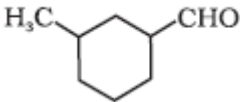
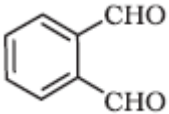
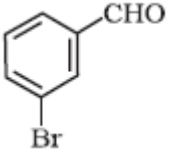
S.No	STRUCTURE	IUPAC NAME
1	$\text{CH}_3\text{CH}_2\text{CH}(\text{Cl})\text{CH}_3$	2-Chlorobutane
2	$(\text{CH}_3)_3\text{CCH}_2\text{Br}$	1-Bromo-2,2-dimethylpropane
3	$(\text{CH}_3)_3\text{CBr}$	2-Bromo-2-methylpropane
4	$\text{CH}_2 = \text{CHCl}$	Chloroethene
5	$\text{CH}_2 = \text{CHCH}_2\text{Br}$	3-Bromopropene
6	$(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{Br}$	1-Bromo-3-methylbutane
7		3-Bromo-2-methylpropene
8		2-Chloroacetophenone
9	$\text{ClCH}_2\text{C}\equiv\text{CCH}_2\text{Br}$	1-Bromo-1-chloro-1,2,2-trifluoroethane
10	$\text{CH}_3\text{C}(\text{p-ClC}_6\text{H}_4)_2\text{CH}(\text{Br})\text{CH}_3$	2-Bromo-3,3 bis(4-chlorophenyl) butane
11	$(\text{CCl}_3)_3\text{CCl}$	2-(trichloromethyl)-1,1,1,2,3,3,3-heptachloropropane
12	$\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{I}$	1-iodo-2,2-dimethyl-1-phenylbutane
13	$\text{CH}_3\text{C}(\text{Cl})(\text{C}_2\text{H}_5)_2\text{CH}_2\text{CH}_3$	3-chloro-5-methylhex-2-ene
14		1,2-Dichlorobenzene
15		3-phenyl-1-bromopropane
16		1-Chloro-2-methylbenzene or 2-Chlorotoluene
17		2,4,6-Trinitrochlorobenzene
18		4-chlorobenzenesulphonic acid
19		p,p'-dichlorodiphenyltrichloroethane
20		1-Chloro-4-ethylcyclohexane

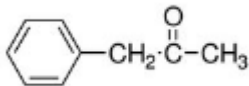
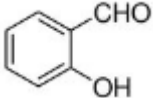
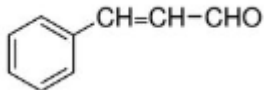
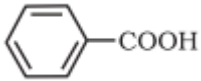
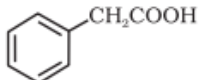
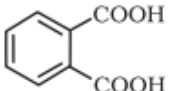
11. ALCOHOL , PHENOLS AND ETHERS

S.No	STRUCTURE	IUPAC NAME
1	$\text{CH}_3\text{-OH}$	Methanol
2	$\text{CH}_3\text{-CH}_2\text{-OH}$	Ethanol
3	$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-OH}$	Propan-1-ol
4	$\begin{array}{c} \text{CH}_3\text{-CH-CH}_2\text{-CH}_3 \\ \\ \text{OH} \end{array}$	Butan-2-ol
5	$\begin{array}{c} \text{CH}_3\text{-CH-CH}_2\text{-OH} \\ \\ \text{CH}_3 \end{array}$	2-Methylpropan-1-ol
6	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{-C-OH} \\ \\ \text{CH}_3 \end{array}$	2-Methylpropan-2-ol
7	$\begin{array}{c} \text{CH}_2\text{-CH-CH}_2 \\ \quad \quad \\ \text{OH} \quad \text{OH} \quad \text{OH} \end{array}$	Propane -1, 2, 3-triol
8		Phenol
9		2-methylphenol
10		3-methylphenol
11		2-hydroxyphenol
12		4-hydroxyphenol
13		2,4,6-trinitrophenol

14	CH_3OCH_3	Methoxymethane
15	$\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$	Ethoxyethane
16	$\text{C}_6\text{H}_5\text{OCH}_3$	Methoxybenzene (Anisole)
17	$\begin{array}{c} \text{CH}_3\text{O}-\text{CH}-\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	2-Methoxypropane
18	$\text{C}_6\text{H}_5-\text{O}-\text{CH}_2-\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_3$	3-Methylbutoxybenzene
19		2-Ethoxy- -1,1-dimethylcyclohexane
20	$\text{CH}_3-\text{O}-\text{CH}_2-\text{CH}_2-\text{OCH}_3$	1,2-Dimethoxyethane

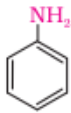
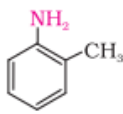
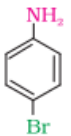
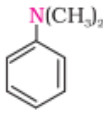
12. ALDEHYDES KETONES CARBOXYLIC ACIDS

S.No	STRUCTURE	IUPAC NAME
1	HCHO	Methanal
2	CH_3CHO	Ethanal
3	$(\text{CH}_3)_2\text{CHCHO}$	2-Methylpropanal
4		3-Methylcyclohexanecarbaldehyde
5	$\text{CH}_3\text{CH}(\text{OCH}_3)\text{CHO}$	2-Methoxypropanal
6	$\text{CH}_2=\text{CHCHO}$	Prop-2-enal
7		Benzene-1,2-dicarbaldehyde
8		3-Bromobenzenecarbaldehyde or 3-Bromobenzaldehyde
9	$\begin{array}{c} \text{O} \\ \\ \text{H}_3\text{C}-\text{C}-\text{CH}_2\text{CH}_3 \end{array}$	2-butanone

10	$\begin{array}{c} \text{CH}_3 \quad \text{O} \\ \quad \\ \text{H}_3\text{C}-\text{C}-\text{CH}_2-\text{C}-\text{CH}_3 \\ \\ \text{Br} \end{array}$	4-bromo-4-methyl-2-pentanone
11	$\begin{array}{c} \text{O} \\ \\ \text{H}_3\text{C}-\text{C}-\text{CH}_3 \end{array}$	Acetone
12		Benzyl methyl ketone
13		Salicylaldehyde
14		Cinnamaldehyde
15	$\begin{array}{c} \text{O} \\ \\ \text{Ph}-\text{C}-\text{Ph} \end{array}$	benzophenone
16	CH_3COOH	Ethanoic acid
17	$\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$	Butanoic acid
18	$(\text{CH}_3)_2\text{CHCOOH}$	2-Methylpropanoic acid
19	$\text{HOOC}-(\text{CH}_2)_2-\text{COOH}$	Butanedioic acid
20	$\text{HOOC}-(\text{CH}_2)_4-\text{COOH}$	Hexanedioic acid
21		Benzenecarboxylic acid (Benzoic acid)
22		2-Phenylethanoic acid
23		Benzene 1,2dicarboxylic acid

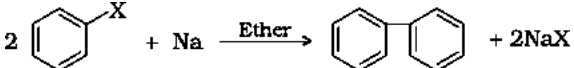

13. AMINES

S.No	STRUCTURE	IUPAC NAME
1	$\text{CH}_3-\text{CH}_2-\text{NH}_2$	Ethanamine
2	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{NH}_2$	Propan-1-amine
3	$\begin{array}{c} \text{CH}_3-\text{N}-\text{CH}_2-\text{CH}_3 \\ \\ \text{H} \end{array}$	N-Methylethanamine
4	$\begin{array}{c} \text{C}_2\text{H}_5-\text{N}-\overset{1}{\text{CH}_2}-\overset{2}{\text{CH}_2}-\overset{3}{\text{CH}_2}-\overset{4}{\text{CH}_3} \\ \\ \text{C}_2\text{H}_5 \end{array}$	N,N-Diethylbutan-1-amine
5	$\begin{array}{c} \text{CH}_3-\text{N}-\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	N,N-Dimethylmethanamine
6	$\text{NH}_2-\overset{1}{\text{CH}_2}-\overset{2}{\text{CH}}=\overset{3}{\text{CH}_2}$	Prop-2-en-1-amine

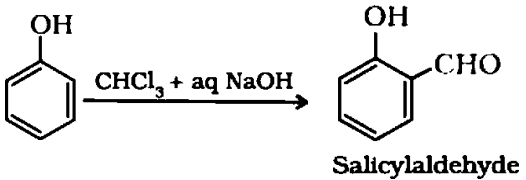
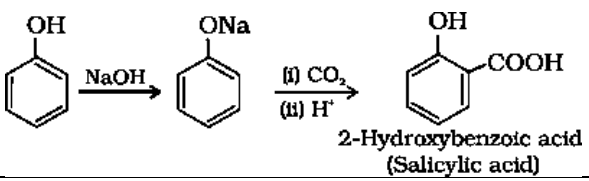
	$\text{NH}_2 - (\text{CH}_2)_6 - \text{NH}_2$	Hexane-1,6-diamine
7		Aniline or Benzenamine
8		2-Methylaniline
9		4-Bromobenzenamine or 4-Bromoaniline
10		N,N-Dimethylbenzenamine

2. NAME REACTION

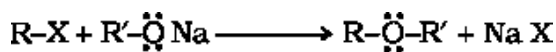
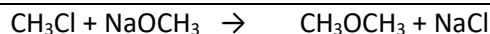
A. HALOALKANES AND HALOARENES

Wurtz reaction : Alkyl halides react with sodium in dry ether to give hydrocarbons(Alkanes) containing double the number of carbon atoms present in the halide.	$2\text{R} - \text{X} + 2\text{Na} \xrightarrow{\text{Dry ether}} \text{R} - \text{R} + 2\text{NaX}$ $2\text{CH}_3 - \text{Br} + 2\text{Na} \xrightarrow{\text{Dry ether}} \text{CH}_3 - \text{CH}_3 + 2\text{NaBr}$
Fittig reaction : Aryl halides(Haloarenes) when treated with sodium in dry ether gives in which two aryl groups are joined together.	$2\text{Ar} - \text{X} + 2\text{Na} \xrightarrow{\text{Dry ether}} \text{Ar} - \text{Ar} + 2\text{NaX}$ 
Wurtz-Fittig reaction : A mixture of an alkyl halide(Haloalkanes) and aryl halide(Haloarenes.) gives an alkylarene when treated with sodium in dry ether.	$\text{Ar} - \text{X} + \text{Na} + \text{R} - \text{X} \xrightarrow{\text{Dry ether}} \text{Ar} - \text{R} + 2\text{NaX}$ 
Finkelstein reaction : Alkyl chlorides/ bromides on reaction with NaI in dry acetone to give Alkyl iodides.	$\text{R} - \text{Cl} + \text{NaI} \xrightarrow{\text{acetone}} \text{R} - \text{I} + \text{NaCl}$ $\text{R} - \text{Br} + \text{NaI} \xrightarrow{\text{acetone}} \text{R} - \text{I} + \text{NaBr}$
Swarts reaction Heating of alkyl chloride/bromide in the presence of a metallic fluoride such as AgF, Hg2F2, CoF2 or SbF3 to give alkyl fluorides	$\text{R} - \text{X} \xrightarrow{\text{AgF, Hg}_2\text{F}_2, \text{CoF}_2 \text{ or } \text{SbF}_3} \text{R} - \text{F}$ $\text{CH}_3 - \text{Br} + \text{AgF} \longrightarrow \text{CH}_3 - \text{F} + \text{AgBr}$

12. ALCOHOLS, PHENOLS AND ETHERS

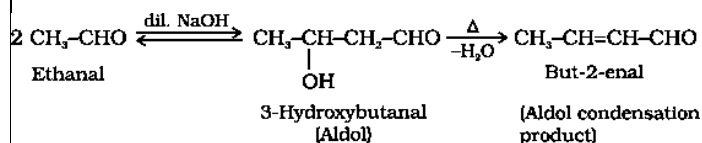
Hydroboration –oxidation reaction : The alcohol obtained corresponds to anti- Markownikov 's addition of water on alkenes.	$\text{CH}_3 - \text{CH} = \text{CH}_2 \xrightarrow{(i) \text{B}_2\text{H}_6 (ii) \text{H}_2\text{O}_2 / \text{OH}^-} \text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{OH}$
Reimer-Tiemann reaction-	 <p>Salicylaldehyde</p>
Kolbe's reaction	 <p>2-Hydroxybenzoic acid (Salicylic acid)</p>

Williamson's synthesis :In this method an alkyl halide (Better results are obtained if the alkyl halide is primary) reacts with a sodium alkoxide to form symmetrical or unsymmetrical ethers.

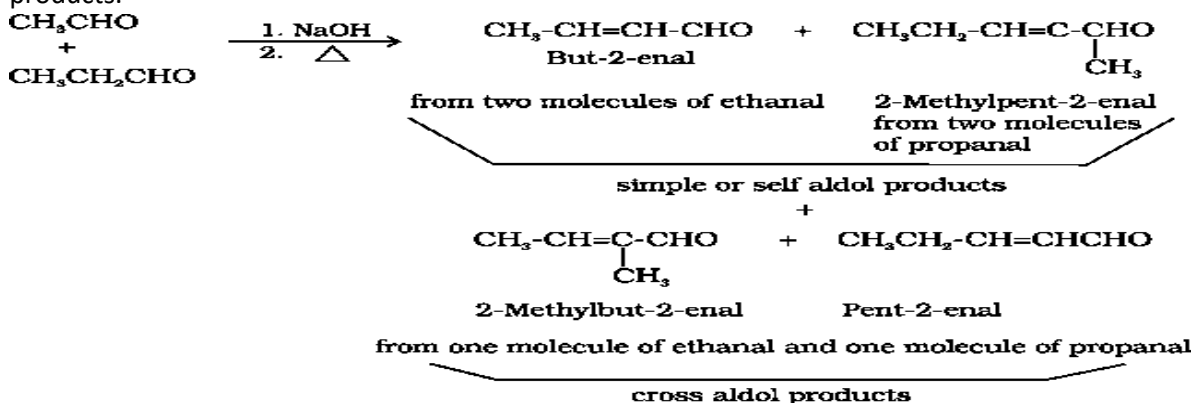


12. ALDEHYDES, KETONES AND CARBOXYLIC ACID

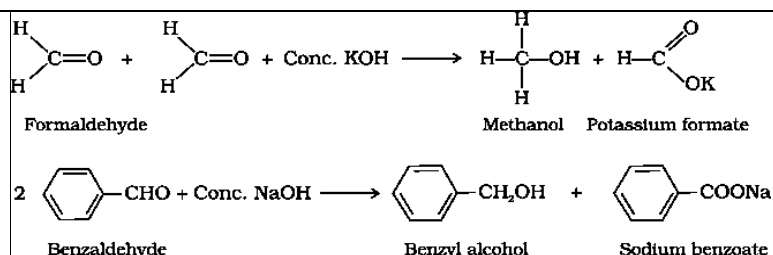
Aldol Condensation : Aldehydes and ketones **having at least one α - hydrogen** undergo a condensation reaction in the presence of **dilute alkali** (NaOH ,KOH etc.) as catalyst to form β -hydroxyaldehyde (aldol) or β - hydroxyketone (ketol) respectively



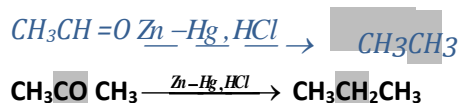
Cross Aldol Condensation: When aldol condensation is carried out between two different aldehydes and / or ketones, it is called **cross aldol condensation**. If both of them contain α -hydrogen atoms, it gives a mixture of four products.



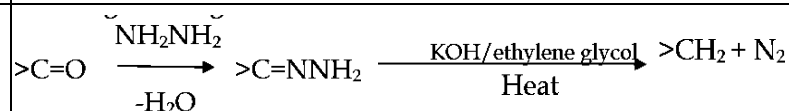
Cannizzaro Reaction: Aldehydes, which do not have an α -hydrogen atom, undergo self oxidation and reduction reaction on treatment with concentrated alkali. In this reaction one molecule of the aldehyde is reduced to alcohol and another is oxidized to carboxylic acid salt.



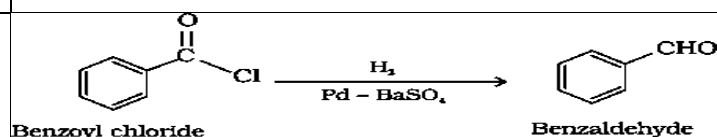
Clemmensen Reaction: The carbonyl group of aldehydes and Ketones are reduced to CH_2 group on treatment with zinc amalgam (Zn/Hg) and concentrated hydrochloric acid. (Conc. HCl)



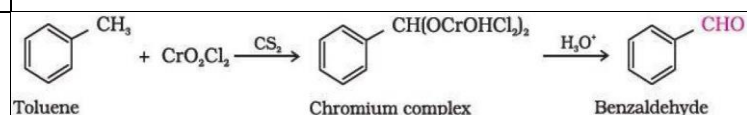
Wolf Kishner Reaction



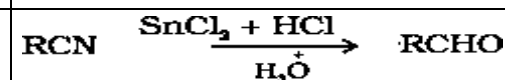
Rosenmund Reaction: Acyl chloride (acid chloride) is hydrogenated over catalyst, palladium on barium sulphate.

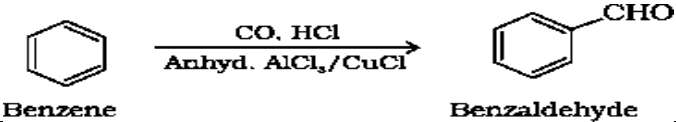


Etard Reaction-

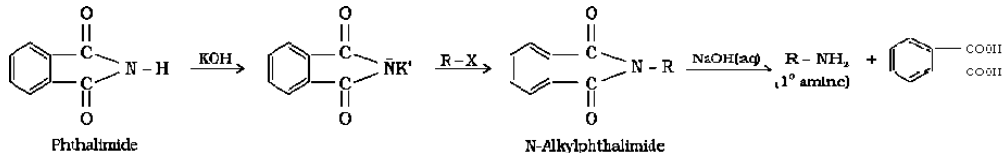
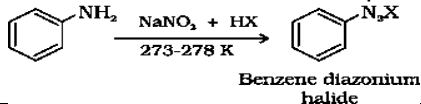
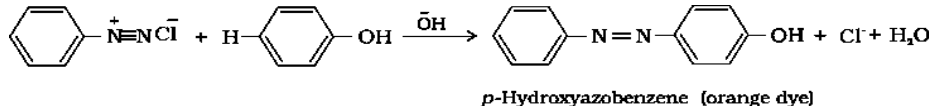
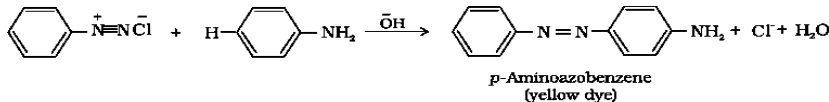


Stephen Reaction:



Gatterman-Koch reaction:	 Benzene Benzaldehyde
Ozonolysis of alkenes involves the addition of ozone molecule to alkene to form ozonide, and then cleavage of the ozonide by Zn-H ₂ O to Aldehyde and/or Ketones.	$\text{CH}_3\text{CH}=\text{CH}_2 \xrightarrow[2. \text{Zn} + \text{H}_2\text{O}]{1. \text{O}_3} \text{CH}_3\text{CHO} + \text{HCHO}$ Propene Ethanal Methanal
Decarboxylation : Sodium salts of acids when heated with soda lime, alkanes are formed.	$\text{CH}_3\text{COONa} + \text{NaOH (CaO)} \rightarrow \text{CH}_4 + \text{Na}_2\text{CO}_3$ Sodium acetate Sodium lime Methane
Hell Volhard Zelinsky: (HVZ) Carboxylic acids having an α-hydrogen are halogenated at the α-position on treatment with chlorine or bromine in the presence of small amount of red phosphorus to give α-halocarboxylic acids	$\text{RCH}_2\text{COOH} \xrightarrow[\text{ii H}_2\text{O}]{\text{i X}_2/\text{Red phosphorus}} \text{R}-\underset{\substack{ \\ \text{X}}}{\text{CH}}-\text{COOH}$ X = Cl, Br α-halocarboxylic acids

13. AMINES

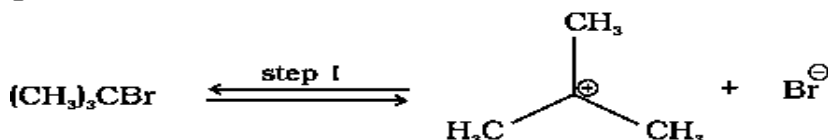
Hoffmann bromamide degradation reaction: primary amides are treated with bromine in the presence of an alkali, a primary amine containing one carbon less than the amide is formed.	$\text{RCONH}_2 + 4\text{NaOH} + \text{Br}_2 \rightarrow \text{RNH}_2 + 2\text{NaBr} + \text{Na}_2\text{CO}_3 + 2\text{H}_2\text{O}$ $\text{CH}_3-\text{CO}-\text{NH}_2 + \text{Br}_2 + 4\text{KOH} \rightarrow \text{CH}_3\text{NH}_2 + \text{K}_2\text{CO}_3 + 2\text{KBr} + 2\text{H}_2\text{O}$
Gabriel phthalimide synthesis: Phthalimide on treatment with KOH which on heating with alkyl halide followed by alkaline hydrolysis produces the corresponding primary amine.	 Phthalimide N-Alkylphthalimide
Carbylamine reaction(Isocyanide test): Aliphatic and aromatic primary amines on heating with chloroform and ethanolic potassium hydroxide form isocyanides or carbylamines which are foul smelling substances.	$\text{R-NH}_2 + \text{CHCl}_3 + 3\text{KOH} \xrightarrow{\text{heat}} \text{R-NC} + 3\text{KCl} + 3\text{H}_2\text{O}$
Diazotization reaction-	 Benzene diazonium halide
Sandmeyer's reaction: The Cl-, Br- and CN- nucleophiles can easily be introduced in the benzene ring in the presence of Cu(I) ion [cuprous chloride or cuprous bromide or cuprous cyanide]	$\text{ArN}_2^+\text{X}^- \begin{cases} \xrightarrow{\text{CuCl/HCl}} \text{ArCl} + \text{N}_2 \\ \xrightarrow{\text{CuBr/HBr}} \text{ArBr} + \text{N}_2 \\ \xrightarrow{\text{CuCN/KCN}} \text{ArCN} + \text{N}_2 \end{cases}$
Gatterman reaction: 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	$\text{ArN}_2^+\text{X}^- \begin{cases} \xrightarrow{\text{Cu/HCl}} \text{ArCl} + \text{N}_2 + \text{CuX} \\ \xrightarrow{\text{Cu/HBr}} \text{ArBr} + \text{N}_2 + \text{CuX} \end{cases}$
Coupling reaction: Benzene diazonium chloride reacts with phenol in which the phenol molecule at its para position is coupled with the diazonium salt to form <i>p</i> -hydroxyazobenzene.. Similarly the reaction of diazonium salt with aniline yields <i>p</i> -aminoazobenzene	
 <i>p</i> -Hydroxyazobenzene (orange dye)	
 <i>p</i> -Aminoazobenzene (yellow dye)	

MECHANISM:

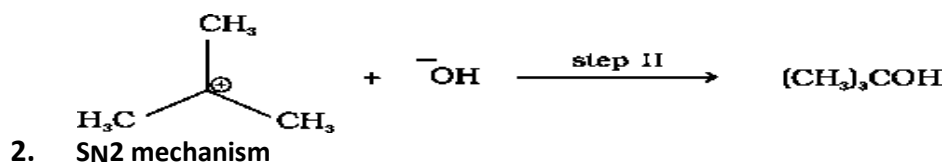
UNIT: 10 HALOALKANES AND HALOARENES.

1. SN1 mechanism

- It is **Two step reactions**.
- Step I:** In the first step slow dissociation of alkyl halide takes place by reversible reaction forming a carbocation.

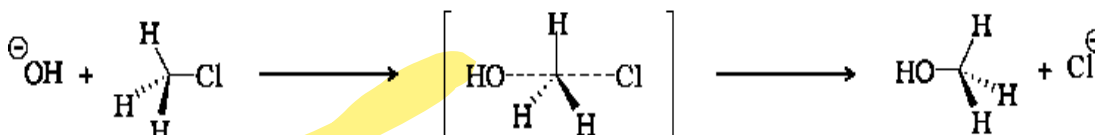


- Step II:** The carbocation at once combines with the nucleophile to form final product (racemic mixture)



2. SN2 mechanism

- It is **One step reaction**.



Comparing the SN1 and the SN2 reactions

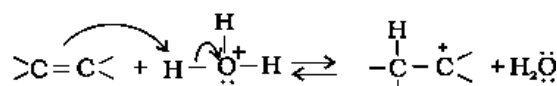
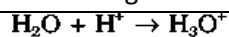
	SN1	SN2
Order of reaction	= 1	= 2
Rate Law	Unimolecular (substrate only) $R = k[\text{RX}]^1 [\text{Nu}]^0$	Bimolecular (substrate and nucleophile) $R = k[\text{RX}]^1 [\text{Nu}]^1$
"Big Barrier"	Carbocation stability	Steric hindrance
Alkyl halide (Reactivity)	$3^\circ > 2^\circ \gg 1^\circ$	$1^\circ > 2^\circ \gg 3^\circ$
Nucleophile	Weak (generally neutral)	Strong (generally bearing a negative charge)
Solvent	Polar protic (e.g. alcohols)	Polar aprotic (e.g. DMSO, acetone)
Stereochemistry	Mix of retention and inversion	Inversion
Optical activity	Racemic mixture = optically inactive	optically active either d or l
Complete in steps	= 2	= 1
Intermediate	Carbocation	Transition state

UNIT: 11 ALCOHOLS, PHENOLS & ETHERS

3. Mechanism for the Hydration of alkenes to alcohol

Mechanism- The mechanism of the reaction involves the following three steps:

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

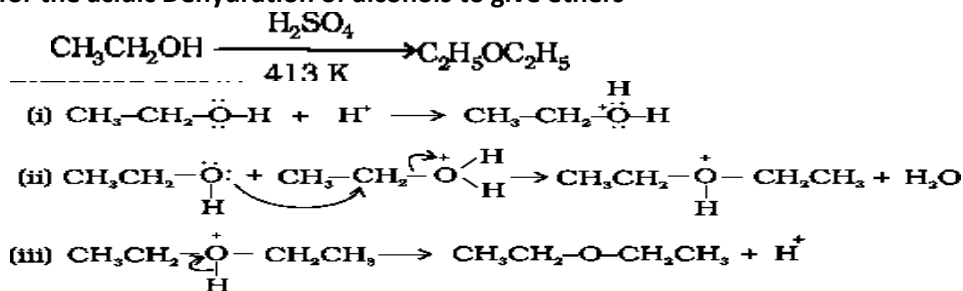


Step 2: Nucleophilic attack of water on carbocation	$\begin{array}{c} \text{H} \\ \\ -\text{C}-\text{C}^+ \\ \end{array} + \text{H}_2\ddot{\text{O}} \rightleftharpoons \begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ -\text{C}-\text{C}-\text{O}^+-\text{H} \end{array}$
Step 3: Deprotonation to form an alcohol	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ -\text{C}-\text{C}-\text{O}^+-\text{H} \end{array} + \text{H}_2\ddot{\text{O}} \rightarrow \begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ -\text{C}-\text{C}-\ddot{\text{O}}\text{H} \end{array} + \text{H}_3\text{O}^+$

4. Mechanism for the acidic Dehydration of alcohols to give alkenes

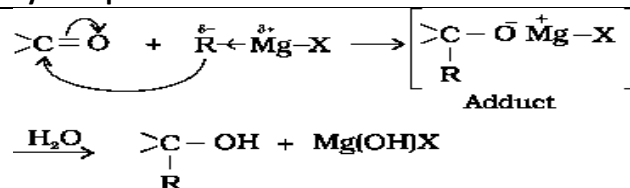
Step 1: Formation of protonated alcohol.	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{H}-\text{C}-\text{C}-\ddot{\text{O}}-\text{H} \\ \quad \\ \text{H} \quad \text{H} \\ \text{Ethanol} \end{array} + \text{H}^+ \xrightleftharpoons{\text{Fast}} \begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \\ \text{H}-\text{C}-\text{C}-\text{O}^+-\text{H} \\ \quad \\ \text{H} \quad \text{H} \\ \text{Protonated alcohol} \\ \text{(Ethyl oxonium ion)} \end{array}$
Step 2: Formation of carbocation: It is the slowest step and hence, the rate determining step of the reaction.	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \\ \text{H}-\text{C}-\text{C}-\text{O}^+-\text{H} \\ \quad \\ \text{H} \quad \text{H} \end{array} \xrightleftharpoons{\text{Slow}} \begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{H}-\text{C}-\text{C}^+ \\ \quad \\ \text{H} \quad \text{H} \end{array} + \text{H}_2\text{O}$
Step 3: Formation of ethene by elimination of a proton	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{H}-\text{C}-\text{C}^+ \\ \quad \\ \text{H} \quad \text{H} \end{array} \rightleftharpoons \begin{array}{c} \text{H} \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \text{H} \\ \text{Ethene} \end{array} + \text{H}^+$
Mechanism for the reaction of HI on Ethoxymethane	Mechanism for the reaction of HI on t-butyl methyl ether-
$\text{CH}_3-\ddot{\text{O}}-\text{CH}_2\text{CH}_3 + \text{H}-\text{I} \rightleftharpoons \text{CH}_3-\ddot{\text{O}}^+-\text{CH}_2\text{CH}_3 + \text{I}^-$ $\text{I}^- + \text{CH}_3-\ddot{\text{O}}^+-\text{CH}_2\text{CH}_3 \rightarrow \left[\text{I}-\text{CH}_3-\ddot{\text{O}}^+-\text{CH}_2\text{CH}_3 \right]^- \rightarrow \text{CH}_3\text{I} + \text{CH}_3\text{CH}_2\text{OH}$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{O}-\text{CH}_3 \\ \\ \text{H} \\ \text{CH}_3 \end{array} \xrightarrow{\text{slow}} \begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}^+ \\ \\ \text{CH}_3 \end{array} + \text{CH}_3\text{OH}$ $\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}^+ \\ \\ \text{CH}_3 \end{array} + \text{I}^- \xrightarrow{\text{fast}} \begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{I} \\ \\ \text{CH}_3 \end{array}$

1. Mechanism for the acidic Dehydration of alcohols to give ethers



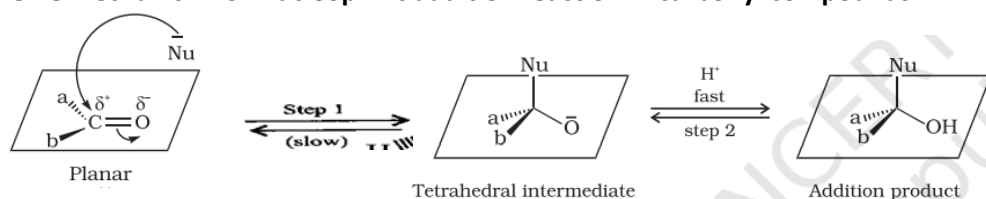
2. Mechanism for the addition Grignard reagent on carbonyl compounds.

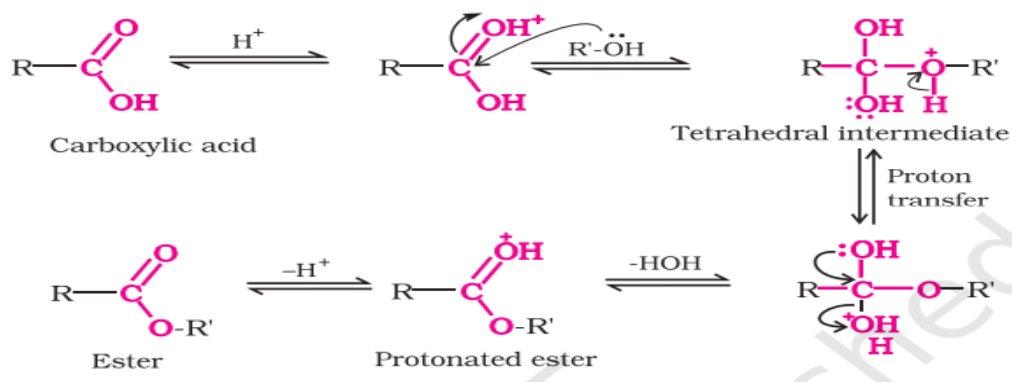
The first step of the reaction is the nucleophilic addition of Grignard reagent to the carbonyl group to form an adduct. Hydrolysis of the adduct yields an alcohol.



UNIT: 12 ALDEHYDES, KETONES & CARBOXYLIC ACIDS

3. Give mechanism for Nucleophilic addition reaction in carbonyl compounds.

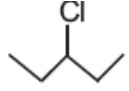

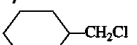
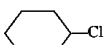
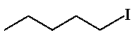
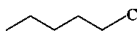
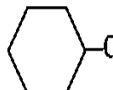


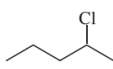
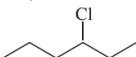
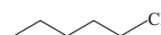
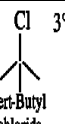
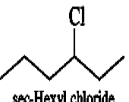




REASONING TYPE OF QUESTIONS

10. HALOALKANES AND HALOARENES

Give **Reasons** for the following :

	QUESTION-REASONING	ANSWER- REASON
1	Benzyl chloride is highly reactive towards the $SN1$ reaction.	Due to the stability of benzyl carbocation/resonance/Diagram
2	2-bromobutane is optically active but 1-bromobutane is optically inactive	Because 2-Bromobutane has a chiral centre
3	Electrophilic substitution reactions in haloarenes occur slowly.	Due to $-I$ effect of halogen.
4	Which would undergo $SN1$ reaction faster in the following pair and why? CH_3-CH_2-Br and $CH_3-\underset{\substack{ \\ CH_3 \\ \\ Br}}{C}-CH_3$	t-Butyl bromide because 3° carbocation intermediate derived from $(CH_3)_3CBr$ is more stable than 1° carbocation from CH_3CH_2Br .
5	why haloarenes are much less reactive than haloalkanes towards nucleophilic substitution reactions	In haloarenes $C-X$ bond acquires a partial double bond character due to resonance
6	Which compound in each of the following pairs will react faster in $SN2$ reaction? Why? (i) CH_3Br or CH_3I (ii) $(CH_3)_3C-Cl$ or CH_3-Cl	(i) CH_3-I reacts faster than CH_3-Br as iodine is a better leaving group because of its larger size. (ii) CH_3-Cl (1° halide) reacts faster than $(CH_3)_3CCl$ (3° halide) since in case tertiary butyl chloride three bulky methyl group hinder the approaching nucleophile
7	Which one of the following reacts faster in an $SN1$ reaction and why?  Or 	Compound (I) reacts faster in $SN1$ reaction as it is a 2° alkyl halide
8	Which ones in the following pairs of substances undergoes $SN2$ substitution reaction faster and why? (i)  or  (ii)  or 	(i)  : It is primary halide therefore undergoes $SN2$ reaction faster. (ii)  : As iodine is a better leaving group because of its large size, it will be released at a faster rate in the presence of incoming nucleophile
9	Which one in the following pairs undergoes $SN1$ substitution reaction faster and why? (i)  or  (ii)  or 	(i)  3° halide reacts faster than 2° halide because of the greater stability of tertiary carbocation. (ii)  2° halide reacts faster than 1° halide because of the greater stability of secondary carbocation than primary.
10	A solution of KOH hydrolyses $CH_3CH(Cl)CH_2CH_3$ and $CH_3CH_2CH_2CH_2Cl$. Which one of these is	$CH_3CH_2CH(Cl)CH_3$ more easily hydrolysed as it forms secondary carbocation which is more

	more easily hydrolysed and why?	stable than primary carbocation
11	Which compound in the following couples will react faster in SN2 displacement and why? (a) 1-Bromopentane or 2-bromopentane (b) 1-Bromo-2-methylbutane or 2-bromo-2-methylbutane	(a) 1-Bromopentane, as it is a primary alkyl halide. (b) 1-Bromo-2-methyl butane, as it is a primary alkylhalide
12	State one use each of DDT and iodoform	DDT: It is used as insecticide to control flies, mosquitoes, etc. Iodoform: Iodoform is used as an antiseptic.
13	Haloalkanes easily dissolve in organic solvents, why?	Both have non polar hydrocarbon chain which have strong Vander Waal forces.
14	What is known as a racemic mixture? Give an example.	An equimolar mixture of d- and l- isomers called racemic mixture. For example, (50:50 d+l) butan-2-ol. A racemic mixture is optically inactive due to external compensation
15	Of the two bromo derivatives, $C_6H_5CH(CH_3)Br$ and $C_6H_5CH(C_6H_5)Br$, which one is more reactive in SN1 substitution reaction and why?	$C_6H_5CH(C_6H_5)Br$ the intermediate obtained from $C_6H_5CH(C_6H_5)Br$ is more stable than obtained from $C_6H_5CH(CH_3)Br$ because it is stabilised by two phenyl groups due to resonance.
16	Rearrange the compounds of each of the following sets in order of reactivity towards SN2 displacement: (i) 2-Bromo-2-methylbutane, 1-Bromopentane, 2-Bromopentane (ii) 1-Bromo-3-methylbutane, 2-Bromo-2-methylbutane, 3-Bromo-2-methylbutane (iii) 1-Bromobutane, 1-Bromo-2, 2-dimethylpropane, 1-Bromo-2-methylbutane	(i) 1-Bromopentane > 2-Bromopentane > 2-Bromo-2methyl butane. (ii) 1-Bromo-2-methyl butane > 3-Bromo-2-methyl butane > 2-Bromo-2-methyl butane (iii) 1-Bromobutane > 1-Bromo-2-methylbutane > 1-Bromo-2,2-dimethyl butane
17	Although chlorine is an electron withdrawing group, yet it is ortho-, para-directing in electrophilic aromatic substitution reactions. Explain why it is so?	Through resonance effect, chlorine tends to stabilize the carbocation and the effect is more pronounced at ortho and para-positions
18	Alkyl halides, though polar, are immiscible with water.	due to inability of alkyl halides to form intermolecular hydrogen bonds with water molecules.
19	Grignard's reagents should be prepared under anhydrous conditions, why?	This is because Grignard reagent forms alkanes by reacting with moisture. $RMgX + H_2O \rightarrow RH + Mg(OH)X$
20	the dipole moment of chlorobenzene is lower than that of cyclohexyl chloride	Since chlorobenzene has lower magnitude of negative charge on Cl atom and shorter C—Cl bond than cyclohexyl chloride due to resonance therefore chlorobenzene has lower dipole moment than cyclohexyl chloride
21	The C—Cl bond length in chlorobenzene is shorter than that in CH_3-Cl	Due to resonance C—Cl bond acquires a partial double bond character which is difficult to cleave.
22	Chloroform is stored in closed dark brown bottles	Because chloroform is slowly oxidised by air in the presence of light to an extremely poisonous gas phosgene. $COCl_2$
23	Chlorobenzene is extremely less reactive towards a nucleophilic substitution reaction	Due to repulsion between nucleophile and electron-rich arenes and C-Cl bond has double bond character.
24	Alkyl halides on treatment with aq KOH forms alcohols but with alc KOH alkenes are produced, Why?	An Aq KOH provides OH^- where as alc KOH provides RO^- (alkoxide) which is a stronger base than OH^- , so it abstracts H^+ from $\beta - C$ of alkyl halide

11. ALCOHOL, PHENOL AND ETHER

Give **Reasons** for the following :

	QUESTION-REASONING	ANSWER- REASON
1	Give Reasons for the following: p-nitrophenol is more acidic than p-methylphenol	Due to -I / -R effect of -NO ₂ group & +I / +R effect of -CH ₃ group or 4-nitrophenoxide ion is more stable than 4-methylphenoxide ion
2	Bond length of C – O bond in phenol is shorter than that in methanol	Due to Resonance effect of – OH group in phenol
3	Arrange in increasing order of boiling point C ₂ H ₅ OH, CH ₃ CH ₂ NH ₂ , CH ₃ NHCH ₃	CH ₃ -NH-CH ₃ < CH ₃ -CH ₂ -NH ₂ < C ₂ H ₅ -OH.
4	(CH ₃) ₃ C – Br on reaction with sodium methoxide (NaOCH ₃) gives alkene as the main product and not an ether	(CH ₃) ₃ C-Br being a 3° halide prefers to undergo β – elimination on reacting with strong base like NaOCH ₃ .
5	p-nitrophenol is more acidic than o-nitrophenol	Due to intramolecular H-bonding in o-nitrophenol it is weak acidic
6	Bond angle C – O – C in ethers is slightly higher than the tetrahedral angle (109°28').	The mutual repulsion between bulky alkyl groups is stronger than the l.p-l.p electronic repulsions
7	o-nitrophenol is more acidic than o-methoxyphenol	Because -NO ₂ is an electron withdrawing group
8	Butan-1-ol has a higher boiling point than diethyl ether	Due to H-Bonding
9	Phenol is more acidic than ethanol.	due to resonance in phenol, oxygen acquires positive charge and releases H ⁺ ion easily whereas there is no resonance in CH ₃ CH ₂ OH OR (after releasing H ⁺ , phenoxide ion get stabilised by resonance)
10	Boiling point of ethanol is higher in comparison to methoxymethane.	Because of hydrogen bonding in ethanol
11	(CH ₃) ₃ C O CH ₃ on reaction with HI gives CH ₃ OH and (CH ₃) ₃ C I as the main products and not (CH ₃) ₃ COH and CH ₃ I	Because it follows S N1 path way which results in the formation of stable (CH ₃) ₃ C ⁺ .
12	The C – O – H bond angle in alcohols is slightly less than the tetrahedral angle (109°28').	Due to lone pair- lone pair repulsion on oxygen
13	o-and p-nitrophenols are more acidic than phenol	Due to -I effect or -R effect of -NO ₂ group
14	Identify chiral in CH ₃ CH(OH)CH ₂ CH ₃ and CH ₃ CH(OH)CH ₃	<div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;"> $\begin{array}{c} \text{H} \\ \\ \text{CH}_3 - \text{C}^* - \text{CH}_2\text{CH}_3 \\ \\ \text{OH} \\ \text{(Chiral)} \end{array}$ </div> <div style="text-align: center;"> $\begin{array}{c} \text{H} \\ \\ \text{CH}_3 - \text{C} - \text{CH}_3 \\ \\ \text{OH} \\ \text{(Non-chiral)} \end{array}$ </div> </div>
15	Alcohols are more soluble in water than the hydrocarbons of comparable molecular masses	due to their ability to form hydrogen bonds with water molecules
16	Of the two alcohols; (a) CH ₂ =CH—CH ₂ OH and (b) CH ₂ =CH—CH ₂ —CH ₂ OH, which one will react more easily with conc. HCl in the presence of ZnCl ₂ ?	CH ₂ = CH – CH ₂ OH
17	O-nitrophenol is steam volatile whereas p-nitrophenol is not	p-nitro phenol has intermolecular H-bond while o-nitro phenol has intramolecular H-bond.

18	In Phenol, the –OH group activates the benzene ring towards electrophilic substitution and directs the substituents to Ortho and para positions in benzene ring	Because the OH group attached to the benzene ring activates it towards electrophilic substitution. Also, it directs the incoming group to <i>ortho</i> and <i>para</i> positions in the ring as these positions become electron rich due to the resonance effect caused by –OH group. (also draw the resonating structures of phenol)
19	In alcohols the boiling point decreases with increase in branching.	because of decrease in vander Waals forces with decrease in surface area
20	Although phenoxide ion has more number of resonating structures than carboxylate ion, carboxylic acid is a stronger acid than phenol.	Carbonyl group of carboxylate ion is stronger electron withdrawing group than phenyl group of phenoxide ion

12. ALDEHYDES KETONES AND CARBOXYLIC ACIDS

Give **Reasons** for the following :

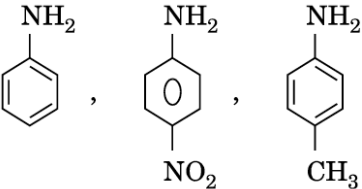
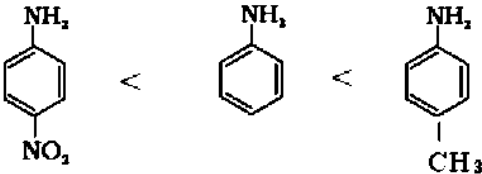
	QUESTION-REASONING	ANSWER- REASON
1	Arrange the following compounds in increasing order of their property as indicated -CH ₃ COCH ₃ , C ₆ H ₅ COC ₆ H ₅ , CH ₃ CHO (reactivity towards nucleophilic addition reaction)	C ₆ H ₅ CO C ₆ H ₅ < CH ₃ COCH ₃ < CH ₃ CHO
2	Cl-CH-COOH, Cl-CH ₂ -COOH, CCl ₃ -COOH (acidic character) Cl	Cl-CH ₂ -COOH < Cl ₂ CH-COOH < CCl ₃ -COOH
3	(i) CH ₃ CHO, C ₆ H ₅ CHO, HCHO (reactivity towards nucleophilic addition reaction)	C ₆ H ₅ CHO < CH ₃ CHO < HCHO
4	2,4-dinitrobenzoic acid, 4-methoxybenzoic acid, 4-nitrobenzoic acid (acidic character)	4-Methoxybenzoic acid < 4-Nitrobenzoic acid < 2,4-Dinitrobenzoic acid
5	(ii) ClCH ₂ COOH, FCH ₂ COOH, CH ₃ COOH (acidic character)	CH ₃ COOH < Cl-CH ₂ -COOH < F-CH ₂ -COOH
6	Arrange the following compounds in an increasing order of their acid strengths: (CH ₃) ₂ CHCOOH, CH ₃ CH ₂ CH(Br)COOH, CH ₃ CH(Br)CH ₂ COOH	(CH ₃) ₂ CHCOOH < CH ₃ -CH(Br)-CH ₂ -COOH < CH ₃ -CH ₂ -CH(Br)-COOH
7	Aldehydes are more reactive than ketones towards nucleophilic addition	due to steric hindrance of alkyl group due to +I effect of alkyl group +ve charge of carbonyl carbon decreases.
8	The boiling points of aldehydes and ketones are lower than of the corresponding acids	due to intermolecular hydrogen bonding in carboxylic acids
9	The aldehydes and ketones undergo nucleophilic addition reactions	Due to greater electronegativity of oxygen than carbon the C atom of the >C=O bond acquires a partial positive charge in aldehydes and ketones and hence readily undergo nucleophilic addition reactions
10	Monochloroethanoic acid has a higher <i>pKa</i> value than dichloroethanoic acid.	Because of two -I group in dichloroethanoic acid, it is a stronger acid than monochloroethanoic acid
11	Ethanoic acid is a weaker acid than benzoic acid	because methyl group due to its positive inductive effect destabilize the acetate anion by intensifying the negative charge.
12	Why are lower members of aldehydes easily miscible with water?	Lower member of aldehydes are able to form intermolecular hydrogen bonds with water molecules. Hence, they are easily miscible with water
13	Arrange the following compounds in an increasing order of their indicated property: (i) Benzoic acid, 4-Nitrobenzoic acid, 3,4-Dinitrobenzoic acid, 4-Methoxybenzoic acid (acid strength)	(i) Acid strength: 4-Methoxy benzoic acid < Benzoic acid < 4-Nitrobenzoic acid < 3, 4-Dinitrobenzoic acid.

14	(ii) $\text{CH}_3\text{CH}_2\text{CH}(\text{Br})\text{COOH}$, $\text{CH}_3\text{CH}(\text{Br})\text{CH}_2\text{COOH}$, $(\text{CH}_3)_2\text{CHCOOH}$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$ (acid strength)	(ii) Acid strength: $(\text{CH}_3)_2\text{CHCOOH} < \text{CH}_3\text{CH}_2\text{CH}_2\text{COOH} < \text{CH}_3\text{CH}(\text{Br})\text{CH}_2\text{COOH} < \text{CH}_3\text{CH}_2\text{CH}(\text{Br})\text{COOH}$
15	What is Tollen's reagent? Write one usefulness of this reagent	A solution of AgNO_3 dissolved in NH_4OH is known as Tollen's reagent. This is used to detect the presence of $-\text{CHO}$ group in an organic compound. For example: $\text{RCHO} + 2\text{Ag}(\text{NH}_3)_2\text{OH} \rightarrow \text{RCOONH}_4 + 2\text{Ag}^+ + \text{H}_2\text{O} + 3\text{NH}_3$.
16	Arrange the following compounds in increasing order of their reactivity in nucleophilic addition reactions: ethanal, propanal, propanone, butanone	Butanone < Propanone < Propanal < Ethanal Reactivity in nucleophilic addition decreases with increasing +I effect and steric hindrance. Aldehydes are more reactive than ketones; among aldehydes and ketones, smaller alkyl groups are more reactive
17	Cyclohexanone forms cyanohydrin in good yield but 2, 4, 6-trimethylcyclohexanone does not.	Due to presence of three methyl groups, the nucleophilic attack by CN^- ion does not occur due to steric hindrance in 2, 4, 6-trimethylcyclohexanone. As there is no such steric hindrance in cyclohexanone so nucleophilic attack by the CN^- ion occurs readily and hence cyclohexanone cyanohydrin is obtained in good yield
18	Acetaldehyde, Acetone, Methyl tert-butyl ketone (reactivity towards HCN)	Methyl tert-butyl ketone < Acetone < Acetaldehyde
19	Benzoic acid, 3,4-Dinitrobenzoic acid, 4-Methoxybenzoic acid (acid strength)	4-Methoxy benzoic acid < Benzoic acid < 3,4-Dinitrobenzoic acid
20	$\text{CH}_3\text{CH}_2\text{CH}(\text{Br})\text{COOH}$, $\text{CH}_3\text{CH}(\text{Br})\text{CH}_2\text{COOH}$, $(\text{CH}_3)_2\text{CHCOOH}$ (acid strength)	$(\text{CH}_3)_2\text{CHCOOH} < \text{CH}_3\text{CH}(\text{Br})\text{CH}_2\text{COOH} < \text{CH}_3\text{CH}_2\text{CH}(\text{Br})\text{COOH}$
21	Ethanal is more reactive than acetone towards nucleophilic addition reaction	due to steric hinderence of alkyl group OR due to +I effect of alkyl group +ve charge of carbonyl carbon decreases.
22	$(\text{CH}_3)_3\text{C}-\text{CHO}$ does not undergo aldol condensation	α -hydrogen is not present in $(\text{CH}_3)_3\text{C}-\text{CHO}$
23	There are two $-\text{NH}_2$ group in semicarbazide however only one is involved in the formation of semicarbazones.	Since the NH_2 group attached to carbonyl group is stabilized by resonance and has double bond character
24	It is necessary to control the pH during the reaction of aldehydes and ketones with ammoniaderivatives.	In weakly acidic medium protonation of carbonyl carbon is required, in case of strongly acidic medium, protonation of ammonia derivative will be also takes place and will not be able to act as a nucleophile
25	Would you expect benzaldehyde to be more reactive or less reactive in nucleophilic addition reactions than propanal.	The carbon atom of the carbonyl group of benzaldehyde is less electrophilic than carbon atom of the carbonyl group present in propanal. The polarity of the carbonyl group is reduced in benzaldehyde due to resonance as shown below and hence it is less reactive than propanal
26	Formaldehyde does not take part in Aldol condensation.	Due to absence of α -hydrogen atom
27	Carboxylic acids are higher boiling liquids than alcohols	due to more extensive association of carboxylic acid molecules through intermolecular hydrogen bonding

13. AMINES AND DIAZONIUM SALT

Give **Reasons** for the following :

	QUESTION-REASONING	ANSWER- REASON
1	Arrange the following in increasing order of basic strength $\text{C}_6\text{H}_5\text{NH}_2$, $\text{CH}_3\text{CH}_2\text{NH}_2$, $\text{C}_6\text{H}_5\text{NHCH}_3$	$\text{C}_6\text{H}_5\text{-NH}_2 < \text{C}_6\text{H}_5\text{-NH-CH}_3 < \text{CH}_3\text{-CH}_2\text{-NH}_2$

2	In increasing order of solubility in water CH ₃ NH ₂ , (CH ₃) ₃ N, CH ₃ NHCH ₃	(CH ₃) ₃ N < CH ₃ NHCH ₃ < CH ₃ NH ₂
3	p-methylaniline is more basic than p-nitroaniline	–CH ₃ group shows +I – effect (electron releasing group) whereas –NO ₂ group shows –I- Effect (electron withdrawing group)
4	Acetylation of –NH ₂ group is done in aniline before preparing its ortho and para compounds.	To reduce activating effect of –NH ₂ group.
5	Arrange in order of basic strength. (ii) 	
6	<i>pK_b</i> for aniline is more than that for methylamine	In aniline due to resonance the lone pair of electrons on the nitrogen atom are delocalized over the benzene ring. As a result, the electron density on the nitrogen decreases. On the other hand, in methyl amine +I effect of CH ₃ increases the electron density on the nitrogen atom. Therefore aniline is a weaker base than methyl amine and hence its <i>pK_b</i> value is higher than that of methyl amine
7	Methylamine solution in water reacts with ferric chloride solution to give a precipitate of ferric hydroxide	$\text{CH}_3\text{—NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{NH}_3^+ + \text{OH}^-$ <p>Due to alkaline nature of solution of methylamine precipitation of Fe(OH)₃ or</p> $\text{FeCl}_3 + 3\text{OH}^- \longrightarrow \text{Fe(OH)}_3 \downarrow + 3\text{Cl}^-$ <p style="text-align: center;">Ferric hydroxide (Brown ppt)</p>
8	Aniline does not undergo Friedel-Crafts reaction	Aniline being a Lewis base, reacts with lewis acid AlCl ₃ to form a salt. Due to this N atom of aniline acquires positive charge and hence acts as a strong deactivation group for further reaction.
9	Why do amines behave as nucleophiles?	Due to the presence of a lone pair of electrons on nitrogen atom
10	<i>pK_b</i> of methylamine is less than that of aniline.	Lone pair of nitrogen in aniline involve in resonance, LP is not available for donation. On the other hand, in methyl amine +I effect of CH ₃ increases the electrondensity on the nitrogen atom. Therefore aniline is a weaker base than methyl amine and hence its <i>pK_b</i> value is higher than that of methyl amine
11	Ethylamine is freely soluble in water whereas aniline is only slightly soluble	because ethylamine forms hydrogen bonds with water, and due to hydrophobic benzene ring, aniline hence aniline is slightly soluble
12	Why is an alkylamine more basic than ammonia?	Due to electron donating nature of alkyl group
13	Arrange the following compounds in an increasing order of basic strengths in their aqueous solutions: NH ₃ , CH ₃ NH ₂ , (CH ₃) ₂ NH, (CH ₃) ₃ N	NH ₃ < (CH ₃) ₃ N < CH ₃ —NH ₂ < (CH ₃) ₂ NH.
14	Arrange the following compounds in an increasing order of their basic strength in aqueous solutions: NH ₃ , C ₂ H ₅ NH ₂ , (C ₂ H ₅) ₂ NH, (C ₂ H ₅) ₃ N	NH ₃ < C ₂ H ₅ NH ₂ < (C ₂ H ₅) ₃ N < (C ₂ H ₅) ₂ NH
15	In an increasing order of basic strength: C ₆ H ₅ NH ₂ , C ₆ H ₅ N(CH ₃) ₂ , (C ₂ H ₅) ₂ NH and	In an increasing order of <i>pK_b</i> values: C ₂ H ₅ NH ₂ , C ₆ H ₅ NHCH ₃ , (C ₂ H ₅) ₂ NH and C ₆ H ₅ NH ₂

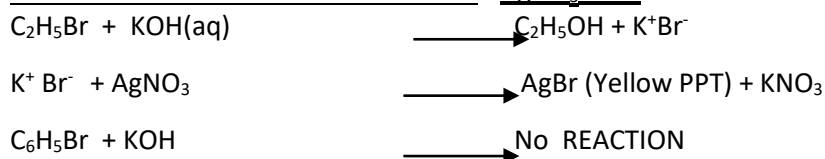
	CH ₃ NH ₂	
16	In a decreasing order of basic strength: Aniline, p-nitroaniline and p-toluidine	<i>p</i> -Toluidine > Aniline > tr-nitroaniline
17	In an increasing order of pK _b values: C ₂ H ₅ NH ₂ , C ₆ H ₅ NHCH ₃ , (C ₂ H ₅) ₂ NH and C ₆ H ₅ NH ₂	(C ₂ H ₅) ₂ NH ₂ < C ₂ H ₅ NH ₂ < C ₆ H ₅ NHCH ₃ < C ₆ H ₅ NH ₂
18	The order of basicity of amines in the gaseous phase follows the order: Tertiary amine > Secondary amine > Primary amine > NH ₃ .	Because the more the number of Electron donating groups (EDG) i.e alkyl groups more is the basicity
19	Aromatic primary amines cannot be prepared by Gabriel phthalimide synthesis.	because in preparation by Gabriel phthalimide synthesis, Ar-X is needed and aryl halides do not undergo nucleophilic substitution easily due to presence of partial double character
20	Although amino group is o- and p- directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of m-nitroaniline.	because Nitration is usually carried out with a mixture of conc HNO ₃ and conc H ₂ SO ₄ . In presence of these acids aniline gets protonated to form the anilinium ion which is <i>meta</i> directing
21	Acetylation of —NH ₂ group of aniline reduces its activating effect	Because with acetylation of aniline results in decrease of electron density on Nitrogen
22	NH ₂ group of aniline acetylated is before carrying out nitration.	Because the acetyl group reduces the reactivity of the ring thus its oxidation does not occur easily with HNO ₃ and mono substitution carried out.
23	Why are diazonium salts of aromatic amines more stable than those of aliphatic amines?	due to dispersal of the positive charge on the benzene ring.

. DISTINGUISH TEST

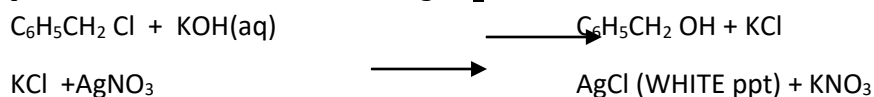
S.N o	Test	Reagent	Inference
1.	Lucas test :To distinguish between Primary (1°), Secondary (2°), & Tertiary (3°) Alcohols	ZnCl ₂ /HCl	(3°) Alcohols gives Turbidity (immediately), 2° Turbidity after sometime (5-10 min) 1° does not give Turbidity at room temperature
2.	Iodoform test (Alcohols containing CH ₃ -CH(OH)-linkage)	I ₂ / NaOH	Yellow Ppt of CHI ₃ .is formed
3.	Neutral ferric chloride test (Phenol)	Neutral FeCl ₃	Phenols give Violet colouration
4.	Tollens test [Aliphatic Aldehydes (e.g. Ethanal, Propanal etc) & Aromatic Aldehydes (Benzaldehyde etc.)]	Ammoniacal .AgNO ₃	Bright silver mirror [Ag] is produced due to the formation of silver metal.
5.	Fehling's test [Only Aliphatic Aldehydes] **Aromatic aldehyde do not give this test	Fehling solution A (aqueous copper sulphate & Fehling solution B alkaline sodium potassium tartarate (Rochelle salt))	Reddish brown precipitate of [Cu ₂ O] is obtained.
6.	Iodoform test (Aldehydes & Ketones containing —COCH ₃ linkage)	I ₂ / NaOH	Yellow Ppt of CHI ₃ .is formed

7.	Sodium bicarbonate test (Aliphatic & Aromatic Carboxylic acids)	NaHCO_3 Sodium Hydrogencarbonate	Effervescence due to evolution of CO_2 gas.
8.	Isocyanide test Primary Aliphatic & Aromatic amines.	Chloroform (CHCl_3) + Alcoholic KOH	Unpleasant odour (foul smelling) of isocyanides or carbylamines.
9.	Heinsberg test (To distinguish between (1°) , (2°) , & (3°) Amines.	Benzenesulphonyl chloride $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$	Product of 1° Amines soluble in alkali. Product of 2° Amines are insoluble in alkali 3° amines do not react.
10.	Azo dye test (Aniline)	($\text{NaNO}_2 + \text{HCl}$) [Nitrous acid] followed by reaction with naphthol	Reaction with $\text{NaNO}_2 + \text{HCl}$ at 273-278 K gives BDC which forms a brilliant orange Azo dye with β -naphthol in sodium hydroxide
11.	Test for Methanoic acid (Formic acid) Tollens test & Fehling's test	Amm. AgNO_3 & Fehling solution A & B	Bright silver mirror $[\text{Ag}]$ is produced due to the formation of silver metal Reddish brown precipitate of $[\text{Cu}_2\text{O}]$ is obtained.

1) **ETHYL BROMIDE AND BROM BENZENE:- AgNO_3 TEST**



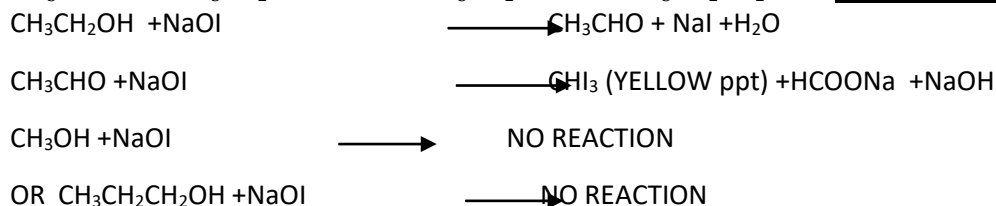
2) **p- $\text{ClC}_6\text{H}_4\text{CH}_3$ AND $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$:- AgNO_3 TEST**



3) **CCl_4 AND CHCl_3 :- CARBYLAMINE TEST**



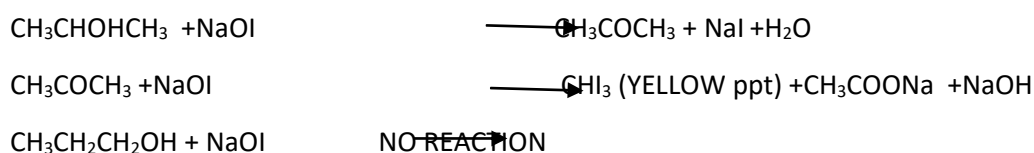
4) **CH_3OH AND $\text{CH}_3\text{CH}_2\text{OH}$ OR $\text{CH}_3\text{CH}_2\text{OH}$ AND $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$:- iodoform TEST**



5) **$\text{CH}_3\text{CH}_2\text{OH}$ AND $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$:- LUCAS TEST**



6) **$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ AND $\text{CH}_3\text{CHOHCH}_3$:- iodoform TEST**

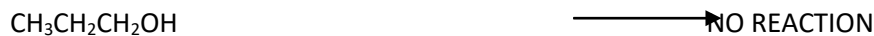


- 7) $\text{CH}_3\text{CHOHCH}_2\text{CH}_3$ AND $(\text{CH}_3)_3\text{COH} :-$ LUCAS TEST OR IODOFORM TEST
 $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_3 + \text{Anhy. ZnCl}_2 + \text{Con. HCl} \longrightarrow \text{CH}_3\text{CHClCH}_3$ (TURBIDITY AFTER 5 MINS.) $(\text{CH}_3)_3\text{COH} + \text{Anhy. ZnCl}_2 + \text{Con. HCl} \longrightarrow (\text{CH}_3)_3\text{CCl}$ (WHITETURBIDITY IMMEDIATELY)
- 8) $\text{CH}_3\text{CH}_2\text{OH}$ AND $\text{C}_6\text{H}_5\text{OH} :-$ FeCl_3 TEST
 $\text{C}_6\text{H}_5\text{OH} + \text{FeCl}_3 \longrightarrow (\text{C}_6\text{H}_5\text{O})_3\text{Fe}$ (VIOLET COLOURATION) + HCl
 $\text{CH}_3\text{CH}_2\text{OH} + \text{FeCl}_3 \longrightarrow \text{NO REACTION}$
- 9) $(\text{R})_2\text{NH}$ AND $\text{RNH}_2 :-$ (CARBYLAMINE TEST)
 $\text{R-NH}_2 + \text{CHCl}_3 + 3\text{KOH} \longrightarrow \text{R-NC} + 3\text{KCl} + 3\text{H}_2\text{O}$ offensive smell of isocyanide
 $(\text{R})_2\text{NH}_2 + \text{CHCl}_3 + 3\text{KOH} \longrightarrow \text{NO REACTION}$
- 10) $\text{C}_2\text{H}_5\text{OH}$ AND $\text{CH}_3\text{CH}_2\text{NH}_2 :-$ (IODOFORMTEST)
 $\text{CH}_3\text{CH}_2\text{OH} + \text{NaOI} \longrightarrow \text{CH}_3\text{CHO} + \text{NaI} + \text{H}_2\text{O}$
 $\text{CH}_3\text{CHO} + \text{NaOI} \longrightarrow \text{CHI}_3$ (YELLOW ppt) + $\text{HCOONa} + \text{NaOH}$
- 11) $\text{CH}_3\text{COCH}_2\text{CH}_2\text{CH}_3$ AND $\text{CH}_3\text{CH}_3\text{COCH}_2\text{CH}_3 :-$ (IODOFORM TEST)
 $\text{CH}_3\text{COCH}_2\text{CH}_2\text{CH}_3 + \text{NaOI} \longrightarrow \text{CHI}_3$ (YELLOW ppt) + $\text{CH}_3\text{CH}_2\text{CH}_2\text{COONa} + \text{NaOH}$
 $\text{CH}_3\text{CH}_3\text{COCH}_2\text{CH}_3 \longrightarrow \text{NO REACTION}$
- 12) $\text{C}_6\text{H}_5\text{COCH}_3$ AND $\text{C}_6\text{H}_5\text{CHO} :-$ (IODOFORM TEST)
 $\text{C}_6\text{H}_5\text{COCH}_3 + \text{NaOI} \longrightarrow \text{CHI}_3$ (YELLOW ppt) + $\text{C}_6\text{H}_5\text{COONa} + \text{NaOH}$
 $\text{C}_6\text{H}_5\text{CHO} + \text{NaOI} \longrightarrow \text{NO REACTION}$
- 13) CH_3CHO AND $\text{CH}_3\text{CH}_2\text{CHO} :-$ (IODOFORM TEST)
 $\text{CH}_3\text{CHO} + \text{NaOI} \longrightarrow \text{CHI}_3$ (YELLOW ppt) + $\text{HCOONa} + \text{NaOH}$
 $\text{CH}_3\text{CH}_2\text{CHO} \longrightarrow \text{NO REACTION}$
- 14) CH_3CHO AND $\text{C}_6\text{H}_5\text{CHO} :-$ (IODOFORM TEST)
 $\text{CH}_3\text{CHO} + \text{NaOI} \longrightarrow \text{CHI}_3$ (YELLOW ppt) + $\text{HCOONa} + \text{NaOH}$
 $\text{C}_6\text{H}_5\text{CHO} \longrightarrow \text{NO REACTION}$
- 15) $\text{C}_6\text{H}_5\text{CHO}$ AND $\text{CH}_3\text{COCH}_3 :-$ (IODOFORMTEST)
 $\text{CH}_3\text{COCH}_3 + \text{NaOI} \longrightarrow \text{CHI}_3$ (YELLOW ppt) + $\text{CH}_3\text{COONa} + \text{NaOH}$
 $\text{C}_6\text{H}_5\text{CHO} \longrightarrow \text{NO REACTION}$
- 16) $\text{CH}_3\text{COC}_6\text{H}_5$ AND $\text{C}_6\text{H}_5\text{COC}_6\text{H}_5 :-$ (IODOFORM TEST)
 $\text{C}_6\text{H}_5\text{COCH}_3 + \text{NaOI} \longrightarrow \text{CHI}_3$ (YELLOW ppt) + $\text{C}_6\text{H}_5\text{COONa} + \text{NaOH}$
 $\text{C}_6\text{H}_5\text{COC}_6\text{H}_5 \longrightarrow \text{NO REACTION}$
- 17) CH_3COCH_3 AND $\text{CH}_3\text{CH}_2\text{CHO} :-$ (IODOFORM TEST)
 $\text{CH}_3\text{COCH}_3 + \text{NaOI} \longrightarrow \text{CHI}_3$ (YELLOW ppt) + $\text{CH}_3\text{COONa} + \text{NaOH}$
 $\text{CH}_3\text{CH}_2\text{CHO} \longrightarrow \text{NO REACTION}$ (TOLLENS TEST IS ALSO POSSIBLE)
- 18) CH_3CHO AND $\text{HCHO} :-$ (IODOFORM TEST)
 $\text{CH}_3\text{CHO} + \text{NaOI} \longrightarrow \text{CHI}_3$ (YELLOW ppt) + $\text{HCOONa} + \text{NaOH}$
 $\text{HCHO} \longrightarrow \text{NO REACTION}$
- 19) $\text{C}_2\text{H}_5\text{Cl}$ AND $\text{CH}_2=\text{CHCl} :-$ (AgNO_3 TEST)
 $\text{C}_2\text{H}_5\text{Cl} + \text{KOH (aq)} + \text{AgNO}_3 \longrightarrow \text{C}_2\text{H}_5\text{OH} + \text{AgCl (WHITE ppt)} + \text{KNO}_3$
 $\text{CH}_2=\text{CHCl} \longrightarrow \text{NO REACTION}$
- 20) $\text{C}_6\text{H}_5\text{Cl}$ AND $\text{C}_6\text{H}_{11}\text{Cl} :-$ (AgNO_3 TEST)
 $\text{C}_6\text{H}_{11}\text{Cl} + \text{KOH (aq)} + \text{AgNO}_3 \longrightarrow \text{C}_6\text{H}_{11}\text{OH} + \text{AgCl (WHITE ppt)} + \text{KNO}_3$
 $\text{C}_6\text{H}_5\text{Cl} \longrightarrow \text{NO REACTION}$

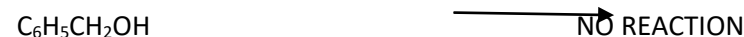
21) $\text{C}_6\text{H}_5\text{Cl}$ AND $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$:- (AgNO_3 TEST)



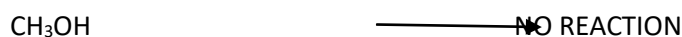
22) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ AND CH_3COCH_3 :- (IODOFORM TEST)



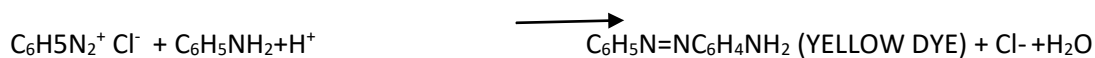
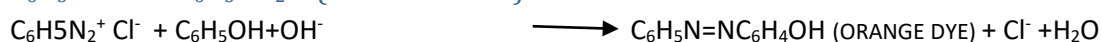
23) $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ AND $\text{CH}_3\text{CHOHCH}_3$:- (IODOFORM TEST)



24) CH_3OH AND $\text{C}_6\text{H}_5\text{OH}$:- (FeCl_3 TEST)



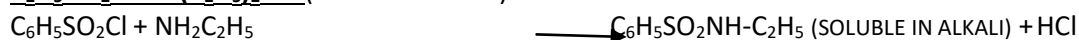
25) C_6H_5OH AND $C_6H_5NH_2$:- (AZO DYE TEST)



26) $\text{C}_6\text{H}_5\text{NH}_2$ AND $\text{C}_6\text{H}_5\text{NH CH}_3$ (CARBYLAMINE TEST)



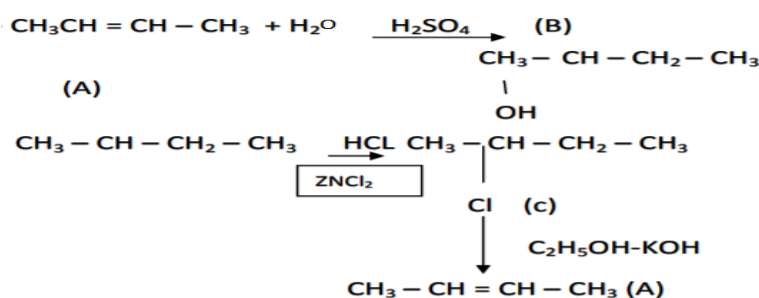
27) $\text{C}_2\text{H}_5\text{NH}_2$ AND $(\text{C}_2\text{H}_5)_2\text{NH}$ (HINSBERG TEST)



4. WORD PROBLEM

10. HALOALKANES AND HALOARENES

1. An organic compound 'A' having molecular formula C_4H_8 on treatment with dil. H_2SO_4 give another compound 'B'. B on treatment with conc. HCl and anhy. $ZnCl_2$ gives 'C'. C on treatment with sodium ethoxide gives back 'A'. Identify the compound. Write the equations involved.

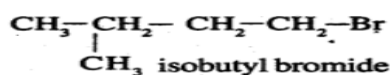


2. A primary alkyl halide (A), C_4H_9Br reacted with hot alcoholic KOH to give compound (B). Compound (B) reacted with HBr to give (C), which is an isomer of (A). When (A) was reacted with sodium metal, it gave a compound (D), C_8H_{18} which was different than the compound when n-butyl bromide was reacted with sodium. Give the structural formula of (A) and write equations of all the reactions.

There are two primary alkyl halides having the formula C_4H_9Br . They are n-butyl bromide and isobutyl bromide

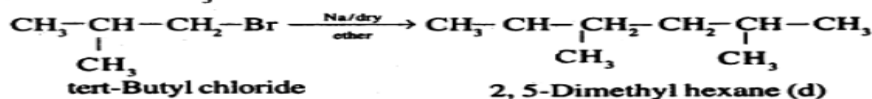
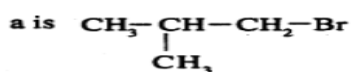


n-Butyl bromide



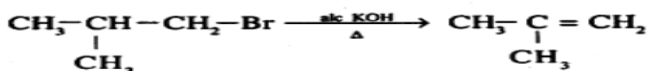
isobutyl bromide

Since (a) reacts with Na to give a compound C_8H_{18} which is different from the compound formed when n-butyl bromide is reacted with Na, (a) has to be isobutyl bromide.

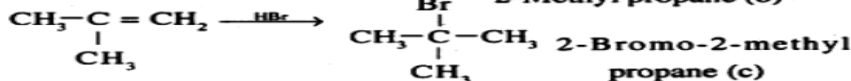


tert-Butyl chloride

2, 5-Dimethyl hexane (d)



2-Methyl propane (b)

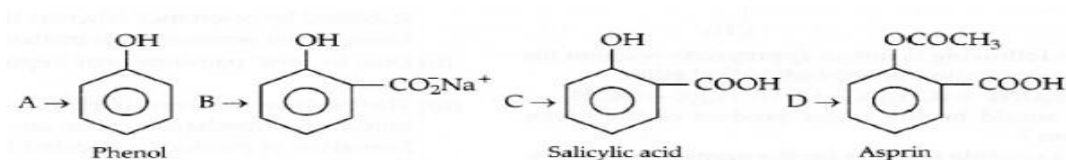


2-Bromo-2-methyl propane (c)

5. ALCOHOLS, PHENOLS AND ETHERS

3. An organic compound (A) having molecular formula C_6H_6O gives a characteristic colour with aqueous $FeCl_3$ solution. (A) on treatment with CO_2 and NaOH at 400 K under pressure gives (B), which on acidification gives a compound (C). The compound (C) reacts with acetyl chloride to give (D) which is a popular pain killer. Identify compounds A, B, C and D.

ANS=



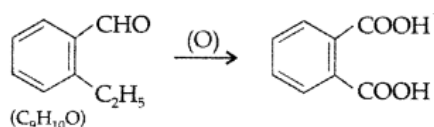
4. A compound A with molecular formula C_3H_8O undergoes oxidation to form compound B. Compound B is widely used in nail polish removers and paint removers. When B is treated with CH_3MgBr it forms an intermediate and on hydrolysis it gives a compound C which is a 3° alcohol. Identify A, B and C and write their structures.

Ans: = A= Propan-2-ol B= Acetone C= 2-methylpropan-2-ol

12. Aldehydes, Ketones and Carboxylic Acids

5. An organic compound A contains 69.77% carbon, 11.63% hydrogen and rest oxygen. The molecular mass of the compound is 86. It does not reduce Tollen's Reagent but forms an addition compound with sodium hydrogen sulphite and gives positive iodoform test. On vigorous oxidation, it gives ethanoic acid and propanoic acids. Identify the structure of compound A.

Ans:



6. An organic compound with molecular formula $C_9H_{10}O$ forms 2,4-DNP derivative., reduces Tollen's reagent and undergoes Cannizzaro reaction. On vigorous oxidation, it gives 1,2-benzenedicarboxylic acid. Identify the compound.

Ans:

(b) Calculation of Molecular formula :

$$C = 69.77\%, \quad H = 11.63\%$$

$$\therefore O = 100 - (69.77 + 11.63) = 18.6\%$$

Element	%	Molar mass	%/Molar mass	Simplest ratio
C	69.77	12	5.88	5
H	11.63	1	11.63	10
O	18.6	16	1.16	1

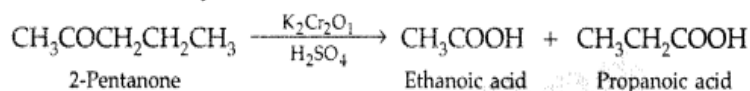
Empirical formula of given compound = $C_5H_{10}O$

Empirical formula mass = $5 \times 12 + 10 \times 1 + 16 = 86$

$$\therefore n = \frac{\text{Empirical formula mass}}{\text{Molar mass}} = \frac{86}{86} = 1$$

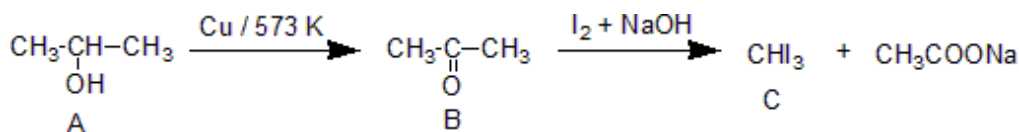
Molecular formula of the given compound = $1 \times C_5H_{10}O = C_5H_{10}O$

Determination of structure : Since the compound does not reduce Tollen's reagent and gives positive iodoform test so it may be a **ketone**.

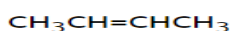


7. An organic compound A (C_3H_8O) on treatment with copper at 573 K gives B. B does not reduce Fehling's solution but gives a yellow ppt. of compound C with $I_2 / NaOH$. Deduce the structures of A, B and C.

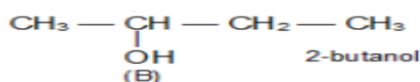
Ans: As B gives negative fehling's test means B is not an aldehyde. Copper at 573 K act as oxidising agent. Therefore, A is alcohol which gives ketone on oxidation. This ketone gives positive iodoform test. In positive iodoform test yellow precipitate of iodoform, CHI_3 are obtained. "C" is iodoform.



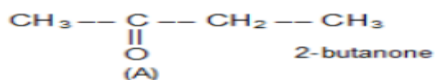
8. A ketone A (C_4H_8O) which undergoes a haloform reaction and gives compound B on reduction. B on heating with sulphuric acid gives a compound C which forms mono-ozonide D. D on hydrolysis with zinc dust gives only E. Identify A, B, C, D and E. Write the reactions involved



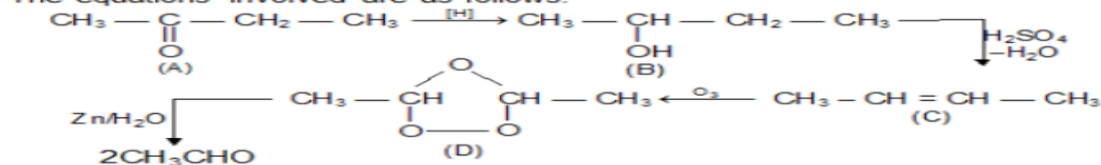
The compound C is obtained by dehydration of B, thus the latter should be



Finally, B is obtained by the reduction of A. Hence, the compound A should be



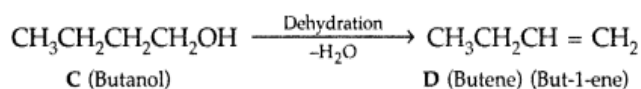
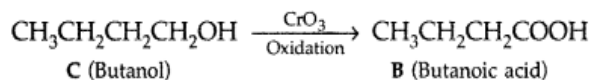
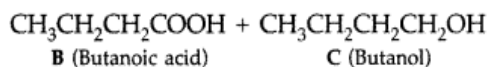
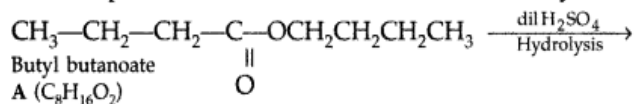
The equations involved are as follows:



9. An organic compound A has the molecular formula $C_8H_{16}O_2$. It gets hydrolysed with dilute sulphuric acid and gives a carboxylic acid B and an alcohol C. Oxidation of C with chromic acid also produced B. C on dehydration reaction gives but-1-ene. Write equations for the reactions involved.

ANS:

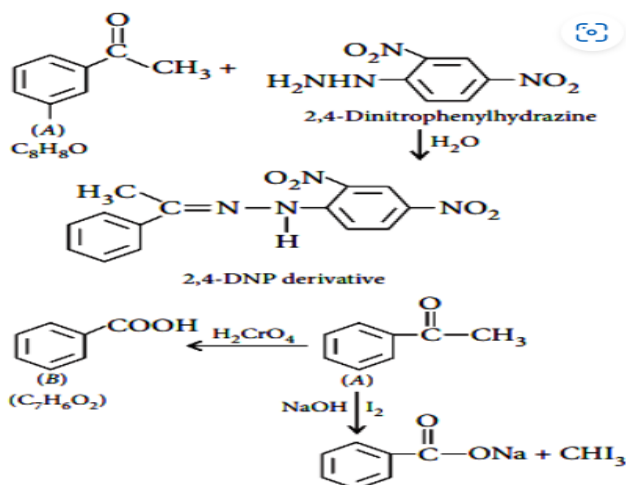
(b) The compound A with molecular formula is **Butyl butanoate**.



10. An organic compound A with molecular formula $\text{C}_8\text{H}_8\text{O}$ forms an orange red precipitate with 2,4-DNP reagent and gives yellow precipitate on heating with I_2 and NaOH . It neither reduces Tollen's reagent nor Fehling's reagent nor does it decolourize bromine water or Baeyer's reagent. On drastic oxidation with chromic acid, it gives a carboxylic acid having molecular formula $\text{C}_7\text{H}_6\text{O}_2$. Identify the compounds A and B and explain the reactions involved.

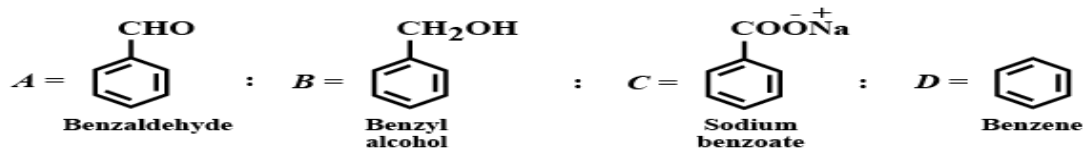
(A) forms, 2, 4-DNP derivative. Therefore, it is an aldehyde or a ketone. Since it does not reduce Tollen's or Fehling reagent, (A) must be a ketone. (A) responds to iodoform test.

Compound (B), being an oxidation product of a ketone should be a carboxylic acid. The molecular formula of (B) indicates that it should be benzoic acid and compound (A) should, therefore, be a mono-substituted aromatic methyl ketone.

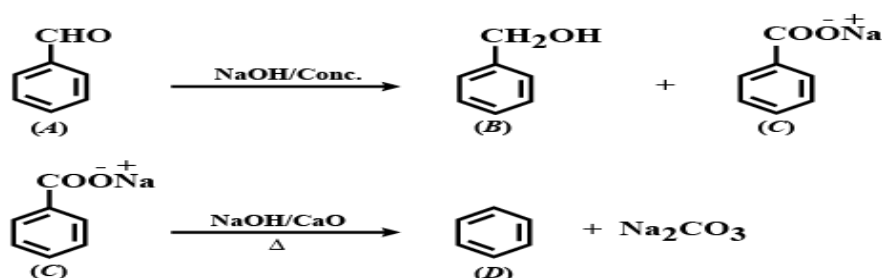


11. An organic compound A which has characteristic odour, on treatment with NaOH forms two compounds B and C. Compound B has the molecular formula $\text{C}_7\text{H}_8\text{O}$ which on oxidation with CrO_3 gives back compound A. Compound C is the sodium salt of the acid. C when heated with soda lime yields an aromatic hydrocarbon D. Deduce the structures of A, B, C and D.

Ans: (A) gives characteristic odour which on treatment with NaOH and forms two compounds



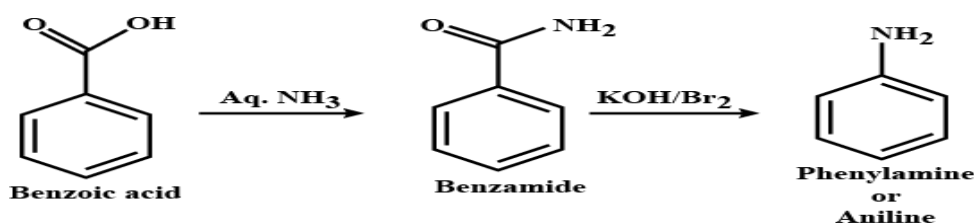
Reaction involved are:



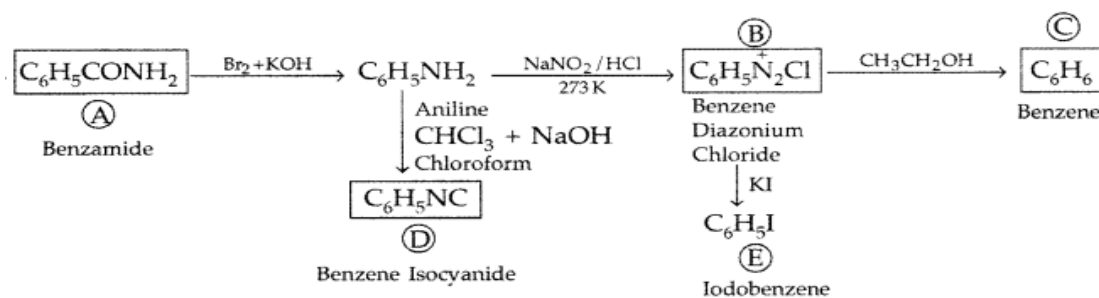
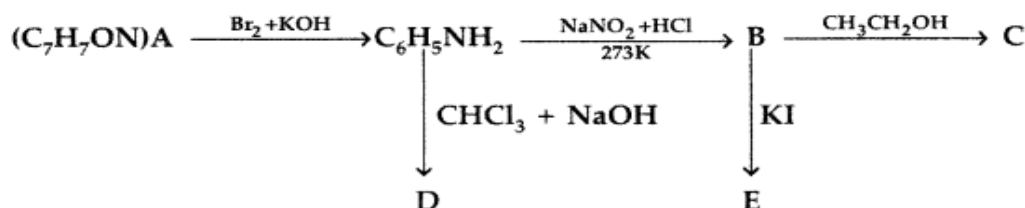
13. AMINES

12. 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 $\text{C}_6\text{H}_7\text{N}$. Write the structure and IUPAC names of compounds A, B and C.

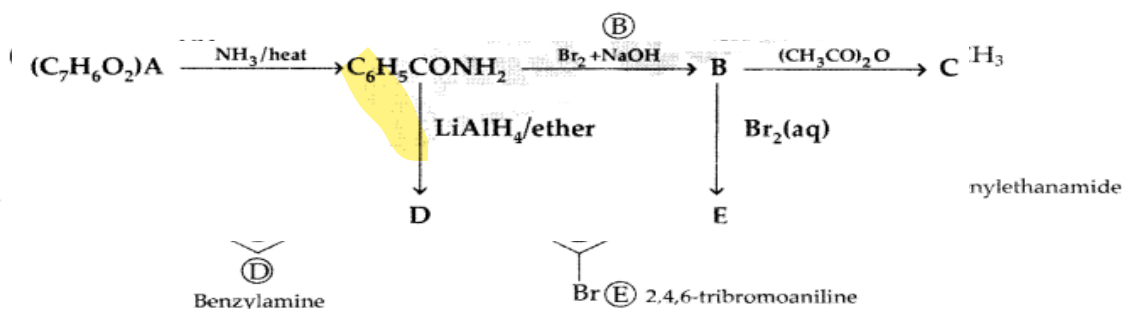
ANS: The aromatic compound A is benzoic acid. On treatment with aqueous ammonia and heating forms compound B, which is benzamide. Benzamide on heating with bromine and KOH forms a compound C, which is aniline. The reaction is called Hoffmann bromamide degradation.



13. An aromatic compound A of molecular formula $\text{C}_7\text{H}_7\text{ON}$ undergoes a series of reactions as shown below. Write the structures of A, B, C, D and E in the following reactions :



14. An aromatic compound A of molecular formula $\text{C}_7\text{H}_6\text{O}_3$ undergoes a series of reactions as shown below. Write



the structures of A, B, C, D and E in the following reactions :

KEY FOR CONVERSIONS

Sl No	Reagent	Group Out	Group In	Remark
1	KMnO ₄ / H ⁺	-CH ₂ OH	-COOH	Strong Oxidation (2° alc → ketone)
2	LiAlH ₄	-COOH	-CH ₂ OH	Strong Reduction (ketone → 2° alc)
3	Cu / 573 K or CrO ₃	-CH ₂ OH	-CHO	Dehydrogenation
4	PCl ₅ or SOCl ₂	-OH	-Cl	
5	Cl ₂ / Δ or Cl ₂ / UV	-H	-Cl	Free radical substitution
6	Aq NaOH / KOH	-X	-OH	Nucleophilic substitution
7	KCN	-X	-CN	Step Up
8	AgCN	-X	-NC	
9	Alcoholic KOH	-HX	=	Dehydrohalogenation (Stzf)
10	Mg / dry ether		Mg	R-X → R-MgX
11	HBr	>=<	H, Br	Merkovnikov
12	H ₂ / Pd-BaSO ₄	-COCl	-CHO	Rosenmund Reduction
13	Zn-Hg / HCl	>C=O	-CH ₂ -	Clemmenson Reduction
14	NH ₃ / Δ	-COOH	-CONH ₂	-COOH + NH ₃ → -COONH ₄
15	Br ₂ /NaOH or NaOBr	-CONH ₂	-NH ₂	Step Down (Hoffmann)
16	HNO ₂ or NaNO ₂ /HCl	-NH ₂	-OH	HONO
17	CHCl ₃ / alc KOH	-NH ₂	-NC	Carbyl amine
18	P ₂ O ₅	-CONH ₂	-CN	Dehydration
19	H ₃ O ⁺	-CN	-COOH	Hydrolysis
20	OH ⁻	-CN	-CONH ₂	
21	LiAlH ₄	-CN	-CH ₂ NH ₂	Reduction
22	Red P / Cl ₂	α-H of acid	-Cl	HVZ Reaction
In benzene ring				
23	Fe / X ₂ / dark	-H	-X	Halogenation
24	CH ₃ Cl / AlCl ₃ (anhyd)	-H	-CH ₃	Friedel Craft alkylation
25	CH ₃ COCl / AlCl ₃ (anhyd)	-H	-COCH ₃	Friedel Craft acylation
26	Conc. HNO ₃ / conc. H ₂ SO ₄	-H	-NO ₂	Nitration
27	Conc H ₂ SO ₄	-H	-SO ₃ H	Sulphonation
28	KMnO ₄ / H ⁺	-R	-COOH	Oxidation
29	CrO ₂ Cl ₂ / H ⁺	-CH ₃	-CHO	Mild oxidation(Etard Reaction)
30	Sn / HCl or Fe/HCl	-NO ₂	-NH ₂	Reduction
31	NaOH / 623K / 300 atm	-Cl	-OH	
32	Zn dust / Δ	-OH	-H	
33	NaNO ₂ / dil HCl / 273- 278 K	-NH ₂	-N ⁺ Cl ⁻ ₂	Diazo reaction
34	CuCl/HCl or Cu/HCl	-N ⁺ Cl ⁻ ₂	-Cl	Sandmeyer or Gattermann
35	CuBr/HBr or Cu/HBr	-N ⁺ Cl ⁻ ₂	-Br	Sandmeyer or Gattermann
36	CuCN / KCN	-N ⁺ Cl ⁻ ₂	-CN	Sandmeyer
37	KI	-N ⁺ Cl ⁻ ₂	-I	
38	BF ₃ / Δ	-N ⁺ Cl ⁻ ₂	-F	
39	H ₃ PO ₂ or CH ₃ CH ₂ OH	-N ⁺ Cl ⁻ ₂	-H	
40	H ₂ O / 283 K	-N ⁺ Cl ⁻ ₂	-OH	
41	BF ₃ / NaNO ₂ ,Cu/ Δ	-N ⁺ Cl ⁻ ₂	-NO ₂	
42	C ₆ H ₅ -OH	-N ⁺ Cl ⁻ ₂	-N=N-C ₆ H ₅ -OH	Coupling (p-hydroxy)
43	C ₆ H ₅ -NH ₂	-N ⁺ Cl ⁻ ₂	-N=N-C ₆ H ₅ -NH ₂	Coupling (p-amino)

Reactions of Grignard Reagent

Grignard reagent +	Any one below + H ₂ O →	Product
	H ₂ O or ROH or RNH ₂	R-H
	H-CHO	R-CH ₂ -OH (1° alc)
	R-CHO	R-CH(OH)-R (2° alc)
	R-CO-R	R ₂ C(OH)-R (3° alc)

R-MgX	CO ₂	R-COOH
	R-CN	R-CO-R
	HCOOR	Aldehyde
	RCOOR	Ketone

Directional Properties of groups in benzene ring for electrophilic substitution

Ortho-para directing group: -R, -OH, -NH₂, -X, -OR, -NHR, -NR₂, -NHCOCH₃, -CH₂Cl, -SH, -Ph

Meta-directing group: -NO₂, -CHO, -COOH, COOR, -CN, -SO₃H, -CH₃, -CCl₃, -NH₃⁺,

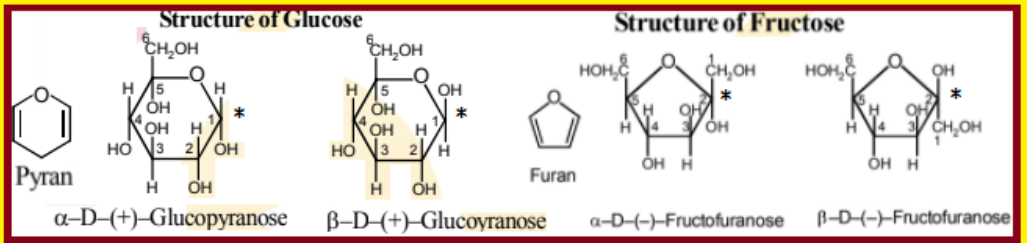
3

BIOMOLECULES

Carbohydrates are classified on the basis of their behavior on hydrolysis :	
Monosaccharides:	A carbohydrate that cannot be hydrolyzed further to give simpler unit of polyhydroxy aldehyde or ketone is called a monosaccharide. examples are glucose, fructose, ribose, etc.
Oligosaccharides:	Carbohydrates that yield two to ten monosaccharide units, on hydrolysis, are called oligosaccharides. They are further classified as disaccharides, trisaccharides, tetra saccharides, etc., depending upon the number of monosaccharides, they provide on hydrolysis. For example, sucrose on hydrolysis gives one molecule each of glucose and fructose.
Polysaccharides:	Carbohydrates which yield a large number of monosaccharide units on hydrolysis are called polysaccharides. Some common examples are starch, cellulose, glycogen, gums, etc. Polysaccharides are not sweet in taste, hence they are also called non-sugars.
Reducing sugars:	All those carbohydrates which reduce Fehling's solution and Tollens' reagent are referred to as reducing sugars. Examples: All monosaccharides, Maltose and Lactose.
Non-reducing sugars:	In disaccharides, if the reducing groups of monosaccharides i.e., aldehydes or ketone groups are bonded, these are non-reducing sugars e.g. All polysaccharides sucrose
Anomers:	α & β - Glucose, which differ in the orientation of - OH group at C ₁ .
Proteins:	proteins are polymer of α - amino acids, joined by peptide bonds. They also known as polyamides.
Types of Proteins:	(i) Fibrous proteins:- The polypeptide chains run parallel and are held by H-bond or disulphide linkage, Insoluble in water Eg: Keratin, Myocin (ii) Globular proteins:- Polypeptides coil around to give a spherical shape, Soluble in water Eg: Insulin, Albumins
Structure and shape of Proteins:	1) Primary structure : It is a specific sequence of amino acids 2) Secondary structure : It represent shape ie. α - helix and β -pleated sheet. i) α - helix : polypeptide chain twisted in to a right handed screw by forming H-bonds b/w NH group and >C=O grup. ii) β- pleated sheet : peptide chains laid side by side and held together by H-bonds 3) Tertiary structure : It represent further folding of the secondary structure. It gives rise to two major molecular shapes viz. fibrous and globular. 4) Quaternary structure of proteins : composed of two or more polypeptide chains referred to as sub-units. The spatial arrangement of these subunits with respect to each other.
Denaturation of proteins	Disturbing the 2 ^o and 3 ^o structures of proteins by heating or changing pH. eg: coagulation of egg white on boiling.

Nucleic acids	Polymer of nucleotides linked by phosphodiester linkage -3' 5' linkage
Nucleotide	Each nucleotide contains N-base, Sugar and Phosphate.
Nucleoside	Contains N-base & Sugar.
Double helical structure of DNA	Two strand of DNA coiled around each other and held together by H-bonds b/w pairs of bases. Such as – C≡G–, and –A =T– Purines : A & G And Pyrimidines : C, U & T
DNA	N-Bases : A,G ,C & T, Double helix, Contains 2-deoxy ribose sugar, Transfer heredity characters.
RNA	N-Bases: A,G C & U, Single helix, Contains Ribose sugar, Helps in proteins synthesis.
Preparation of Glucose	<p>(I) From Cane sugar: (Sucrose) : When sucrose is hydrotysed by boiling with dil HCl or dil H₂SO₄ in alcoholic solution</p> $\text{C}_{12}\text{H}_{22}\text{O}_{11} + \text{H}_2\text{O} \xrightarrow{\text{H}^+} \text{C}_6\text{H}_{12}\text{O}_6 + \text{C}_6\text{H}_{12}\text{O}_6$ <p style="text-align: center;">Sucrose Glucose Fructose</p> <p>(II) From Starch : Commercially Glucose is obtained by hydrolysis of starch by boiling it with dil H₂SO₄ at 393 K</p> $(\text{C}_6\text{H}_{10}\text{O}_5)_n + n\text{H}_2\text{O} \xrightarrow[393\text{K, 2-3 atm}]{\text{H}^+} n\text{C}_6\text{H}_{12}\text{O}_6$ <p style="text-align: center;">Starch Glucose</p>
Structure of Glucose	<p style="text-align: center;">GLUCOSE (OPEN CHAIN /Cyclic STRUCTURE)</p> <div style="display: flex; align-items: center;"> <div style="margin-right: 20px;"> <p>CHO ← One aldehyde group</p> <p>CH(OH)₄ ← Four 2° alcoholic group</p> <p>CH₂OH ← One 1° Alcoholic group</p> </div> <div style="text-align: center;"> <p>$\alpha\text{-D-(+)-Glucose}$ $\beta\text{-D-(+)-Glucose}$</p> </div> </div>
Reactions of Glucose	
Reactions that prove cyclic structure of Glucose	<ol style="list-style-type: none"> Aldehyde group present but glucose does not react with NaHSO₃ & NH₃. Glucose does not give the Schiff's Test & 2,4-DNP test for aldehyde. Glucose penta-acetate does not react hydroxyl amine, which shows that aldehyde group is absent in glucose. Glucose exist in two stereo-isomeric forms (α & β). <p>➤ All observations indicate that free aldehydic group is not present in glucose.</p>

Cyclic Structure of Glucose



Structure of Nucleotide

