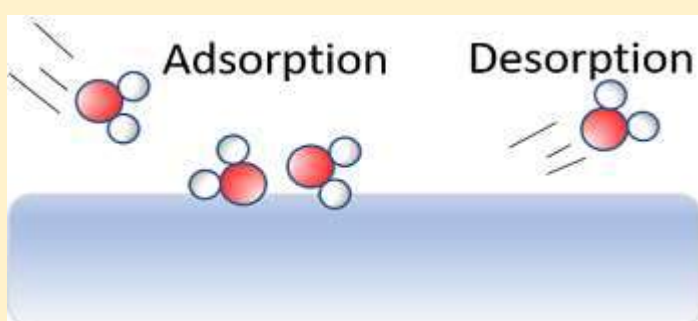


COMPLETE STUDY PACK AS PER REVISED SYLLABUS

# CBSE TERM -2

## XII

# CHEMISTRY



**SYLLABUS FOR SESSION 2021-22 CLASS XII Term-II**

S.No	UNIT	No. of Periods	MARKS
1	Electrochemistry	7	13
2	Chemical Kinetics	5	
3	Surface Chemistry	5	
4	d-and f-Block Elements	7	9
5	Coordination Compounds	8	
6	Aldehydes, Ketones and Carboxylic Acids	10	13
7	Amines	7	
	TOTAL	49	35

- ELECTROCHEMISTRY:** Redox reactions, EMF of a cell, standard electrode potential, Nernst equation and its application to chemical cells, Relation between Gibbs energy change and EMF of a cell, conductance in electrolytic solutions, specific and molar conductivity, variations of conductivity with concentration, Kohlrausch's Law, electrolysis.
- CHEMICAL KINETICS:** Rate of a reaction (Average and instantaneous), factors affecting rate of reaction: concentration, temperature, catalyst; order and molecularity of a reaction, rate law and specific rate constant, integrated rate equations and half-life (only for zero and first order reactions).
- SURFACE CHEMISTRY:** Adsorption - physisorption and chemisorption, factors affecting adsorption of gases on solids, colloidal state: distinction between true solutions, colloids and suspension; lyophilic, lyophobic, multi-molecular and macromolecular colloids; properties of colloids; Tyndall effect, Brownian movement, electrophoresis, coagulation.
- d-and f-BLOCK ELEMENTS:** General introduction, electronic configuration, occurrence and characteristics of transition metals, general trends in properties of the first row transition metals – metallic character, ionization enthalpy, oxidation states, ionic radii, colour, catalytic property, magnetic properties, interstitial compounds, alloy formation. Lanthanoids - Electronic configuration, oxidation states and lanthanoid contraction and its consequences. Coordination Compounds: Coordination compounds - Introduction, ligands, coordination number, colour, magnetic properties and shapes, IUPAC nomenclature of mononuclear coordination compounds. Bonding, Werner's theory, VBT, and CFT.
- ALDEHYDES, KETONES AND CARBOXYLIC ACIDS:** Aldehydes and Ketones: Nomenclature, nature of carbonyl group, methods of preparation, physical and chemical properties, mechanism of nucleophilic addition, reactivity of alpha hydrogen in aldehydes, uses. Carboxylic Acids: Nomenclature, acidic nature, methods of preparation, physical and chemical properties; uses.
- AMINES:** Nomenclature, classification, structure, methods of preparation, physical and chemical properties, uses, identification of primary, secondary and tertiary amines.

# A c k n o w l e d g e m e n t

## A c k n o w l e d g e m e n t

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**It gives me great pleasure in placing the Complete study pack CBSE TERM -II of chemistry for the students of class XII.**

**With the focus on equipping the learner with essential skills and granting him confidence, the present Complete study pack has been aptly designed for obtaining desired tangible output.**

**I owe a special sense of gratitude to my Parents for constant source of inspiration, support & encouragement.**

**It is hoped that this material will instill a sense of confidence among the students to heighten their proficiency in learning the subject.**

**I am sure it will be a path finder for high achievers aspiring for JEE (MAINS) & NEET.**

**It is hoped that the book will be warmly received and will prove to be beneficial to the learners.**

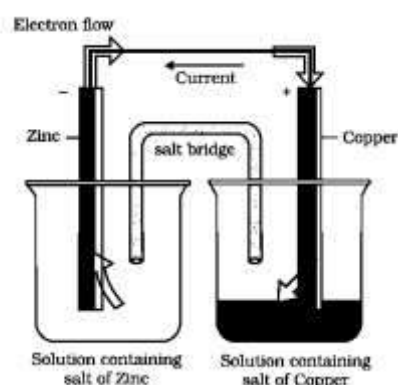
**All the Best for your coming Exams.....**

**NEERAJ AGRAWAL  
P.G.T (CHEMISTRY)**

# ELECTROCHEMISTRY

## TOPIC :ELECTROCHEMICAL CELLS NERNST EQUATION,EQUILLIBRIUM CONSTANT,& GIBBS ENERGY

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

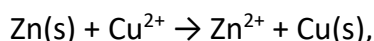


### 2. Electrochemical Cells (Daniell cell)

Reaction at **Anode (Oxidation half reaction):**  $\text{Zn(s)} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$

Reaction at **Cathode (Reduction half reaction):**  $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu(s)}$

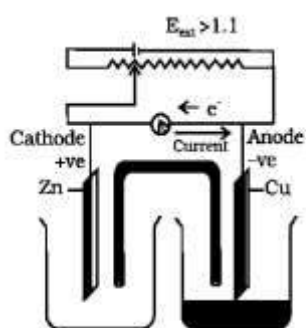
**Overall cell reaction:**



The cell can be represented as:  $\text{Zn(s)} | \text{Zn}^{2+}(\text{aq}) || \text{Cu}^{2+}(\text{aq}) | \text{Cu(s)}$

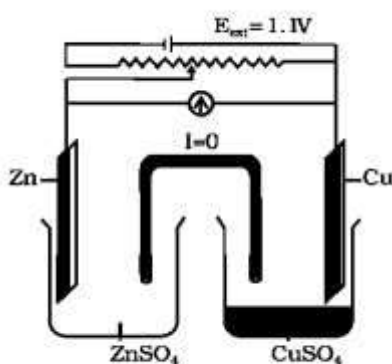
Tip to remember: **LOAN** which means **LEFT OXIDATION ANODE NEGATIVE**

3. **DANIEL CELL** converts the chemical energy liberated during the redox reaction to electrical energy and has an electrical potential equal to 1.1 V . when concentration of  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$  ions is unity. Such a device is called a **galvanic** or a **voltaic** cell.
4. **GALVANIC CELL** is an electrochemical cell that converts the chemical energy of a spontaneous redox reaction into electrical energy. In this device the Gibbs energy of the spontaneous redox reaction is converted into electrical work which may be used for running a motor or other electrical gadgets like heater, fan, geyser, etc.
5. If an external opposite potential becomes greater than  $E^\circ_{\text{cell}}$  of the reaction gets reversed and electrochemical cell now functions as an **electrolytic cell**.
- 6.



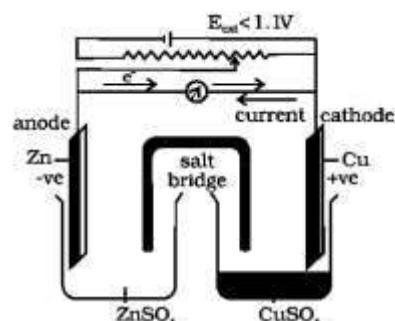
When  $E_{\text{ext}} > 1.1\text{V}$

- (i) Electrons flow from Cu to Zn and current flows from Zn to Cu.
- (ii) Zinc is deposited at the zinc electrode and copper dissolves at copper electrode.



When  $E_{\text{ext}} = 1.1\text{V}$

- (i) No flow of electrons or current.
- (ii) No chemical reaction.



When  $E_{\text{ext}} < 1.1\text{V}$

- (i) Electrons flow from Zn rod to Cu rod hence current flows from Cu to Zn.
- (ii) Zn dissolves at anode and copper deposits at cathode.

7.  $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$  or  $E^\circ_{\text{cell}} = E^\circ_{\text{right}} - E^\circ_{\text{left}}$

8. **STANDARD HYDROGEN ELECTRODE (SHE)** :It consists of a platinum wire sealed in a glass tube, The wire is coated with finely divided platinum black. Platinum black catalyze the reaction  $2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_{2(\text{ag})}$  Pure hydrogen gas at 1 atmosphere pressure is bubbled through HCl solution containing  $\text{H}^+$  ions at 1.0M concentration continuously over platinum black electrode. The temperature is 298K. **It is assigned a value of zero** for it electrode potential and is used as reference electrode.

9. **NERNST'S EQUATION** : It is a relationship that relates electrode potential and concentration of

metal ion. 
$$E_{cell} = E^{\circ}_{cell} - \frac{2.303RT}{nF} \log \theta$$

At T = 298 K substituting R=8.314 F= 96500 C,  $\left[ \frac{2.303RT}{F} = 0.059 \right]$

$$E_{cell} = E^{\circ} - \frac{0.0591}{n} \log Q \quad \text{Where } Q = \text{Reaction Quotient, Quotient}$$

$Q = \frac{[Pr\ oducts]}{[Re\ ac\ tan\ ts]}$ , n=number of electrons

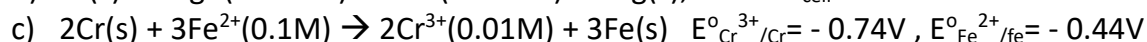
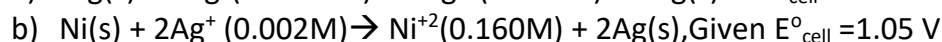
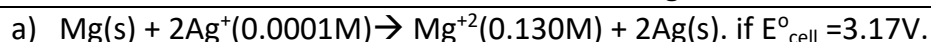
**Example:** Mg /Mg<sup>2+</sup>// Cr<sup>3+</sup>/Cr 
$$E_{cell} = E^{\circ}_{cell} - \frac{2.303RT}{6F} \log \frac{[Mg^{+2}]^3}{[Cr^{+3}]^2}$$

10. **Relation between E<sup>o</sup><sub>cell</sub> and Equilibrium constant K<sub>c</sub>** : At equilibrium Q = K<sub>c</sub> and E<sub>cell</sub> = 0

$$E_{cell} = E_{cell}^{\circ} - \frac{2.303RT}{nF} \log K_c, \quad \therefore \log K_c = \frac{E_{cell}^{\circ} \times nF}{2.303RT} = \frac{E_{cell}^{\circ} \times n}{0.059}$$

### QUESTIONS BASED ON NERNST EQUATION, EQUILIBRIUM CONSTANT, & GIBBS ENERGY

- Define Electrochemical cell. What happens when applied external opposite potential becomes greater than E<sup>o</sup><sub>cell</sub> of electrochemical cell.
- Explain the working of the galvanic cell by taking an example.
- Explain the function of the salt bridge.
- Write the Nernst equation and emf of the following cells at 298K:
  - Mg(s)/Mg<sup>2+</sup>(0.001M)//Cu<sup>2+</sup>(0.0001)/Cu(s); E<sup>o</sup><sub>Cu<sup>2+</sup>/Cu</sub> = +0.34V, E<sup>o</sup><sub>Mg<sup>2+</sup>/Mg</sub> = -2.36
  - Fe(s)/Fe<sup>2+</sup>(0.001M)//H<sup>+</sup>(1M)/H<sub>2</sub>(g)/Pt(s) E<sup>o</sup><sub>Fe<sup>2+</sup>/Fe</sub> = -0.44 V
  - Zn/Zn<sup>2+</sup>(0.1M)//Cd<sup>2+</sup>(0.01)/Cd; E<sup>o</sup><sub>Zn<sup>2+</sup>/Zn</sub> = -0.76V, E<sup>o</sup><sub>Cd<sup>2+</sup>/Cd</sub> = -0.40V
  - Cu/Cu<sup>2+</sup>(2M)//Ag<sup>+</sup>(0.05M)/Ag; E<sup>o</sup><sub>Cu<sup>2+</sup>/Cu</sub> = +0.34V, E<sup>o</sup><sub>Ag<sup>+</sup>/Ag</sub> = + 0.80V
  - Mg(s)/Mg<sup>2+</sup>(10<sup>-3</sup>M)//Cu<sup>2+</sup>(10<sup>-4</sup>M)/Cu(s); E<sup>o</sup><sub>Cu<sup>2+</sup>/Cu</sub> = +0.34V, E<sup>o</sup><sub>Mg<sup>2+</sup>/Mg</sub> = -2.36
  - Zn/Zn<sup>2+</sup>(2M)//Cu<sup>2+</sup>(0.5M)/Cu; E<sup>o</sup><sub>Zn<sup>2+</sup>/Zn</sub> = -0.76V, E<sup>o</sup><sub>Cu<sup>2+</sup>/Cu</sub> = 0.34V
  - Sn/Sn<sup>2+</sup>(0.050M)//H<sup>+</sup>(0.020M)/H<sub>2</sub>(g)/Pt(s) E<sup>o</sup><sub>Sn<sup>2+</sup>/Sn</sub> = - 0.14V
  - Sn/Sn<sup>2+</sup>(0.04M)//H<sup>+</sup>(0.02M)/H<sub>2</sub>(g)/Pt(s) E<sup>o</sup><sub>Sn<sup>2+</sup>/Sn</sub> = - 0.14V
  - Pt(s)/Br<sub>2</sub>(l)/Br<sup>-</sup>(0.010)// H<sup>+</sup>(0.030M)/H<sub>2</sub>(g)/Pt(s)
- Calculate the emf of the cell at 25°C for the following :



- The emf of the cell Zn/Zn<sup>2+</sup>(0.1M)//Cd<sup>2+</sup>(M<sub>1</sub>)/Cd has been found to be 0.3035 V at 298K. Calculate the value of M<sub>1</sub>. E<sup>o</sup><sub>Zn<sup>2+</sup>/Zn</sub> = -0.76V, E<sup>o</sup><sub>Cd<sup>2+</sup>/Cd</sub> = - 0.40V.
- Calculate the potential for half cell containing .10M K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>(aq), 0.20M Cr<sup>3+</sup>(aq) and 1.0x 10<sup>-4</sup> H<sup>+</sup>(aq), The half cell reaction is Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>(aq) + 14 H<sup>+</sup>(aq) + 6e<sup>-</sup> → 2Cr<sup>3+</sup>(aq) + 7H<sub>2</sub>O(l) and the Standard cell potential E<sup>o</sup><sub>cell</sub> = 1.33V
- How would you determine the standard electrode potential of the system Mg<sup>2+</sup>|Mg?
- Calculate the potential of hydrogen electrode in contact with a solution whose pH is 10.
- A Zinc rod is dipped in 0.1M solution of ZnSO<sub>4</sub>. The salt is 95% dissociated at this dilution at 298K. Calculate the electrode potential.
- Using the E<sup>o</sup> values of X & Y predict which is better for coating the surface of iron to prevent rust and why? E<sup>o</sup><sub>Fe<sup>2+</sup>/Fe</sub> = -0.44V, E<sup>o</sup><sub>X<sup>2+</sup>/X</sub> = -2.36V, E<sup>o</sup><sub>Y<sup>2+</sup>/Y</sub> = -0.14V
- Calculate the emf of the cell . The following chemical reaction is occurring in an electrochemical cell.  
Mg(s) + 2Ag<sup>+</sup> (0.0001 M) → Mg<sup>2+</sup>(0.10M) + 2 Ag(s) The electrode values are Mg<sup>2+</sup> / Mg = - 2. 36 V Ag<sup>+</sup> / Ag = 0.81 V. For this cell calculate / write (a) (i) E<sup>o</sup> value

- for the electrode  $2\text{Ag}^+ / \text{Ag}$  (ii) Standard cell potential  $E^\circ_{\text{cell}}$ . (b) Cell potential (E)cell (c) (i) Symbolic representation of the above cell. (ii) Will the above cell reaction be spontaneous?
13. A voltaic cell is constructed at  $25^\circ\text{C}$  with the following half cell  $\text{Ag}^+(0.001\text{M})/\text{Ag}$  and  $\text{Cu}^{2+}(0.01\text{M})/\text{Cu}$  what would be the voltage of this cell? Given  $E^\circ_{\text{Ag}^+/\text{Ag}} = +0.80\text{V}$ ,  $E^\circ_{\text{Cu}^{2+}/\text{Cu}} = +0.34\text{V}$ .
14. A Copper –silver is set up. The copper ion concentration in it is  $0.10\text{M}$ . The concentration of silver is not known. The cell potential measured  $0.422\text{V}$ . Determine the concentration of silver ion in the cell.  $E^\circ_{\text{Ag}^+/\text{Ag}} = +0.80\text{V}$ ,  $E^\circ_{\text{Cu}^{2+}/\text{Cu}} = +0.34\text{V}$ .
15. One half cell in a voltaic cell is constructed from a silver wire dipped in silver nitrate solution of unknown concentration. The other half cell consists of a zinc electrode in a  $0.10\text{M}$  solution of Zinc nitrate. A voltage of  $1.48\text{V}$  is measured for this cell. Use this information to calculate the concentration of silver nitrate solution. ( $E^\circ_{\text{Zn}^{2+}/\text{Zn}} = -0.763\text{V}$ ,  $E^\circ_{\text{Ag}^+/\text{Ag}} = +0.80\text{V}$ )
16. A voltaic cell is set up at  $25^\circ\text{C}$  With the following half cells :  $\text{Al}(\text{s})/\text{Al}^{3+}(0.001\text{M})$  and  $\text{Ni}^{2+}(0.50)/\text{Ni}(\text{s})$ , Write the equation for the cell reaction that occurs when the cell generates an electric current and determine the cell potential (given  $E^\circ_{\text{Ni}^{2+}/\text{Ni}} = -0.25\text{V}$ ,  $E^\circ_{\text{Al}^{3+}/\text{Al}} = -1.66\text{V}$ )
17. Calculate  $\Delta_r G^\circ$  & value of equilibrium constant for the following :
- $\text{Mg}(\text{s})/\text{Mg}^{2+} // \text{Cu}^{2+}/\text{Cu}(\text{s})$ ;  $E^\circ_{\text{Cu}^{2+}/\text{Cu}} = +0.34\text{V}$ ,  $E^\circ_{\text{Mg}^{2+}/\text{Mg}} = -2.36$
  - $\text{Zn}(\text{s}) + \text{Cu}^{2+} \rightleftharpoons \text{Zn}^{2+} + \text{Cu}$   $E^\circ_{\text{Cu}^{2+}/\text{Cu}} = +0.34\text{V}$ ,  $E^\circ_{\text{Zn}^{2+}/\text{Zn}} = -0.76\text{V}$
  - $\text{Cu}(\text{s}) + 2\text{Ag}^+ \rightleftharpoons \text{Cu}^{2+} + 2\text{Ag}(\text{s})$   $E^\circ_{\text{Cu}^{2+}/\text{Cu}} = +0.34\text{V}$ ,  $E^\circ_{\text{Ag}^+/\text{Ag}} = +0.80\text{V}$
  - $2\text{Fe}^{3+} + 2\text{I}^- \rightarrow 2\text{Fe}^{2+} + \text{I}_2$  has  $E^\circ_{\text{cell}} = 0.236\text{V}$
  - $\text{Fe}^{2+}(\text{aq}) + \text{Ag}^+ \rightarrow \text{Fe}^{3+}(\text{aq}) + \text{Ag}(\text{s})$ ,  $E^\circ_{\text{Ag}^+/\text{Ag}} = +0.80\text{V}$ ,  $E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} = +0.77\text{V}$
  - $2\text{Cr}(\text{s}) + 3\text{Cd}^{2+} \rightarrow 2\text{Cr}^{3+} + 3\text{Cd}(\text{s})$   $E^\circ_{\text{Cr}^{3+}/\text{Cr}} = -0.74\text{V}$ ,  $E^\circ_{\text{Cd}^{2+}/\text{Cd}} = -0.40\text{V}$
18. Calculate the equilibrium constant for the reaction Calculate the equilibrium constant for the reaction In the button cell widely used in watches and devices the following reaction takes place:  $\text{Zn}(\text{s}) + \text{Ag}_2\text{O}(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{Ag}(\text{s}) + 2\text{OH}^-(\text{aq})$  Determine  $\Delta_r G^\circ$  &  $E^\circ$  for the reaction.  $E^\circ_{\text{Zn}^{2+}/\text{Zn}} = -0.76\text{V}$ ,  $E^\circ_{\text{Ag}^+/\text{Ag}} = +0.80\text{V}$
19. Calculate emf and  $\Delta G$  for the following cell :  $\text{Mg}(\text{s})/\text{Mg}^{2+}(0.001\text{M}) // \text{Cu}^{2+}(0.0001\text{M})/\text{Cu}(\text{s})$ ;  $E^\circ_{\text{Cu}^{2+}/\text{Cu}} = +0.34\text{V}$ ,  $E^\circ_{\text{Mg}^{2+}/\text{Mg}} = -2.37\text{V}$
20. Calculate  $\Delta_r G^\circ$  for the reaction at  $25^\circ\text{C}$  :  $\text{Au}(\text{s}) + \text{Ca}^{2+}(1\text{M}) \rightarrow \text{Au}^{3+}(1\text{M}) + \text{Ca}(\text{s})$ ,  $E^\circ_{\text{Ca}^{2+}/\text{Ca}} = -2.87\text{V}$ ,  $E^\circ_{\text{Au}^{3+}/\text{Au}} = +1.50\text{V}$ . Predict whether the reaction will be spontaneous or not at  $25^\circ\text{C}$  which of the above two half cells will act as an oxidizing agent and which one will be a reducing agent?
21. Depict the galvanic cell in which the reaction:  $\text{Zn} + \text{Ag}^+ \rightarrow \text{Zn}^{2+} + 2\text{Ag}$  takes place. Further show: (a) Which of the electrode is negatively charged? (b) The carriers of the current in the cell. (c) Individual reaction at each electrode.
22. Two half cell reactions of an electrochemical cell are given below: (i)  $\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$   $E^\circ = +1.51\text{V}$  (ii)  $\text{Sn}^{2+} \rightarrow \text{Sn}^{4+} + 2\text{e}^-$   $E^\circ = +0.15\text{V}$ . Construct the redox reaction from the two half cell reaction and predict if the reaction favours formation of reactants or product shown in the reaction
23. Given the standard electrode potentials:  $\text{K}^+/\text{K} = -2.93\text{V}$ ,  $\text{Ag}^+/\text{Ag} = 0.80\text{V}$ ,  $\text{Hg}^{2+}/\text{Hg} = 0.79\text{V}$   $\text{Mg}^{2+}/\text{Mg} = -2.37\text{V}$ ,  $\text{Cr}^{3+}/\text{Cr} = -0.74\text{V}$ . Arrange these metals in their increasing order of reducing power
24. Tarnished silver contains  $\text{Ag}_2\text{S}$ . Can this tarnish be removed by placing tarnished silver ware in an aluminium pan containing an inert electrolytic solution such as  $\text{NaCl}$ . The standard electrode potential for half reaction :  $\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$  is  $-1.66$  and  $\text{Ag}_2\text{S} + 2\text{e}^- \rightarrow 2\text{Ag}^+ + \text{S}^{2-}$  is  $-0.71$

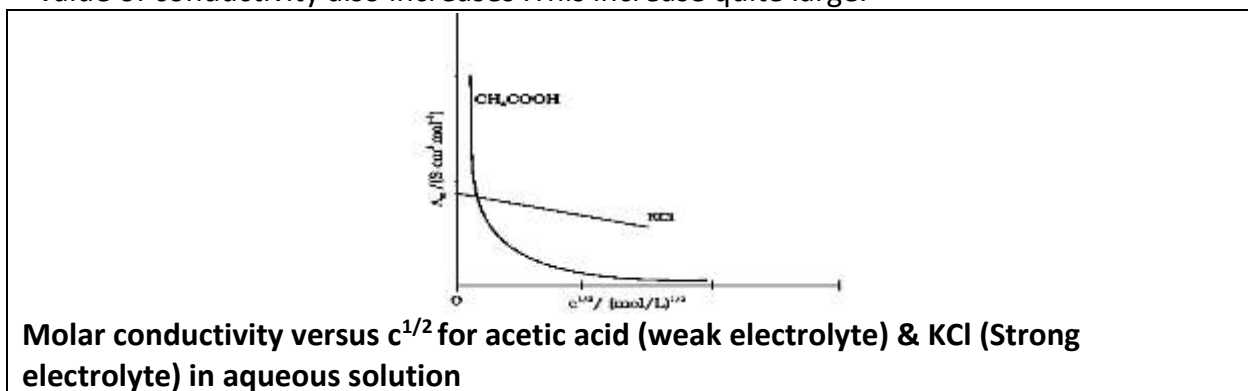
## TOPIC : CONDUCTIVITY, MOLAR CONDUCTIVITY, CELL CONSTANT, KOHLRAUSCH LAW AND ITS APPLICATION.

- Electrical conductance** through metals is called metallic or electronic conductance and is due to the movement of electrons. The electronic conductance depends on (i) the nature and structure of the metal (ii) the number of valence electrons per atom (iii) temperature (it decreases with increase of temperature)

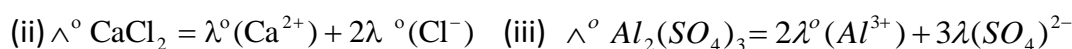
2. **Electrolytic or ionic conductance:** The conductance of electricity by ions present in the solutions is called electrolytic or ionic conductance. The conductivity of electrolytic (ionic) solutions depends on: (i) the nature of the electrolyte added (ii) size of the ions produced and their solvation (iii) the nature of the solvent and its viscosity (iv) concentration of the electrolyte (v) temperature (it increases with the increase of temperature).
3. **Resistance:** The electrical resistance is represented by the symbol 'R' and it is measured in ohm ( $\Omega$ ). The electrical resistance of any object is directly proportional to its length,  $l$ , and inversely proportional to its area of cross section,  $A$ .  $R \propto \frac{l}{A}$  or  $R = \rho \left(\frac{l}{A}\right)$  Where  $\rho$  is the constant which depends upon the nature of conductor. It is called specific resistance or resistivity. Unit is ohm-cm
4. The **resistivity** for a substance is its resistance when it is one metre long and its area of cross section is one  $\text{m}^2$ .
5. **Conductance** : The ease with which carried flows through conductor is called its conductance. It is reciprocal of the resistance  $G = \frac{1}{R}$ . The SI unit of conductance is siemens, represented by the symbol 'S' and is equal to  $\text{ohm}^{-1}$  ( $\Omega^{-1}$ ) (also known as mho).
6. **Specific Conductance or Conductivity** : of any conductor is the reciprocal of specific resistance and is denoted by  $\kappa$  (Greek work Kappa). The SI units of conductivity are  $\text{Sm}^{-1}$  but quite often,  $\kappa$  is expressed in  $\text{S cm}^{-1}$ . Conductivity of a material in  $\text{S m}^{-1}$  is its conductance when it is 1 m long and its area of cross section is  $1 \text{ m}^2$ . It may be noted that  $1 \text{ S cm}^{-1} = 100 \text{ S m}^{-1}$ .  $\kappa = \frac{1}{\rho} \Rightarrow \kappa = \frac{1}{R} \frac{l}{A} \Rightarrow \kappa = G \frac{l}{A}$  The quantity  $l/A$  is called cell constant denoted by the symbol,  $G^*$ . It depends on the distance between the electrodes and their area of cross-section and has the dimension of  $\text{length}^{-1}$  and can be calculated if we know  $l$  and  $A$ . ( $G^*(\text{cell constant}) = \frac{l}{A}$ ) The conductivity of a solution at any given concentration is the conductance of one unit volume of solution kept between two platinum electrodes with unit area of cross section and at a distance of unit length.
7. **Superconductivity:** Certain materials called superconductors by definition have zero resistivity or infinite conductivity. Earlier, only metals and their alloys at very low temperatures (0 to 15 K) were known to behave as superconductors, but nowadays a number of ceramic materials and mixed oxides are also known to show superconductivity at temperatures as high as 150 K.
8. **Molar Conductivity** : It is defined as the conducting power of all the ions produced by one gram mol of an electrolyte in a solution.  $\Lambda_m = \frac{\kappa}{C}$  In the above equation, if  $\kappa$  is expressed in  $\text{Sm}^{-1}$  and the concentration,  $c$  in  $\text{mol m}^{-3}$  then the units of  $\Lambda_m$  are in  $\text{Sm}^2\text{mol}^{-1}$
- $$\Lambda_m (\text{Sm}^2\text{mol}^{-1}) = \frac{\kappa (\text{Sm}^{-1})}{1000 (\text{Lm}^{-3}) \times \text{Molarity} (\text{molL}^{-1})}$$
- If we use  $\text{Scm}^{-1}$  as the units for  $\kappa$  and  $\text{molcm}^{-3}$ , the units of concentration, then the units for  $\Lambda_m$  are  $\text{Scm}^2 \text{mol}^{-1}$ .
- $$\Lambda_m (\text{Scm}^2\text{mol}^{-1}) = \frac{\kappa (\text{Scm}^{-1}) \times 1000 (\text{Lcm}^{-3})}{\text{Molarity} (\text{molL}^{-1})}$$
9. **Limiting molar conductivity** : When concentration approaches zero, the molar conductivity is known as limiting molar conductivity and is represented by the symbol  $\Lambda^0$
10. Conductivity of a solution decrease with dilution because on dilution the number of ions per unit volume decreases. so the conductivity decreases

11. **Variation of molar conductivity with dilution (concentration is decreased)** : The increase in conductivity of strong and weak electrolyte upon dilution is due to different reasons:

- a) **FOR STRONG ELECTROLYTES** molar conductivity increases slowly with dilution because in strong electrolytes the dissociation of the electrolyte into ions is almost complete however interionic forces are quite strong. Upon dilution ionic attractions are reduced. This leads to increase in ionic mobility thus molar conductivity increases with dilution(or decrease in concentration)
- b) **FOR WEAK ELECTROLYTES** molar conductivity increases Steeply with dilution because in weak electrolytes the dissociation of electrolyte into ions is comparatively less. Dilution helps in dissociation of electrolyte .As a result more ions are formed and corresponding value of conductivity also increases .This increase quite large.



12. **Kohlrausch's Law** : The law states that limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte. (i)  $\Lambda^{\circ} NaCl = \lambda^{\circ}(Na^{+}) + \lambda^{\circ}(Cl^{-})$



13. **Application of Kohlrausch's Law** 1. Calculation of limiting molar conductivity 2. Calculation of degree of dissociation : Degree of Dissociation is ratio of molar conductivity at a specific concentration 'C' to limiting molar conductivity. It is denoted by  $\alpha$   $\alpha = \frac{\Lambda_m^c}{\Lambda_m^{\circ}}$  3. Calculation of

dissociation constant

$$K_a = \frac{c\alpha^2}{(1-\alpha)} = \frac{c\Lambda^2}{\Lambda^{\circ}(\Lambda^{\circ} - \Lambda)}$$

### QUESTIONS BASED ON CONDUCTIVITY MOLAR CONDUCTIVITY, CELL CONSTANT, KOHLRAUSCH LAW AND ITS APPLICATION

- Define conductivity, molar conductivity & limiting molar conductivity.
- Distinguish between Electrical conductance & Electrolytic (ionic conductance)
- Express the relation among the cell constant, the resistance of the solution in the cell and the conductivity of the solution. How is the conductivity of a solution related to its molar conductivity.
- The resistance of 0.01M NaCl solution at 25°C is 200ohm. The cell constant of the conductivity cell is unity. Calculate the molar conductivity of the solution.
- The conductivity of 0.20M solution of KCl at 298 K is 0.0248S $cm^{-1}$ . Calculate its molar conductivity.
- The Molar conductivity of a 1.5M solution of an electrolyte is found to be 138.9 S $cm^2 mol^{-1}$ . Calculate the conductivity of this solution.
- The resistance of conductivity cell containing 0.001M KCl at 298K is 1500 ohm. What is cell constant if conductivity of 0.001M KCl at 298K is 0.146X 10<sup>-3</sup>S $cm^{-1}$ .



8. When a certain conductance cell was filled with 0.1M KCl solution it has resistance of 85 ohm at 25°C. When the same cell was filled with an aqueous solution of 0.052M of unknown electrolyte the resistance was 96ohm. Calculate the molar conductivity of electrolyte. The conductivity of 0.1 M solution of KCl is  $1.29 \times 10^{-2} \text{Scm}^{-1}$ .
9. Resistance of conductivity cell filled with  $0.1 \text{molL}^{-1}$  KCl solution is 100 ohm. If the resistance of the same cell when filled with  $0.02 \text{molL}^{-1}$  KCl solution is 520 ohm. Calculate the conductivity & molar conductivity of  $0.02 \text{molL}^{-1}$  KCl solution. The conductivity of  $0.1 \text{molL}^{-1}$  solution of KCl is  $1.29 \text{Sm}^{-1}$ .
10. Resistance of conductivity cell filled with  $0.1 \text{molL}^{-1}$  KCl solution is 100 ohm. If the resistance of the same cell when filled with  $0.02 \text{molL}^{-1}$  KCl solution is 520 ohm. Calculate the conductivity & molar conductivity of  $0.02 \text{molL}^{-1}$  KCl solution. The conductivity of  $0.1 \text{molL}^{-1}$  solution of KCl is  $1.29 \text{Sm}^{-1}$ .
11. The electrical resistance of a column of  $0.05 \text{molL}^{-1}$  NaOH solution of diameter 1 cm and length 50 cm is  $5.55 \times 10^3$  ohm. Calculate its resistivity, conductivity & molar conductivity.
12. State Kohlrausch law and its application. Limiting molar conductivity of NaCl, HCl and NaAc are 126.4, 425.9 & 91  $\text{Scm}^2 \text{mol}^{-1}$ . Calculate Limiting molar conductivity of HAC.
13. Define the term degree of dissociation. Write an expression that relates the molar conductivity of a weak electrolyte to its degree of dissociation.
14. Calculate the degree of dissociation of acetic at 298K, given that  $\Lambda_{\text{m}(\text{CH}_3\text{COOH})} = 11.7 \text{Scm}^2 \text{mol}^{-1}$ ,  $\Lambda_{\text{m}(\text{CH}_3\text{COO}^-)} = 40.9 \text{Scm}^2 \text{mol}^{-1}$ ,  $\Lambda_{\text{m}(\text{H}^+)} = 349.1 \text{Scm}^2 \text{mol}^{-1}$
15. Conductivity of 0.00241M acetic acid is  $7.896 \times 10^{-6} \text{S cm}^{-1}$ . Calculate its molar conductivity. If  $\Lambda^0$  for acetic acid is  $390.5 \text{S cm}^2 \text{mol}^{-1}$ . What is its dissociation constant?
16. Conductivity of 0.001028 M acetic acid is  $4.95 \times 10^{-5} \text{S cm}^{-1}$ . Calculate its molar conductivity. If  $\Lambda^0$  for acetic acid is  $390.5 \text{S cm}^2 \text{mol}^{-1}$ . What is its dissociation constant?
17. The molar Conductivity of  $0.025 \text{molL}^{-1}$  methanoic acid is  $46.1 \text{S cm}^2 \text{mol}^{-1}$ . Calculate its degree of dissociation & dissociation constant. If  $\lambda^0(\text{H}^+)$  is  $349.6 \text{S cm}^2 \text{mol}^{-1}$  and  $\lambda^0(\text{HCOO}^-) = 54.6 \text{S cm}^2 \text{mol}^{-1}$ .
18. How do you account for molar conductivity of strong and weak electrolyte with concentration? Plot the graphs also.
19. Why does the conductivity of a solution decrease with dilution?

### TOPIC: PRODUCTS OF ELECTROLYSIS

Products of electrolysis depend on the nature of material being electrolysed and the type of electrodes being used. If the electrode is inert (e.g., Pt or Gold), it does not participate in the chemical reaction and acts only as source or sink for electrons. On the other hand, if the electrode is reactive, it participates in the electrode reaction. Thus, the products of electrolysis may be different for reactive and inert electrodes. The products of electrolysis depend on the different oxidizing and reducing species present in the electrolytic cell and their standard electrode potentials. Moreover, some of the electrochemical processes although feasible, are so slow kinetically that at lower voltages these don't seem to take place and extra potential (called *overpotential*) has to be applied, which makes such process more difficult to occur.

**Note: (i) The reaction at a Cathode with higher value of  $E_{red}^o$  is preferred (ii) The reaction at anode with lower value of  $E_{red}^o$  is preferred**

S.No	Electrolysis of	CATHODE	ANODE
1	Aqueous solution of $\text{AgNO}_3$ with silver electrodes	Ag metal ( $\text{Ag}^+$ are discharged compared to $\text{H}^+$ as its $E_{red}^o$ is higher)	$\text{Ag}^+$ ions (Silver electrode being reactive dissolves to produce $\text{Ag}^+$ ions)
S.No	Electrolysis of	CATHODE	ANODE
2	Aqueous solution of $\text{AgNO}_3$ with platinum electrodes	Ag metal ( $\text{Ag}^+$ are discharged compared to $\text{H}^+$ as its $E_{red}^o$ is	$\text{O}_2$ gas ( $\text{OH}^-$ ions discharged compared to

		higher)	$\text{NO}_3^-$ as its $E_{red}^{\circ}$ is lower)
3	Aqueous solution of $\text{CuCl}_2$ with platinum electrodes	Copper metal	$\text{Cl}_2$ gas
4	Molten $\text{NaCl}$	Sodium metal	$\text{Cl}_2$ gas
5	Aqueous sodium chloride solution	$\text{H}_2$ gas	$\text{Cl}_2$ gas
6	Dilute Sulphuric acid with platinum electrodes	$\text{H}_2$ gas	$\text{O}_2$ gas
7	Copper sulphate using inert electrodes (Pt)	Copper metal	$\text{O}_2$ gas
8	Aqueous sodium bromide	$\text{H}_2$ gas	$\text{Br}_2$ gas

### QUESTIONS BASED ON PRODUCTS OF ELECTROLYSIS

- Predict the products of electrolysis: (a) An aq. Solution of  $\text{AgNO}_3$  with silver electrodes. (b) An aq. Solution of  $\text{AgNO}_3$  with platinum electrodes. (c). An aq. Solution of  $\text{H}_2\text{SO}_4$  with platinum electrodes. (d). An aq. Solution of  $\text{CuCl}_2$  with platinum electrodes. (e) Aqueous sodium bromide (f) Copper sulphate using inert electrodes (Pt) (g) Molten  $\text{NaCl}$  (h) Aqueous sodium chloride solution
- Following reactions occur at cathode during electrolysis of Aqueous solution of  $\text{AgCl}$  solution: (a)  $\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s})$   $E^{\circ} = +0.80\text{V}$  (b)  $\text{H}^+(\text{aq}) + \text{e}^- \rightarrow \text{H}_2(\text{s})$   $E^{\circ} = 0.00\text{V}$  on the basis of their standard electrode potential values which reaction is feasible at the cathode and why?
- During electrolysis of Aqueous solution of  $\text{NaBr}$  solution there are two possible reactions (a)  $2\text{H}_2\text{O}(\text{l}) \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$   $E^{\circ} = +1.23\text{V}$  (b)  $2\text{Br}^-(\text{aq}) \rightarrow \text{Br}_2(\text{s}) + 2\text{e}^-$   $E^{\circ} = 1.08\text{V}$  on the basis of their standard electrode potential values which reaction is feasible at the anode and why?

**KEEP ON ENJOYING AND LOVING CHEMISTRY**

**IMPORTANT QUESTIONS FOR TERM -2 ELECTROCHEMISTRY**

- Define Electrochemical cell. What happens when applied external opposite potential becomes greater than  $E^{\circ}_{\text{cell}}$  of electrochemical cell.
- Explain the working of the galvanic cell by taking an example.
- Explain the function of the salt bridge.
- Which reference electrode is used to measure the electrode potential of other electrodes?
- Write the Nernst equation for the cell reaction in the Daniel cell. How will the  $E_{\text{cell}}$  be affected when concentration of  $\text{Zn}^{2+}$  ions is increased?
- Consider a cell given below  $\text{Cu} | \text{Cu}^{2+} || \text{Cl}^- | \text{Cl}_2, \text{Pt}$  Write the reactions that occur at anode and cathode
- A galvanic cell has electrical potential of 1.1V. If an opposing potential of 1.1V is applied to this cell, what will happen to the cell reaction and current flowing through the cell?
- Write the Nernst equation and emf of the following cells at 298K:
  - $\text{Mg(s)} / \text{Mg}^{2+}(0.001\text{M}) // \text{Cu}^{2+}(0.0001) / \text{Cu(s)}$ ;  $E^{\circ}_{\text{Cu}^{2+}/\text{Cu}} = +0.34\text{V}$ ,  $E^{\circ}_{\text{Mg}^{2+}/\text{Mg}} = -2.36$
  - $\text{Fe(s)} / \text{Fe}^{2+}(0.001\text{M}) // \text{H}^+(1\text{M}) / \text{H}_2(\text{g}) / \text{Pt(s)}$   $E^{\circ}_{\text{Fe}^{2+}/\text{Fe}} = -0.44\text{V}$
  - $\text{Zn/Zn}^{2+}(0.1\text{M}) // \text{Cd}^{2+}(0.01) / \text{Cd}$ ;  $E^{\circ}_{\text{Zn}^{2+}/\text{Zn}} = -0.76\text{V}$ ,  $E^{\circ}_{\text{Cd}^{2+}/\text{Cd}} = -0.40\text{V}$
  - $\text{Cu/Cu}^{2+}(2\text{M}) // \text{Ag}^+(0.05\text{M}) / \text{Ag}$ ;  $E^{\circ}_{\text{Cu}^{2+}/\text{Cu}} = +0.34\text{V}$ ,  $E^{\circ}_{\text{Ag}^+/\text{Ag}} = +0.80\text{V}$
  - $\text{Mg(s)} / \text{Mg}^{2+}(10^{-3}\text{M}) // \text{Cu}^{2+}(10^{-4}\text{M}) / \text{Cu(s)}$ ;  $E^{\circ}_{\text{Cu}^{2+}/\text{Cu}} = +0.34\text{V}$ ,  $E^{\circ}_{\text{Mg}^{2+}/\text{Mg}} = -2.36$
  - $\text{Zn/Zn}^{2+}(2\text{M}) // \text{Cu}^{2+}(0.5\text{M}) / \text{Cu}$ ;  $E^{\circ}_{\text{Zn}^{2+}/\text{Zn}} = -0.76\text{V}$ ,  $E^{\circ}_{\text{Cu}^{2+}/\text{Cu}} = 0.34\text{V}$
  - $\text{Sn/Sn}^{2+}(0.050\text{M}) // \text{H}^+(0.020\text{M}) / \text{H}_2(\text{g}) / \text{Pt(s)}$   $E^{\circ}_{\text{Sn}^{2+}/\text{Sn}} = -0.14\text{V}$
  - $\text{Sn/Sn}^{2+}(0.04\text{M}) // \text{H}^+(0.02\text{M}) / \text{H}_2(\text{g}) / \text{Pt(s)}$   $E^{\circ}_{\text{Sn}^{2+}/\text{Sn}} = -0.14\text{V}$
  - $\text{Pt(s)} / \text{Br}_2(\text{l}) / \text{Br}^-(0.010) // \text{H}^+(0.030\text{M}) / \text{H}_2(\text{g}) / \text{Pt(s)}$
- Calculate the emf of the cell at 25°C for the following :
  - $\text{Mg(s)} + 2\text{Ag}^+(0.0001\text{M}) \rightarrow \text{Mg}^{2+}(0.130\text{M}) + 2\text{Ag(s)}$ . if  $E^{\circ}_{\text{cell}} = 3.17\text{V}$ .
  - $\text{Ni(s)} + 2\text{Ag}^+(0.002\text{M}) \rightarrow \text{Ni}^{2+}(0.160\text{M}) + 2\text{Ag(s)}$ , Given  $E^{\circ}_{\text{cell}} = 1.05\text{V}$
  - $2\text{Cr(s)} + 3\text{Fe}^{2+}(0.1\text{M}) \rightarrow 2\text{Cr}^{3+}(0.01\text{M}) + 3\text{Fe(s)}$   $E^{\circ}_{\text{Cr}^{3+}/\text{Cr}} = -0.74\text{V}$ ,  $E^{\circ}_{\text{Fe}^{2+}/\text{Fe}} = -0.44\text{V}$
- The emf of the cell  $\text{Zn/Zn}^{2+}(0.1\text{M}) // \text{Cd}^{2+}(M_1) / \text{Cd}$  has been found to be 0.3035 V at 298K. Calculate the value of  $M_1$ .  $E^{\circ}_{\text{Zn}^{2+}/\text{Zn}} = -0.76\text{V}$ ,  $E^{\circ}_{\text{Cd}^{2+}/\text{Cd}} = -0.40\text{V}$ .
- Calculate the potential for half cell containing .10M  $\text{K}_2\text{Cr}_2\text{O}_7(\text{aq})$ , 0.20M  $\text{Cr}^{3+}(\text{aq})$  and  $1.0 \times 10^{-4}\text{H}^+(\text{aq})$ , The half cell reaction is  $\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 6\text{e}^- \rightarrow 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l})$  and the Standard cell potential  $E^{\circ}_{\text{cell}} = 1.33\text{V}$
- How would you determine the standard electrode potential of the system  $\text{Mg}^{2+} | \text{Mg}$ ?
- Calculate the potential of hydrogen electrode in contact with a solution whose pH is 10.
- A Zinc rod is dipped in 0.1M solution of  $\text{ZnSO}_4$ . The salt is 95% dissociated at this dilution at 298K. Calculate the electrode potential.
- Using the  $E^{\circ}$  values of X & Y predict which is better for coating the surface of iron to prevent rust and why?  $E^{\circ}_{\text{Fe}^{2+}/\text{Fe}} = -0.44\text{V}$ ,  $E^{\circ}_{\text{X}^{2+}/\text{X}} = -2.36\text{V}$ ,  $E^{\circ}_{\text{Y}^{2+}/\text{Y}} = -0.14\text{V}$
- Calculate the emf of the cell . The following chemical reaction is occurring in an electrochemical cell.  $\text{Mg(s)} + 2\text{Ag}^+(0.0001\text{M}) \rightarrow \text{Mg}^{2+}(0.10\text{M}) + 2\text{Ag(s)}$  The electrode values are  $\text{Mg}^{2+} / \text{Mg} = -2.36\text{V}$   $\text{Ag}^+ / \text{Ag} = 0.81\text{V}$ . For this cell calculate / write (a) (i)  $E^{\circ}$  value for the electrode  $2\text{Ag}^+ / \text{Ag}$  (ii) Standard cell potential  $E^{\circ}_{\text{cell}}$ . (b) Cell potential (E)cell (c) (i) Symbolic representation of the above cell. (ii) Will the above cell reaction be spontaneous?
- A voltaic cell is constructed at 25°C with the following half cell  $\text{Ag}^+(0.001\text{M}) / \text{Ag}$  and  $\text{Cu}^{2+}(0.01\text{M}) / \text{Cu}$  what would be the voltage of this cell? Given  $E^{\circ}_{\text{Ag}^+/\text{Ag}} = +0.80\text{V}$ ,  $E^{\circ}_{\text{Cu}^{2+}/\text{Cu}} = +0.34\text{V}$ .
- A Copper –silver is set up. The copper ion concentration in its is 0.10M. The concentration of silver is not known. The cell potential measured 0.422V. Determine the concentration of silver ion in the cell.  $E^{\circ}_{\text{Ag}^+/\text{Ag}} = +0.80\text{V}$ ,  $E^{\circ}_{\text{Cu}^{2+}/\text{Cu}} = +0.34\text{V}$ .
- One half cell in a voltaic cell is constructed from a silver wire dipped in silver nitrate solution of unknown concentration . The other half cell consists of a zinc electrode in a 0.10M solution of

- Zinc nitrate .A voltage of 1.48V is measured for this cell.Use this information to calculate the concentration of silver nitrate solution.(  $E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} = -0.763\text{V}$ ,  $E_{\text{Ag}^{+}/\text{Ag}}^{\circ} = + 0.80\text{V}$ )
20. A voltaic cell is set up at 25°C With the following half cells :Al(s)/Al<sup>3+</sup>(0.001M) and Ni<sup>2+</sup>(0.50)/Ni(s) ,Write the equation for the cell reaction that occurs when the cell generates an electric current and determine the cell potential (given  $E_{\text{Ni}^{2+}/\text{Ni}}^{\circ} = -0.25\text{V}$ ,  $E_{\text{Al}^{3+}/\text{Al}}^{\circ} = -1.66\text{V}$ )
  21. What is the relationship between Gibbs free energy of the cell reaction in a galvanic cell and the emf of the cell? When will the maximum work be obtained from a galvanic cell?
  22. Calculate  $\Delta_r G^{\circ}$  & value of equilibrium constant for the following :
    - a) Mg(s)/Mg<sup>2+</sup>//Cu<sup>2+</sup>/Cu(s);  $E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} = +0.34\text{V}$ ,  $E_{\text{Mg}^{2+}/\text{Mg}}^{\circ} = -2.36$
    - a) Zn(s) + Cu<sup>2+</sup>  $\rightleftharpoons$  Zn<sup>2+</sup> + Cu  $E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} = +0.34\text{V}$ ,  $E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} = -0.76\text{V}$
    - b) Cu (s) + 2Ag<sup>+</sup>  $\rightleftharpoons$  Cu<sup>2+</sup> + 2Ag(s)  $E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} = +0.34\text{V}$ ,  $E_{\text{Ag}^{+}/\text{Ag}}^{\circ} = + 0.80\text{V}$
    - c) 2Fe<sup>3+</sup> + 2I<sup>-</sup>  $\rightarrow$  2Fe<sup>2+</sup> + I<sub>2</sub> has  $E_{\text{cell}}^{\circ} = 0.236\text{V}$
    - d) Fe<sup>2+</sup>(aq) + Ag<sup>+</sup>  $\rightarrow$  Fe<sup>3+</sup>(aq) + Ag(s),  $E_{\text{Ag}^{+}/\text{Ag}}^{\circ} = + 0.80\text{V}$ ,  $E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{\circ} = +0.77\text{V}$
    - e) 2Cr(s) + 3Cd<sup>2+</sup>  $\rightarrow$  2Cr<sup>3+</sup> + 3Cd(s)  $E_{\text{Cr}^{3+}/\text{Cr}}^{\circ} = - 0.74\text{V}$  ,  $E_{\text{Cd}^{2+}/\text{Cd}}^{\circ} = - 0.40\text{V}$
  23. Calculate the equilibrium constant for the reaction Calculate the equilibrium constant for the reaction In the button cell widely used in watches and devices the following reaction takes place: Zn (s)+ Ag<sub>2</sub>O(s) + H<sub>2</sub>O(l)  $\rightarrow$  Zn<sup>2+</sup>(aq) + 2 Ag(s) + 2OH<sup>-</sup> (aq) Determine  $\Delta_r G^{\circ}$  &  $E^{\circ}$  for the reaction.  $E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} = -0.76\text{V}$ ,  $E_{\text{Ag}^{+}/\text{Ag}}^{\circ} = + 0.80\text{V}$
  24. Calculate emf and  $\Delta G$  for the following cell : Mg(s)/Mg<sup>2+</sup>(0.001M)//Cu<sup>2+</sup>(0.0001M)/Cu(s);  $E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} = +0.34\text{V}$ ,  $E_{\text{Mg}^{2+}/\text{Mg}}^{\circ} = -2.37\text{V}$
  25. Calculate  $\Delta_r G^{\circ}$  for the reaction at 25°C :Au(s) +Ca<sup>2+</sup> (1 M)  $\rightarrow$  Au<sup>3+</sup>(1M) + Ca (s) ,  $E_{\text{Ca}^{2+}/\text{Ca}}^{\circ} = -2.87\text{V}$ ,  $E_{\text{Au}^{3+}/\text{Au}}^{\circ} = +1.50\text{V}$ . Predict whether the reaction will be spontaneous or not at 25°C which of the above two half cells will act as an oxidizing agent and which one will be a reducing agent?
  26. Depict the galvanic cell in which the reaction:Zn+Ag<sup>+</sup> $\rightarrow$ Zn<sup>2+</sup>+2Ag takes place. Further show:(a)Which of the electrode is negatively charged?(b)The carriers of the current in the cell. (c)Individual reaction at each electrode.
  27. Two half cell reactions of an electrochemical cell are given below:
    - (i)MnO<sub>4</sub><sup>-</sup> + 8 H<sup>+</sup> + 5 e<sup>-</sup>  $\rightarrow$  Mn<sup>2+</sup> + 4 H<sub>2</sub>O  $E^{\circ} = +1.51\text{V}$
    - (ii)Sn<sup>2+</sup>  $\rightarrow$  Sn<sup>4+</sup> + 2e<sup>-</sup>  $E^{\circ} = +0.15\text{V}$ . Construct the redox reaction from the two half cell reaction and predict if the reaction favours formation of reactants or product shown in the reaction
  28. Given the standard electrode potentials,:K<sup>+</sup>/K = -2.93V, Ag<sup>+</sup>/Ag = 0.80V, Hg<sup>2+</sup>/Hg = 0.79V Mg<sup>2+</sup>/Mg = -2.37 V, Cr<sup>3+</sup>/Cr = - 0.74V.Arrange these metals in their increasing order of reducing power
  29. Tarnished silver contains Ag<sub>2</sub>S. Can this tarnish be removed by placing tarnished silver ware in an aluminium pan containing an inert electrolytic solution such as NaCl. The standard electrode potential for half reaction : Al<sup>3+</sup> + 3e  $\rightarrow$  Al is -1.66 and Ag<sub>2</sub>S + 2e  $\rightarrow$  2Ag<sup>+</sup> + S<sup>2-</sup> is -0.71
  30. Define conductivity, molar conductivity & limiting molar conductivity.
  31. Distinguish between Electrical conductance & Electrolytic (ionic conductance)
  32. Express the relation among the cell constant ,the resistance of the solution in the cell and the conductivity of the solution .How is the conductivity of a solution related to its molar conductivity.
  33. The resistance of 0.01M NaCl solution at 25°C is 200ohm.The cell constant of the conductivity cell is unity .calculate the molar conductivity of the solution.
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  36. The resistance of conductivity cell containing 0.001M KCl at 298K is 1500 ohm. What is cell constant if conductivity of 0.001M KCl at 298K is 0.146X 10<sup>-3</sup>S cm<sup>-1</sup>.

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38. Resistance of conductivity cell filled with  $0.1 \text{molL}^{-1}$  KCl solution is 100 ohm. If the resistance of the same cell when filled with  $0.02 \text{molL}^{-1}$  KCl solution is 520 ohm. Calculate the conductivity & molar conductivity of  $0.02 \text{molL}^{-1}$  KCl solution. The conductivity of  $0.1 \text{molL}^{-1}$  solution of KCl is  $1.29 \text{Sm}^{-1}$ .
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41. State Kohlrausch law and its application. Limiting molar conductivity of NaCl, HCl and NaAc are 126.4, 425.9 & 91  $\text{Scm}^2 \text{mol}^{-1}$ . Calculate Limiting molar conductivity of HAC.
42. Define the term degree of dissociation. Write an expression that relates the molar conductivity of a weak electrolyte to its degree of dissociation.
43. Calculate the degree of dissociation of acetic at 298K, given that  $\Lambda_{\text{m}(\text{CH}_3\text{COOH})} = 11.7 \text{Scm}^2 \text{mol}^{-1}$ ,  $\Lambda_{\text{m}(\text{CH}_3\text{COO}^-)} = 40.9 \text{Scm}^2 \text{mol}^{-1}$ ,  $\Lambda_{\text{m}(\text{H}^+)} = 349.1 \text{Scm}^2 \text{mol}^{-1}$
44. Conductivity of 0.00241M acetic acid is  $7.896 \times 10^{-6} \text{S cm}^{-1}$ . Calculate its molar conductivity. If  $\Lambda^0$  for acetic acid is  $390.5 \text{S cm}^2 \text{mol}^{-1}$ . What is its dissociation constant?
45. Conductivity of 0.001028 M acetic acid is  $4.95 \times 10^{-5} \text{S cm}^{-1}$ . Calculate its molar conductivity. If  $\Lambda^0$  for acetic acid is  $390.5 \text{S cm}^2 \text{mol}^{-1}$ . What is its dissociation constant?
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47. How do you account for molar conductivity of strong and weak electrolyte with concentration? Plot the graphs also.
48. Why on dilution the  $\Lambda_{\text{m}}$  of  $\text{CH}_3\text{COOH}$  increases drastically, while that of  $\text{CH}_3\text{COONa}$  increases gradually?
49. Solutions of two electrolytes 'A' and 'B' are diluted. The  $\Lambda_{\text{m}}$  of 'B' increases 1.5 times while that of A increases 25 times. Which of the two is a strong electrolyte? Justify your answer.
50. In an aqueous solution how does specific conductivity of electrolytes change with addition of water?
51. Why does the conductivity of a solution decrease with dilution?
52. Predict the products of electrolysis: (a) An aq. Solution of  $\text{AgNO}_3$  with silver electrodes. (b) An aq. Solution of  $\text{AgNO}_3$  with platinum electrodes. (c). An aq. Solution of  $\text{H}_2\text{SO}_4$  with platinum electrodes. (d). An aq. Solution of  $\text{CuCl}_2$  with platinum electrodes. (e) Aqueous sodium bromide (f) Copper sulphate using inert electrodes (Pt) (g) Molten NaCl (h) Aqueous sodium chloride solution
53. How will the pH of brine (aq. NaCl solution) be affected when it is electrolysed?
54. Following reactions occur at cathode during electrolysis of Aqueous solution of AgCl solution:  
 (a)  $\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s})$   $E^0 = +0.80\text{V}$  (b)  $\text{H}^+(\text{aq}) + \text{e}^- \rightarrow \text{H}_2(\text{s})$   $E^0 = 0.00\text{V}$  on the basis of their standard electrode potential values which reaction is feasible at the cathode and why?
55. During electrolysis of Aqueous solution of NaBr solution there are two possible reactions  
 (a)  $2\text{H}_2\text{O}(\text{l}) \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$   $E^0 = +1.23\text{V}$  (b)  $2 \text{Br}^-(\text{aq}) \rightarrow \text{Br}_2(\text{s}) + 2\text{e}^-$   $E^0 = 1.08 \text{V}$  on the basis of their standard electrode potential values which reaction is feasible at the anode and why?

## CHEMICAL KINETICS

**TOPIC : RATE OF REACTION AVERAGE RATE OF REACTION, INSTANTANEOUS RATE OF REACTION RATE LAW, RATE CONSTANT, ORDER OF REACTION, MOLECULARITY & UNITS OF RATE CONSTANTS**

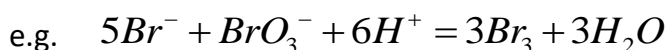
- CHEMICAL KINETICS** : The branch of chemistry, which deals with the study of reaction rates and their mechanisms, called **chemical kinetics**. The word kinetics is derived from the Greek word 'kinesis' meaning movement. chemical kinetics tells about the rate of a reaction
- RATE OF REACTION**: The rate of a reaction can be defined as the change in concentration of a reactant or product in unit time. To be more specific, it can be expressed in terms of: (i) the rate of decrease in concentration of any one of the reactants, or (ii) the rate of increase in concentration of any one of the products.
- AVERAGE RATE OF REACTION** : It is the appearance of products or disappearance of reactants over a long time interval : Consider a reaction:  $aA + bB \rightarrow cC + dD$

$$R_{av} = -\frac{1}{a} \frac{\Delta[A]}{\Delta t} = -\frac{1}{b} \frac{\Delta[B]}{\Delta t} = +\frac{1}{c} \frac{\Delta[C]}{\Delta t} = +\frac{1}{d} \frac{\Delta[D]}{\Delta t}$$

- *Negative sign indicates that the concentration of reactant is decreasing & positive sign indicates that the concentration of product is increasing*

- INSTANTANEOUS RATE OF REACTION** : It is defined as the change in concentration of any one of the reactants or products at that particular instant of time. Consider a reaction:  $aA + bB \rightarrow cC + dD$

$$R_{ins} = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = +\frac{1}{c} \frac{d[C]}{dt} = +\frac{1}{d} \frac{d[D]}{dt}$$



$$R_{ins} = -\frac{1}{5} \frac{d(Br^-)}{dt} = -\frac{d(BrO_3^-)}{dt} = -\frac{1}{6} \frac{d(H^+)}{dt} = +\frac{1}{3} \frac{d(Br_2)}{dt}$$

- UNITS OF RATE OF A REACTION**: The units of rate are concentration time<sup>-1</sup>. For example, if concentration is in mol L<sup>-1</sup> and time is in seconds then the units will be mol L<sup>-1</sup>s<sup>-1</sup>. However, in gaseous reactions, when the concentration of gases is expressed in terms of their partial pressures, then the units of the rate equation will be atm s<sup>-1</sup>
- FACTORS INFLUENCING RATE OF A REACTION**: (a) concentration of reactants (pressure in case of gases) (b) Surface area of reactants (c) temperature (d) catalyst
- RATE LAW** : Consider a reaction:  $aA + bB \rightarrow cC + dD$

Rate  $\propto [A]^x[B]^y \rightarrow$  Rate =  $K[A]^x[B]^y$  (Note: The value of x & y may and may not be equal to a &

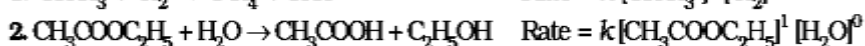
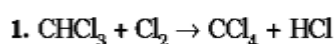
b)  $\rightarrow \frac{-dR}{dt} = K[A]^x[B]^y$ , This form of equation is known as differential rate equation, where k is

a proportionality constant called rate constant.

**Statement:** Rate law is the expression in which reaction rate is given in terms of molar concentration of reactants with each term raised to some power, which may or may not be same as the stoichiometric coefficient of the reacting species in a balanced chemical equation..

- RATE CONSTANT** may be defined as the rate of reaction when the concentration of each reactant in the reaction is unity.
- Rate law for any reaction cannot be predicted by merely looking at the balanced chemical equation, i.e., theoretically but must be determined experimentally.

Reaction	Experimental rate expression
1. $CHCl_3 + Cl_2 \rightarrow CCl_4 + HCl$	Rate = $k [CHCl_3] [Cl_2]^{1/2}$
2. $CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$	Rate = $k [CH_3COOC_2H_5]^1 [H_2O]^0$



- ORDER OF REACTION**: The sum of powers of the concentration of the reactants in the rate law expression is called the order of that chemical reaction. Order of a reaction is an experimental quantity.

Consider a reaction:  $aA + bB \rightarrow cC + dD$ , Rate =  $K[A]^x[B]^y$  **Order of Reaction = x + y**

Order of a reaction can be 0, 1, 2, 3 and even a fraction

11. **ELEMENTARY & COMPLEX REACTIONS:** A balanced chemical equation never gives us a true picture of how a reaction takes place since rarely a reaction gets completed in one step. The reactions taking place in one step are called **elementary reactions**. When a sequence of elementary reactions (called mechanism) gives us the products, the reactions are called **complex reactions**.
12. **UNITS OF RATE CONSTANT (K)=**  $(\text{Conc})^{1-n} \text{Time}^{-1}$  where n is order of reaction, Taking SI units of concentration,  $\text{mol L}^{-1}$  and time, s, the units of  $k = (\text{mol L}^{-1})^{1-n} \text{s}^{-1}$  where n is order of reaction  
For example

Reaction	Order	Unit
Zero order of reaction	0	$K = \text{mol L}^{-1} \text{s}^{-1}$
First order of reaction	1	$K = \text{Sec}^{-1}$
Second order of reaction	2	$K = \text{mol}^{-1} \text{L Sec}^{-1}$

13. **MOLECULARITY OF A REACTION:** The number of reacting species (atoms, ions or molecules) taking part in an elementary reaction, which must collide simultaneously in order to bring about a chemical reaction is called molecularity of a reaction.
- **Unimolecular Reaction:** When one reacting species is involved, for example, decomposition of ammonium nitrite.  $\text{NH}_4\text{NO}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$
  - **Bimolecular Reactions:** When two reacting species involve simultaneous collision, for example, dissociation of hydrogen iodide.  $2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$
  - **Trimolecular Reactions** involve simultaneous collision between three reacting species, for example,  $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$
  - **Note: The molecularity greater than three is not observed.** Because the probability that more than three molecules can collide and react simultaneously is very small.
  - **Molecularity Cannot Be Zero Or A Non Integer.**
14. **RATE DETERMINING STEP:** The overall rate of the reaction is controlled by the slowest step in a reaction called the **rate determining step**. Like for example, chances to win the relay race competition by a team depend upon the slowest person in the team.  
Consider the decomposition of hydrogen peroxide which is catalysed by iodide ion in an alkaline medium
- $$2\text{H}_2\text{O}_2 \xrightarrow{\Gamma, \text{Alkaline}} 2\text{H}_2\text{O} + \text{O}_2, \text{Rate} = \frac{-d[\text{H}_2\text{O}_2]}{dt} = K[\text{H}_2\text{O}_2][\Gamma^-]$$
- Mechanism:** Evidences suggest that this reaction takes place in two steps (i)  $\text{H}_2\text{O}_2 + \Gamma^- \rightarrow \text{H}_2\text{O} + \text{IO}^-$  (**slow**) (ii)  $\text{H}_2\text{O}_2 + \text{IO}^- \rightarrow \text{H}_2\text{O} + \Gamma^- + \text{O}_2$

**Question based on Rate of Reaction Average rate of reaction, Instantaneous rate of reaction Rate law, rate constant, order of reaction, Molecularity & units of rate constants**

1. Define the term rate of reaction.
2. Explain the difference between average rate & Instantaneous rate of reaction
3. For the reaction  $\text{R} \rightarrow \text{P}$ , the concentration of a reactant changes from 0.03M to 0.02M in 25 minutes. Calculate the average rate of reaction using units of time both in minutes and seconds.
4. In a reaction  $2\text{A} \rightarrow \text{Products}$ , the concentration of A decreases from  $0.5 \text{ mol L}^{-1}$  to  $0.4 \text{ mol L}^{-1}$  in 10 minutes. Calculate the rate during this interval?
5. For the reaction  $2\text{N}_2\text{O}_5(\text{g}) \rightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$  the rate of formation of  $\text{NO}_2(\text{g})$  is  $2.8 \times 10^{-3} \text{ Ms}^{-1}$ . Calculate the rate of disappearance of  $\text{N}_2\text{O}_5(\text{g})$
6. For the reaction  $\text{H}_2 + \text{Cl}_2 \rightarrow 2 \text{HCl}$ , Rate = k, Write the order, Molecularity & unit of k.
7. For the reaction  $2\text{NH}_3 \rightarrow \text{N}_2 + 3\text{H}_2$  Rate = k, Write the order, Molecularity & unit of k.

8. The decomposition of  $\text{N}_2\text{O}_5$  in  $\text{CCl}_4$  at 318K has been studied by monitoring the concentration of  $\text{N}_2\text{O}_5$  in the solution. Initially the concentration of  $\text{N}_2\text{O}_5$  is  $2.33 \text{ mol L}^{-1}$  and after 184 minutes, it is reduced to  $2.08 \text{ mol L}^{-1}$ . The reaction takes place according to the equation  $2 \text{N}_2\text{O}_5 (\text{g}) \rightarrow 4 \text{NO}_2 (\text{g}) + \text{O}_2 (\text{g})$ . Calculate the average rate of this reaction in terms of hours, minutes and seconds. What is the rate of production of  $\text{NO}_2$  during this period?
9. Explain the term rate law.
10. Define rate constant.
11. Write a short note on Order of reaction.
12. Give the units of rate constant for zero, first & second order reaction.
13. Express the rate of the following reaction in terms of disappearance of hydrogen & formation of ammonia in the reaction :  $3\text{H}_2 + \text{N}_2 \rightarrow 2\text{NH}_3$
14. For a reaction,  $\text{A} + \text{B} \rightarrow \text{product}$ , the rate law is given by  $r = k [\text{A}]^{1/2} [\text{B}]^2$  what is the order of the reaction?
15. Write the rate equation for the reaction  $2\text{A} + \text{B} \rightarrow \text{C}$  if the order of the reaction is zero.
16. The conversion of molecules x to y follows second order kinetics. If the concentration of x is increased to three times, how will it affect the rate of formation of y?
17. Calculate the overall order of a reaction which has the rate expression (a)  $\text{Rate} = k [\text{A}]^{1/2} [\text{B}]^{3/2}$   
(b)  $\text{Rate} = k [\text{A}]^{3/2} [\text{B}]^{-1}$
18. Identify the reaction order from of the following rate constants. (i)  $k = 2.3 \times 10^{-5} \text{ L mol}^{-1}\text{s}^{-1}$   
(ii)  $k = 3 \times 10^{-4} \text{ s}^{-1}$
19. From the rate expression for the following reactions determine their order of reaction and dimensions of the rate constants.
 

a) $\text{H}_2\text{O}_2 (\text{aq}) + 3 \text{I}^- (\text{aq}) + 2\text{H}^+ \rightarrow 2\text{H}_2\text{O} (\text{l}) + 3\text{I}^-$	Rate = $k [\text{H}_2\text{O}_2] [\text{I}^-]$
b) $\text{CH}_3\text{CHO} (\text{g}) \rightarrow \text{CH}_4(\text{g}) + \text{CO}(\text{g})$	Rate = $k [\text{CH}_3\text{CHO}]^{3/2}$
c) $3\text{NO} \rightarrow \text{N}_2\text{O} (\text{g})$	Rate = $k [\text{NO}]^2$
d) $\text{C}_2\text{H}_5\text{Cl} \rightarrow \text{C}_2\text{H}_4 + \text{HCl}$	Rate = $k[\text{C}_2\text{H}_5\text{Cl}]$
20. The decomposition reaction of ammonia gas on platinum surface has a rate constant =  $2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$ . What is the order of the reaction?
21. For the reaction:  $2\text{A} + \text{B} \rightarrow \text{A}_2\text{B}$  the rate =  $k[\text{A}][\text{B}]^2$  with  $k = 2.0 \times 10^{-6} \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-1}$ . Calculate the initial rate of the reaction when  $[\text{A}] = 0.1 \text{ mol L}^{-1}$ ,  $[\text{B}] = 0.2 \text{ mol L}^{-1}$ . Calculate the rate of reaction after  $[\text{A}]$  is reduced to  $0.06 \text{ mol L}^{-1}$ .
22. A reaction is first order in A and second order in B. Write differential rate equation.
  - ii) How is the rate affected when concentration of B is tripled?
  - iii) How is the rate affected when the concentration of both A and B is doubled?
23. A reaction is second order with respect to a reactant. How is the rate of reaction affected if the concentration of the reactant is (i) doubled (ii) reduced to half ?
24. For the reaction  $\text{A} \rightarrow \text{B}$  the rate becomes 27 times when the concentration of A is increased 3 times. What is the order of reaction?
25. For the reaction  $\text{A} \rightarrow \text{B}$ , the rate of reaction becomes three times when the concentration of A is increased nine times. What is the order of the reaction ?
26. The conversion of molecules x to y follows second order kinetics. If the concentration of x is increased to three times, how will it affect the rate of formation of y?
27. For the reaction  $2\text{X} \rightarrow \text{X}_2$ , the rate of reaction becomes three times when the concentration of X is increased 27 times. What is the order of the reaction ?
28. For the reaction  $\text{A} \rightarrow \text{B}$ , the rate of reaction becomes three times when the concentration of A is increased nine times. What is the order of the reaction ?
29. The decomposition of  $\text{NH}_3$  on platinum surface is zero order reaction. What are the rates of production of  $\text{N}_2$  and  $\text{H}_2$  if  $k = 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$ ?
30. The decomposition of dimethyl ether leads to the formation of  $\text{CH}_4$ ,  $\text{H}_2$  and  $\text{CO}$  and the reaction rate is given by  $\text{Rate} = k [\text{CH}_3\text{CHO}]^{3/2}$  The rate of reaction is followed by increase in



pressure in a closed vessel, so the rate can also be expressed in terms of the partial pressure of dimethyl ether, i.e., Rate =  $k (p_{\text{CH}_3\text{CHO}})^{3/2}$  If the pressure is measured in bar and time in minutes, then what are the units of rate and rate constants?

31. Explain the term Molecularity with example.
32. Define Rate determining step, Elementary & Complex reactions
33. Distinguish between order of reaction & Molecularity.
34. For which type of reactions, order and molecularity have the same value?
35. For a reaction  $A + B \rightarrow \text{Products}$ , the rate law is — Rate =  $k [A][B]^{3/2}$
36. Can the reaction be an elementary reaction? Explain
37. For a zero order reaction will the molecularity be equal to zero? Explain.
38. Why can't molecularity of any reaction be equal to zero?
39. Why molecularity is applicable only for elementary reactions and order is applicable for elementary as well as complex reactions?
40. Why can we not determine the order of a reaction by taking into consideration the balanced chemical equation?
41. Mention the factors that affect the rate of a chemical reaction.
42. The possible mechanism for the reaction :  $2\text{NO} (\text{g}) + \text{O}_2 (\text{g}) \rightarrow 2\text{NO}_2 (\text{g})$  is  
 (i)  $\text{NO} + \text{O}_2 \xrightleftharpoons{K} \text{NO}_3$  (fast)                      (ii)  $\text{NO}_3 + \text{NO} \xrightarrow{K_2} \text{NO}_2 + \text{NO}_2 (\text{g})$  (slow).  
 Write the rate law for the reaction
43. For a reaction  $2\text{H}_2\text{O}_2 \xrightarrow{\text{I}^-, \text{Alkaline}} 2\text{H}_2\text{O} + \text{O}_2$  the proposed mechanism is as follows  
 (i)  $\text{H}_2\text{O}_2 + \text{I}^- \rightarrow \text{H}_2\text{O} + \text{IO}^-$  (slow) (ii)  $\text{H}_2\text{O}_2 + \text{IO}^- \rightarrow \text{H}_2\text{O} + \text{I}^- + \text{O}_2$  (fast)  
 (a) Write the rate law for the reaction. (b) Write the overall order of reaction. (iii) Out of steps (i) & (ii) which one is rate determining step.
44. For a chemical reaction  $A + 2B \rightarrow 2C + D$ . The experimentally obtained information is given below.

Experiment	[A]₀	[B]₀	Initial rate
1	0.30	0.30	0.096
2	0.60	0.30	0.384
3	0.30	0.60	0.192
4	0.60	0.60	0.768

- (i) Derive the order of reaction w.r.t. both the reactants A and B. (ii) write the rate law. (iii) calculate the value of rate constant k (iv) Write the expression for the rate of reaction in terms of A and C.

45. For a certain chemical reaction  $2A + B \rightarrow C + D$  The following result has been obtained :

Experiment	[A] mol L <sup>-1</sup>	[B] mol L <sup>-1</sup>	Initial rate mol L <sup>-1</sup> min <sup>-1</sup>
I	0.1	0.1	$6.0 \times 10^{-3}$
II	0.3	0.2	$7.2 \times 10^{-2}$
III	0.3	0.4	$2.88 \times 10^{-1}$
IV	0.4	0.1	$2.40 \times 10^{-2}$

Determine the rate law and rate constant for the reaction

46. The reaction between A and B is first order with respect to A and zero order with respect to B. Fill in the blanks in the following table:

Experiment	[A] mol L <sup>-1</sup>	[B] mol L <sup>-1</sup>	Initial rate mol L <sup>-1</sup> min <sup>-1</sup>
I	0.1	0.1	$2.0 \times 10^{-2}$
II	—	0.2	$4.0 \times 10^{-2}$
III	0.4	0.4	—
IV	—	0.2	$2.0 \times 10^{-2}$

47. In a reaction between A and B, the initial rate of reaction ( $r_0$ ) was measured for different initial concentrations of A and B as given below:

A/ mol L <sup>-1</sup>	0.20	0.20	0.40
B/ mol L <sup>-1</sup>	0.30	0.10	0.05
$r_0$ /mol L <sup>-1</sup> s <sup>-1</sup>	$5.07 \times 10^{-5}$	$5.07 \times 10^{-5}$	$1.43 \times 10^{-4}$

What is the order of the reaction with respect to A and B?

### TOPIC : INTEGRATED RATE LAW EQUATIONS:- ZERO ORDER REACTIONS & FIRST ORDER REACTIONS

1. **ZERO ORDER REACTION:** In this the rate of the reaction is proportional to zero power of the concentration of reactants.

Consider the reaction,  $R \rightarrow P$

$$\text{Rate} = \frac{-d[R]}{dt} \dots\dots\dots(i) \qquad \text{Rate} = K[R]^0 \dots\dots\dots(ii)$$

$$\text{From (i) \& (ii)} \quad \frac{-d[R]}{dt} = K[R]^0 \quad \Rightarrow \quad \frac{-d[R]}{dt} = K \quad \Rightarrow \quad d[R] = -K dt$$

Integrating both sides

$$\Rightarrow \int d[R] = -K \int dt$$

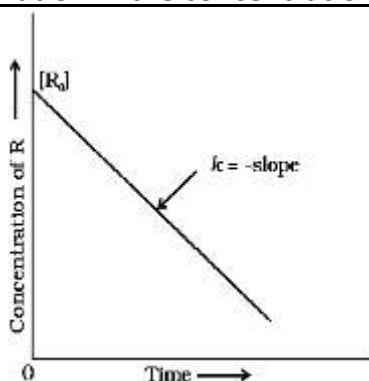
$$\Rightarrow [R] = -Kt + C \dots\dots(iii) \text{ where, } C \text{ is the constant of integration.}$$

At  $t = 0$ , the concentration of the reactant  $R = [R]_0$ , where  $[R]_0$  is initial concentration of the reactant.  
 $[R]_0 = -K \times 0 + C \Rightarrow [R]_0 = C$ , Substituting the value of C in equation (iii)

$$\Rightarrow [R] = -Kt + [R]_0$$

$$\Rightarrow K = \frac{[R]_0 - [R]}{t}$$

#### Variation in the concentration vs time plot for a zero order reaction:-



If we plot  $[R]$  against  $t$ , we get a straight line with **slope =  $-k$**  and intercept equal to  $[R]_0$ .

#### Half life period for a zero order reaction

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

$$\text{At } t_{1/2}, [R] = \frac{[R]_0}{2}$$

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

$$\Rightarrow t_{1/2} = \frac{[R]_0}{2K}$$

**Examples of zero order reaction** (a) The decomposition of gaseous ammonia on a hot platinum surface is a zero order reaction at high pressure (b) The thermal decomposition of HI on gold surface.

2. **FIRST ORDER REACTIONS:** The rate of the reaction is proportional to the first power of the concentration of the reactant R.

Consider the reaction,  $R \rightarrow P$

$$\text{Rate} = \frac{-d[R]}{dt} \dots\dots\dots(i) \qquad \text{Rate} = K[R]^1 \dots\dots\dots(ii)$$

$$\text{From (i) \& (ii)} \quad \frac{-d[R]}{dt} = K[R]^1 \quad \Rightarrow \quad \frac{-d[R]}{[R]} = K dt$$

$$\text{Integrating both sides} \quad \int \frac{-d[R]}{[R]} = K \int dt$$

$-\ln[R]=kt + C$  .....(iii) where, C is the constant of integration

At  $t = 0$ , the concentration of the reactant  $R = [R]_0$ , where  $[R]_0$  is initial concentration of the reactant.

$$-\ln[R]_0 = k \times 0 + C \Rightarrow C = -\ln[R]_0, \text{ Substituting the value of } C \text{ in equation (iii)} \Rightarrow -\ln[R] = kt - \ln[R]_0$$

$$k = \frac{1}{t} \{ \ln[R]_0 - \ln[R] \}$$

$$k = \frac{1}{t} \ln \frac{[R]_0}{[R]} \Rightarrow k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$$

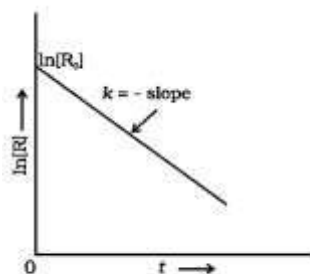


Fig. 4.4: A plot between  $\ln[R]$  and  $t$  for a first order reaction

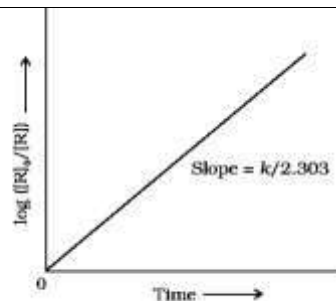


Fig. 4.5: Plot of  $\log [R]_0/[R]$  vs time for a first order reaction

- If we plot  $\ln [R]$  against  $t$  (Fig. 4.4) we get a straight line with slope =  $-k$  and intercept equal to  $\ln [R]_0$
- If we plot a graph between  $\log [R]_0/[R]$  vs  $t$ , (Fig. 4.5), the slope =  $k/2.303$

#### Half life period for a First order reaction

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

$$\text{At } t_{1/2}, [R] = \frac{[R]_0}{2}$$

$$\Rightarrow t_{1/2} = \frac{2.303}{k} \log \frac{[R]_0}{[R]_0/2}$$

$$\Rightarrow t_{1/2} = \frac{2.303}{k} \log 2$$

- **Examples** : All natural and artificial radioactive decay of unstable nuclei take place by first order kinetics.

$$\Rightarrow t_{1/2} = \frac{2.303}{k} \times 0.3010$$

$$\Rightarrow t_{1/2} = \frac{0.693}{K}$$

**It can be seen that for a first order reaction, half-life period is constant, i.e., it is independent of initial concentration of the reacting species**

- Decomposition of  $N_2O_5$  and  $N_2O$  are some more examples of first order reactions

first order gas phase reaction

#### 3. INTEGRATED RATE EQUATION FOR FIRST ORDER GAS PHASE REACTION $A(g) \rightarrow B(g) + C(g)$

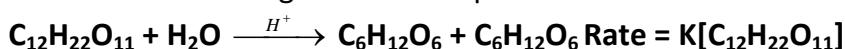
$$k = \frac{2.303}{t} \log \frac{[P]_i}{[2P_i - P_t]}$$

4. **PSEUDO FIRST ORDER REACTION** : The reaction which is bimolecular but order is one is known as Pseudo first order reaction. In this type of reaction one of the reactant is present in large excess i.e. the concentration does not get altered much during the course of the reaction e.g.

##### Hydrolysis of ester



Inversion of cane sugar is another pseudo first order reaction



#### QUESTION ON INTEGRATED RATE LAW EQUATIONS: - ZERO ORDER REACTIONS & FIRST ORDER REACTIONS, PSEUDO FIRST ORDER REACTION

1. Derive the Integrated rate equation for Zero order reaction. Find half life period and plot the graph associated to it.

2. For a zero order chemical reaction: (a) Plot variation in the concentration in [R] vs. time .(b) what are the units of rate constant k? (c) give the relationship between k and  $t_{1/2}$  (half life period) (d) Give the slope
3. A substance with initial concentration 'a' follow zero order kinetics with rate constant 'k' mol L<sup>-1</sup> s<sup>-1</sup>. In how much time will the reaction go to completion?
4. The rate constant for a reaction of zero order reaction in A is 0.0030 mol L<sup>-1</sup> s<sup>-1</sup>. How long will it take for the initial concentration of A to fall from 0.10 M to 0.075M?
5. The decomposition of NH<sub>3</sub> on platinum surface is zero order reaction. If rate constant is 4 x 10<sup>-3</sup> Ms<sup>-1</sup>, how long will it take to reduce the initial concentration of NH<sub>3</sub> from 0.1M to 0.064M.
6. Derive the Integrated rate equation for first order reaction. Find half life period and plot the graph associated to it.
7. For a first order chemical reaction: (i) Plot variation in the concentration in ln[R] vs. time & Give the slope (s) (ii) Draw the plot log [R]<sub>0</sub> / [R] vs. time t(s) & Give the slope (iii) what are the units of rate constant k? (iii) give the relationship between k and  $t_{1/2}$  (half life period) (iv) Give the slope
8. For a reaction R → P half-life period is independent of initial concentration of the reacting species. What is the order of reaction.
9. (a) Define half life period of a reaction .(b) Write the expressions of half life for (i) first order chemical reaction (ii) zero order chemical reaction
10. What are pseudo first order reactions? Give one example of such reaction.
11. A first order reaction has a rate constant 1.15 x 10<sup>-3</sup> s<sup>-1</sup>. How long will 5 g of this reactant take to reduce to 3 g?
12. Time required to decompose SO<sub>2</sub>Cl<sub>2</sub> to half of its initial amount is 60 minutes. If the decomposition is a first order reaction, calculate the rate constant of the reaction.
13. The initial concentration of N<sub>2</sub>O<sub>5</sub> in the following first order reaction N<sub>2</sub>O<sub>5</sub>(g) → NO<sub>2</sub>(g) + 1/2O<sub>2</sub>(g) was 1.24 x 10<sup>-2</sup> mol L<sup>-1</sup> at 318 K. The concentration of N<sub>2</sub>O<sub>5</sub> after 60 minutes was 0.20 x 10<sup>-2</sup> mol L<sup>-1</sup>. Calculate the rate constant of the reaction at 318 K.
14. A first order reaction is found to have a rate constant. k = 5.5 x 10<sup>-4</sup> s<sup>-1</sup>. Find the half-life of the reaction.
15. Show that in a first order reaction, time required for completion of 99.9% is 10 times of half-life ( $t_{1/2}$ ) of the reaction.
16. For a first order reaction, show that time required for 99% completion is twice the time required for the completion of 90% of reaction.
17. Calculate the half-life of a first order reaction from their rate constants given :(i) 200 s<sup>-1</sup> (ii) 2 min<sup>-1</sup> (iii) 4 years<sup>-1</sup>.
18. The half-life for radioactive decay of <sup>14</sup>C is 5730 years. An archaeological artifact containing wood had only 80% of the <sup>14</sup>C found in a living tree. Estimate the age of the sample
19. The rate constant for a first order reaction is 60 s<sup>-1</sup>. How much time will it take to reduce the initial concentration of the reactant to its 1/16<sup>th</sup> value?
20. .During nuclear explosion, one of the products is <sup>90</sup>Sr with half-life of 28.1 years. If 1 μg of <sup>90</sup>Sr was absorbed in the bones of a newly born baby instead of calcium, how much of it will remain after 10 years and 60 years if it is not lost metabolically.
21. H<sub>2</sub>O<sub>2</sub> decomposes to H<sub>2</sub>O and O<sub>2</sub> in a reaction that is first order and has rate constant k = 1.06 x 10<sup>-3</sup> min<sup>-1</sup>. How long will it take 15% of a sample of H<sub>2</sub>O<sub>2</sub> to decompose.
22. A first order reaction takes 30 minutes for 50% decomposition. Calculate the time required for 90% completion for this reaction
23. A first order reaction takes 100 minutes for 60% decomposition. Calculate the time required for 90% completion for this reaction
24. A first order reaction takes 20 minutes for 25% decomposition. Calculate the time required for 75% completion for this reaction
25. A first order reaction takes 40 min for 30% decomposition. Calculate  $t_{1/2}$ .

26. Consider a certain reaction  $A \rightarrow \text{Products}$  with  $k = 2.0 \times 10^{-2} \text{ s}^{-1}$ . Calculate the concentration of A remaining after 100 s if the initial concentration of A is  $1.0 \text{ mol L}^{-1}$ .
27. Sucrose decomposes in acid solution into glucose and fructose according to the first Order rate law, with  $t_{1/2} = 3.00$  hours. What fraction of sample of sucrose remains after 8 hours?
28. A first order reaction has a rate constant  $0.0051 \text{ min}^{-1}$ . If we begin with  $0.10 \text{ M}$  concentration of the reactant, what concentration of the reactant will be left after 3 hours. The
29. A reactant has a half life of 10 min. (i) Calculate the rate constant for the first order reaction (ii) what fraction of the reactant will be left after an hour of the reaction has occurred.
30. The decomposition of phosphine  $\text{PH}_3$  proceeds according to the following equation:  $4\text{PH}_3 \rightarrow \text{P}_4 + 6\text{H}_2$ , It is found that the reaction follows rate reaction rate  $= k[\text{PH}_3]$ . The half life of  $\text{PH}_3$  is 37.9 second at  $120^\circ\text{C}$ . (i) How much time is required for  $3/4^{\text{th}}$  of  $\text{PH}_3$  to decompose? (ii) What fraction of the original sample of  $\text{PH}_3$  remains behind after 1 minute?
31. For a first order reaction, time taken for half of the reaction to complete is  $t_1$ , whereas that for  $3/4^{\text{th}}$  of the reaction to complete is  $t_2$ . How are  $t_1$  and  $t_2$  related?
32. For the decomposition of azoisopropane to hexane and nitrogen at 543k, the following data were obtained. Calculate the rate constant.

t (sec)	P(mm of Hg)
0	35.0
360	54.0
720	63.0

33. For the first order thermal decomposition  $\text{C}_2\text{H}_5\text{Cl}(\text{g}) \rightarrow \text{C}_2\text{H}_4(\text{g}) + \text{HCl}(\text{g})$ . Calculate the rate constant.

Experiment	Time	Pressure (atm)
1	0	0.30
2	300	0.50

34. The Following data were obtained during the first order thermal decomposition of  $\text{SO}_2\text{Cl}_2$  at a constant volume:  $\text{SO}_2\text{Cl}_2(\text{g}) \rightarrow \text{SO}_2(\text{g}) + \text{Cl}_2(\text{g})$ . Calculate the rate constant.

Experiment	Time	Pressure (atm)
1	0	0.4
2	100	0.7

35. The following data were obtained during the first order thermal decomposition of  $\text{N}_2\text{O}_5(\text{g})$  at constant volume:  $2\text{N}_2\text{O}_5(\text{g}) \rightarrow 2\text{N}_2\text{O}_4(\text{g}) + \text{O}_2(\text{g})$ . Calculate the rate constant.

S.No	Time	Pressure (atm)
1	0	0.5
2	100	0.512

36. Following data were obtained for the reaction:  $\text{N}_2\text{O}_5(\text{g}) \rightarrow 2\text{NO}_2(\text{g}) + 1/2 \text{O}_2(\text{g})$ .

Time (s)	0	300	600
$[\text{N}_2\text{O}_5(\text{g})]$ (mol/l)	$1.6 \times 10^{-2}$	$0.8 \times 10^{-2}$	$0.4 \times 10^{-2}$

- (i) Show that it follows first order reaction (ii) Calculate the half life

37. In a pseudo first order hydrolysis of ester in water, the following results were obtained:

Time (s)	0	30	60	90
[Ester] (mol/l)	0.55	0.31	0.17	0.85

- (i) Calculate the average rate of reaction between the time interval 30 to 60 seconds. (ii) Calculate the pseudo first order rate constant for the hydrolysis of ester.



24. For the reaction  $A \rightarrow B$  the rate becomes 27 times when the concentration of A is increased 3 times. What is the order of reaction?
25. For the reaction  $A \rightarrow B$ , the rate of reaction becomes three times when the concentration of A is increased nine times. What is the order of the reaction ?
26. The conversion of molecules x to y follows second order kinetics. If the concentration of x is increased to three times, how will it affect the rate of formation of y?
27. For the reaction  $2X \rightarrow X_2$ , the rate of reaction becomes three times when the concentration of X is increased 27 times. What is the order of the reaction ?
28. For the reaction  $A \rightarrow B$ , the rate of reaction becomes three times when the concentration of A is increased nine times. What is the order of the reaction ?
29. The decomposition of  $NH_3$  on platinum surface is zero order reaction. What are the rates of production of  $N_2$  and  $H_2$  if  $k = 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ S}^{-1}$ ?
30. The decomposition of dimethyl ether leads to the formation of  $CH_4$ ,  $H_2$  and  $CO$  and the reaction rate is given by  $\text{Rate} = k [CH_3CHO]^{3/2}$ . The rate of reaction is followed by increase in pressure in a closed vessel, so the rate can also be expressed in terms of the partial pressure of dimethyl ether, i.e.,  $\text{Rate} = k (p_{CH_3CHO})^{3/2}$ . If the pressure is measured in bar and time in minutes, then what are the units of rate and rate constants?
31. Explain the term Molecularity with example.
32. Define Rate determining step, Elementary & Complex reactions
33. Distinguish between order of reaction & Molecularity.
34. For which type of reactions, order and molecularity have the same value?
35. For a reaction  $A + B \rightarrow \text{Products}$ , the rate law is —  $\text{Rate} = k [A][B]^{3/2}$
36. Can the reaction be an elementary reaction? Explain
37. For a zero order reaction will the molecularity be equal to zero? Explain.
38. Why can't molecularity of any reaction be equal to zero?
39. Why molecularity is applicable only for elementary reactions and order is applicable for elementary as well as complex reactions?
40. Why can we not determine the order of a reaction by taking into consideration the balanced chemical equation?
41. Mention the factors that affect the rate of a chemical reaction.
42. The possible mechanism for the reaction :  $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$  is  
 (i)  $NO + O_2 \xrightleftharpoons{K} NO_3$  (fast)                      (ii)  $NO_3 + NO \xrightarrow{K_2} NO_2 + NO_2$  (g) (slow).  
 Write the rate law for the reaction
43. .For a reaction  $2H_2O_2 \xrightarrow{I^-, Alkaline} 2H_2O + O_2$  the proposed mechanism is as follows  
 (i)  $H_2O_2 + I^- \rightarrow H_2O + IO^-$  (slow) (ii)  $H_2O_2 + IO^- \rightarrow H_2O + I^- + O_2$  (fast)  
 (a) Write the rate law for the reaction.  
 (b) Write the overall order of reaction.  
 (iii) Out of steps (i) & (ii) which one is rate determining step.
44. For a chemical reaction  $A + 2B \rightarrow 2C + D$ . The experimentally obtained information is given below.

Experiment	[A]0	[B]0	Initial rate
1	0.30	0.30	0.096
2	0.60	0.30	0.384
3	0.30	0.60	0.192
4	0.60	0.60	0.768

- (i) Derive the order of reaction w.r.t. both the reactants A and B. (ii) Write the rate law.  
 (iii) Calculate the value of rate constant k  
 (iv) Write the expression for the rate of reaction in terms of A and C.

45. For a certain chemical reaction  $2A + B \rightarrow C + D$  The following result has been obtained:

Experiment	[A] mol L <sup>-1</sup>	[B] mol L <sup>-1</sup>	Initial rate mol L <sup>-1</sup> min <sup>-1</sup>
I	0.1	0.1	$6.0 \times 10^{-3}$
II	0.3	0.2	$7.2 \times 10^{-2}$
III	0.3	0.4	$2.88 \times 10^{-1}$
IV	0.4	0.1	$2.40 \times 10^{-2}$

Determine the rate law and rate constant for the reaction

48. The reaction between A and B is first order with respect to A and zero order with respect to B. Fill in the blanks in the following table:

Experiment	[A] mol L <sup>-1</sup>	[B] mol L <sup>-1</sup>	Initial rate mol L <sup>-1</sup> min <sup>-1</sup>
I	0.1	0.1	$2.0 \times 10^{-2}$
II	–	0.2	$4.0 \times 10^{-2}$
III	0.4	0.4	–
IV	–	0.2	$2.0 \times 10^{-2}$

49. In a reaction between A and B, the initial rate of reaction ( $r_0$ ) was measured for different initial concentrations of A and B as given below:

A/ mol L <sup>-1</sup>	0.20	0.20	0.40
B/ mol L <sup>-1</sup>	0.30	0.10	0.05
$r_0$ /mol L <sup>-1</sup> s <sup>-1</sup>	$5.07 \times 10^{-5}$	$5.07 \times 10^{-5}$	$1.43 \times 10^{-4}$

What is the order of the reaction with respect to A and B?

50. Derive the Integrated rate equation for Zero order reaction. Find half life period and plot the graph associated to it.
51. For a zero order chemical reaction: (a) Plot variation in the concentration in [R] vs. time. (b) what are the units of rate constant k? (c) give the relationship between k and  $t_{1/2}$  (half life period) (d) Give the slope
52. A substance with initial concentration 'a' follow zero order kinetics with rate constant 'k' mol L<sup>-1</sup> s<sup>-1</sup>. In how much time will the reaction go to completion?
53. The rate constant for a reaction of zero order reaction in A is  $0.0030 \text{ mol L}^{-1} \text{ s}^{-1}$ . How long will it take for the initial concentration of A to fall from 0.10 M to 0.075M?
54. The decomposition of NH<sub>3</sub> on platinum surface is zero order reaction. If rate constant is  $4 \times 10^{-3} \text{ Ms}^{-1}$ , how long will it take to reduce the initial concentration of NH<sub>3</sub> from 0.1M to 0.064M.
55. Derive the Integrated rate equation for first order reaction. Find half life period and plot the graph associated to it.
56. For a first order chemical reaction: (i) Plot variation in the concentration in  $\ln[R]$  vs. time & Give the slope (s) (ii) Draw the plot  $\log [R]_0 / [R]$  vs. time t(s) & Give the slope (iii) what are the units of rate constant k? (iv) give the relationship between k and  $t_{1/2}$  (half life period) (iv) Give the slope
57. For a reaction  $R \rightarrow P$  half-life period is independent of initial concentration of the reacting species. What is the order of reaction.
58. (a) Define half life period of a reaction. (b) Write the expressions of half life for (i) first order chemical reaction (ii) zero order chemical reaction
59. What are pseudo first order reactions? Give one example of such reaction.



60. A first order reaction has rate constant  $1.15 \times 10^{-3} \text{ s}^{-1}$ . How long will 5 g of this reactant take to reduce to 3 g?
61. Time required to decompose  $\text{SO}_2\text{Cl}_2$  to half of its initial amount is 60 minutes. If the decomposition is a first order reaction, calculate the rate constant of the reaction.
62. The initial concentration of  $\text{N}_2\text{O}_5$  in the following first order reaction  $\text{N}_2\text{O}_5(\text{g}) \rightarrow \text{NO}_2(\text{g}) + 1/2\text{O}_2(\text{g})$  was  $1.24 \times 10^{-2} \text{ mol L}^{-1}$  at 318 K. The concentration of  $\text{N}_2\text{O}_5$  after 60 minutes was  $0.20 \times 10^{-2} \text{ mol L}^{-1}$ . Calculate the rate constant of the reaction at 318 K.
63. A first order reaction is found to have a rate constant.  $k = 5.5 \times 10^{-4} \text{ s}^{-1}$ . Find the half-life of the reaction.
64. Show that in a first order reaction, time required for completion of 99.9% is 10 times of half-life ( $t_{1/2}$ ) of the reaction.
65. For a first order reaction, show that time required for 99% completion is twice the time required for the completion of 90% of reaction.
66. Calculate the half-life of a first order reaction from their rate constants given : (i)  $200 \text{ s}^{-1}$  (ii)  $2 \text{ min}^{-1}$  (iii)  $4 \text{ years}^{-1}$ .
67. The half-life for radioactive decay of  $^{14}\text{C}$  is 5730 years. An archaeological artifact containing wood had only 80% of the  $^{14}\text{C}$  found in a living tree. Estimate the age of the sample
68. The rate constant for a first order reaction is  $60 \text{ s}^{-1}$ . How much time will it take to reduce the initial concentration of the reactant to its  $1/16^{\text{th}}$  value?
69. During nuclear explosion, one of the products is  $^{90}\text{Sr}$  with half-life of 28.1 years. If  $1 \mu\text{g}$  of  $^{90}\text{Sr}$  was absorbed in the bones of a newly born baby instead of calcium, how much of it will remain after 10 years and 60 years if it is not lost metabolically.
70.  $\text{H}_2\text{O}_2$  decomposes to  $\text{H}_2\text{O}$  and  $\text{O}_2$  in a reaction that is first order and has rate constant  $k = 1.06 \times 10^{-3} \text{ min}^{-1}$ . How long will it take 15% of a sample of  $\text{H}_2\text{O}_2$  to decompose.
71. A first order reaction takes 30 minutes for 50% decomposition. Calculate the time required for 90% completion for this reaction
72. A first order reaction takes 100 minutes for 60% decomposition. Calculate the time required for 90% completion for this reaction
73. A first order reaction takes 20 minutes for 25% decomposition. Calculate the time required for 75% completion for this reaction
74. A first order reaction takes 40 min for 30% decomposition. Calculate  $t_{1/2}$ .
75. Consider a certain reaction  $\text{A} \rightarrow \text{Products}$  with  $k = 2.0 \times 10^{-2} \text{ s}^{-1}$ . Calculate the concentration of A remaining after 100 s if the initial concentration of A is  $1.0 \text{ mol L}^{-1}$ .
76. Sucrose decomposes in acid solution into glucose and fructose according to the first Order rate law, with  $t_{1/2} = 3.00$  hours. What fraction of sample of sucrose remains after 8 hours?
77. A first order reaction has a rate constant  $0.0051 \text{ min}^{-1}$ . If we begin with 0.10 M concentration of the reactant, what concentration of the reactant will be left after 3 hours. The
78. A reactant has a half life of 10 min.  
 (i) Calculate the rate constant for the first order reaction  
 (ii) what fraction of the reactant will be left after an hour of the reaction has occurred.
79. The decomposition of phosphine  $\text{PH}_3$  proceeds according to the following equation:  $4\text{PH}_3 \rightarrow \text{P}_4 + 6\text{H}_2$ , It is found that the reaction follows rate reaction rate =  $k[\text{PH}_3]$  The half life of  $\text{PH}_3$  is 37.9 second at  $120^\circ\text{C}$ .  
 (i) How much time is required for  $3/4^{\text{th}}$  of  $\text{PH}_3$  to decompose?  
 (ii) What fraction of the original sample of  $\text{PH}_3$  remains behind after 1 minute?
80. For a first order reaction, time taken for half of the reaction to complete is  $t_1$ , whereas that for  $3/4^{\text{th}}$  of the reaction to complete is  $t_2$ . How are  $t_1$  and  $t_2$  related ?

81. For the decomposition of azoisopropane to hexane and nitrogen at 543k, the following data were obtained. Calculate the rate constant.

t (sec)	P(mm of Hg)
0	35.0
360	54.0
720	63.0

82. The Following data were obtained during the first order thermal decomposition of  $\text{SO}_2\text{Cl}_2$  at a constant volume:  $\text{SO}_2\text{Cl}_2(\text{g}) \rightarrow \text{SO}_2(\text{g}) + \text{Cl}_2(\text{g})$ . Calculate the rate constant.

Experiment	Time	Pressure (atm)
1	0	0.4
2	100	0.7

83. The following data were obtained during the first order thermal decomposition of  $\text{N}_2\text{O}_5$  (g) at constant volume:  $2\text{N}_2\text{O}_5(\text{g}) \rightarrow 2\text{N}_2\text{O}_4(\text{g}) + \text{O}_2(\text{g})$ . Calculate the rate constant.

S.No	Time	Pressure (atm)
1	0	0.5
2	100	0.512

84. Following data were obtained for the reaction :  $\text{N}_2\text{O}_5(\text{g}) \rightarrow 2\text{NO}_2(\text{g}) + 1/2 \text{O}_2(\text{g})$ .

Time (s)	0	300	600
$[\text{N}_2\text{O}_5(\text{g})]$ (mol/l)	$1.6 \times 10^{-2}$	$0.8 \times 10^{-2}$	$0.4 \times 10^{-2}$

- (i) Show that it follows first order reaction  
(ii) Calculate the half life

85. In a pseudo first order hydrolysis of ester in water, the following results were obtained:

Time (s)	0	30	60	90
[Ester] (mol/l)	0.55	0.31	0.17	0.085

- (i) Calculate the average rate of reaction between the time interval 30 to 60 seconds. (ii) Calculate the pseudo first order rate constant for the hydrolysis of ester

**KEEP ON ENJOYING AND LOVING CHEMISTRY .....**

## SURFACE CHEMISTRY

**TOPIC : ADSORPTION , ABSORPTION, DESORPTION ,SORPTION,TYPES OF ADSORPTION, ADSORPTION ISOTHERMS, APPLICATIONS OF ADSORPTION**

1. **SURFACE CHEMISTRY** deals with phenomena that occur at the surfaces or interfaces.
2. **ADSORPTION:** The accumulation of molecular species at the surface rather than in the bulk of a solid or liquid is termed adsorption.
3. **ADSORBATE:** The molecular species or substance, which accumulates at the surface, is termed adsorbate.
4. **ADSORBENT:** The material on the surface of which the adsorption takes place is called adsorbent. Solids, particularly in finely divided state, have large surface area and therefore, charcoal, silica gel, alumina gel, clay, colloids, metals in finely divided state, etc. act as good adsorbents. Activation of adsorbent means increasing the adsorbing power of an adsorbent. This is done by increasing the surface area of the adsorbent. It can be done by making the surface rough and subdividing the adsorbent into smaller pieces
5. **ADSORPTION IN ACTION:**
  - (a) If a gas like  $O_2$ ,  $H_2$ ,  $CO$ ,  $Cl_2$ ,  $NH_3$  or  $SO_2$  is taken in a closed vessel containing powdered charcoal, it is observed that the pressure of the gas in the enclosed vessel decreases. The gas molecules concentrate at the surface of the charcoal, i.e., gases are adsorbed at the surface.
  - (b) In a solution of an organic dye, say methylene blue, when animal charcoal is added and the solution is well shaken, it is observed that the filtrate turns colourless. The molecules of the dye, thus, accumulate on the surface of charcoal, i.e., are adsorbed.
  - (c) Aqueous solution of raw sugar, when passed over beds of animal charcoal, becomes colourless as the colouring substances are adsorbed by the charcoal.
  - (d) The air becomes dry in the presence of silica gel because the water molecules get adsorbed on the surface of the gel. It is clear from the above examples that solid surfaces can hold the gas or liquid molecules by virtue of adsorption.
6. **DESORPTION:** The process of removing an adsorbed substance from a surface on which it is adsorbed is called desorption.
7. **DISTINCTION BETWEEN ADSORPTION & ABSORPTION**

Adsorption	Absorption
In adsorption, the substance is concentrated only at the surface and does not penetrate through the surface to the bulk of the adsorbent	In absorption, the substance is uniformly distributed throughout the bulk of the solid
In adsorption the concentration of the adsorbate increases only at the surface of the adsorbent	In absorption the concentration is uniform throughout the bulk of the solid
Water vapours are adsorbed by silica gel.	Water vapours are absorbed by anhydrous calcium chloride

7. **SORPTION:** Both adsorption and absorption can take place simultaneously also. The term sorption is used to describe both the processes
8. **MECHANISM OF ADSORPTION.**
  - (a) Adsorption arises due to the fact that the surface particles of the adsorbent are not in the same environment as the particles inside the bulk. Inside the adsorbent all the forces acting between the particles are mutually balanced but on the surface the particles are not surrounded by atoms or molecules of their kind on all sides, and hence they possess unbalanced or residual attractive forces. These forces of the adsorbent are responsible for attracting the adsorbate particles on its surface.
  - (b) **The extent of adsorption increases with the increase of surface area** per unit mass of the adsorbent at a given temperature and pressure. Thus, finely divided metals and porous substances having large

surface areas are good adsorbents. Also powdered substances are more effective adsorbents than their crystalline forms

- (c) **Adsorption is always exothermic** : During adsorption, there is always a decrease in residual forces of the surface, i.e., there is decrease in surface energy which appears as heat. Adsorption, therefore, is invariably an exothermic process. In other words,  $\Delta H$  of adsorption is always negative.
- (d) **Adsorption is accompanied by decrease in entropy**: When a gas is adsorbed, the freedom of movement of its molecules become restricted. This amounts to decrease in the entropy of the gas after adsorption, i.e.,  $\Delta S$  is negative.
- (e) Adsorption is thus accompanied by decrease in enthalpy as well as decrease in entropy of the system
- (f) **Adsorption of a gas on the surface of solid is spontaneous process**. For a process to be spontaneous, the thermodynamic requirement is that, at constant temperature and pressure,  $\Delta G$  must be negative. On the basis of equation,  $\Delta G = \Delta H - T\Delta S$ ,  $\Delta G$  can be negative if  $\Delta H$  has sufficiently high negative value as  $-T\Delta S$  is positive. Thus, in an adsorption process, which is spontaneous, a combination of these two factors makes  $\Delta G$  negative.

#### 9. TYPES OF ADSORPTION: PHYSISORPTION & CHEMISORPTION

PROPERTY	PHYSISORPTION	CHEMISORPTION
<b>TYPE OF FORCES/ BOND</b>	1. It arises because of van der Waals' forces.	1. It is caused by chemical bond formation.
<b>SPECIFICITY</b>	2. It is not specific in nature	2. It is highly specific in nature.
<b>REVERSIBILITY</b>	3. It is reversible in nature	3. It is irreversible.
<b>NATURE OF GAS</b>	4. It depends on the nature of gas. More easily liquefiable gases are adsorbed readily.	4. It also depends on the nature of gas. Gases which can react with the adsorbent show chemisorptions
<b>ENTHALPY OF ADSORPTION</b>	5. Enthalpy of adsorption is low (20-40 kJ mol <sup>-1</sup> ).	5. Enthalpy of adsorption is high (80-240 kJ mol <sup>-1</sup> ).
<b>TEMPERATURE</b>	6. Low temperature is favourable for physisorption. It decreases with increase of temperature.	6. High temperature is favourable for chemisorption. It increases with the increase of temperature.
<b>ACTIVATION ENERGY</b>	7. No appreciable activation energy is needed.	7. High activation energy is sometimes needed.
<b>SURFACE AREA.</b>	8. It depends on the surface area. It increases with an increase of surface area.	8. It also depends on the surface area. It too increases with an increase of surface area.
<b>FORMATION OF LAYERS</b>	9. It results into multimolecular layers on adsorbent surface under high pressure. because there are weak van der Waals' forces. of attraction	9. It results into unimolecular layer. because there are strong forces. of attraction therefore it is monolayered

#### 10. CHARACTERISTICS OF PHYSISORPTION

- (a) **Lack of specificity**: A given surface of an adsorbent does not show any preference for a particular gas as the van der Waals' forces are universal. **It is not specific in nature**.
- (b) **Nature of adsorbate**: The amount of gas adsorbed by a solid depends on the nature of gas. In general, easily liquefiable gases (i.e., with higher critical temperatures) are readily adsorbed as van der Waals' forces are stronger near the critical temperatures. Thus, 1g of activated charcoal adsorbs more sulphur dioxide (critical temperature 630K), than methane (critical temperature 190K) which is still more than 4.5 mL of dihydrogen (critical temperature 33K).
- (c) **Reversible nature & exothermic**: Physical adsorption of a gas by a solid is generally reversible & exothermic.  $\text{Solid} + \text{Gas} \rightleftharpoons \text{Gas/Solid} + \text{Heat}$ , According to Le-Chatelier's principle if we increase

temperature equilibrium will shift in the backward direction i.e gas is released from the absorbed surface. **Physisorption decrease with the increase of temperature.**

- (d) **Surface area of adsorbent:** The extent of adsorption increases with the increase of surface area of the adsorbent. Thus, finely divided metals and porous substances having large surface areas are good adsorbents.
- (e) **Enthalpy of adsorption:** Enthalpy of adsorption is quite low (**20– 40 kJ mol<sup>-1</sup>**). This is because the attraction between gas molecules and solid surface is only due to weak van der Waals' forces.

#### 11. CHARACTERISTICS OF CHEMISORPTIONS:

- (a) **High specificity:** Chemisorption is highly specific and it will only occur if there is some possibility of chemical bonding between adsorbent and adsorbate. For example, oxygen is adsorbed on metals by virtue of oxide formation and hydrogen is adsorbed by transition metals due to hydride formation.
- (b) **Irreversibility:** As chemisorption involves compound formation, it is usually irreversible in nature. Chemisorption is also an exothermic process but the process is very slow at low temperatures on account of high energy of activation. Like most chemical changes, adsorption often increases with rise of temperature. Physisorption of a gas adsorbed at low temperature may change into chemisorption at a high temperature. Usually high pressure is also favourable for chemisorption.
- (c) **Surface area:** Like physical adsorption, chemisorption also increases with increase of surface area of the adsorbent.
- (d) **Enthalpy of adsorption:** Enthalpy of chemisorption is high (80-240 kJ mol<sup>-1</sup>) as it involves chemical bond formation.
- (e) **It is monolayered** as there are strong forces of attraction.

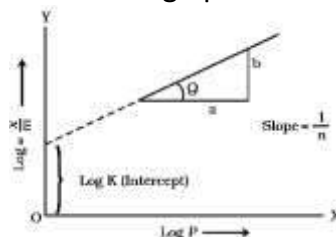
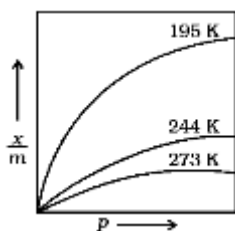
12. **ADSORPTION ISOTHERMS:** The variation in the amount of gas adsorbed by the adsorbent with pressure at constant temperature can be expressed by means of a curve termed as adsorption isotherm.

13. **FREUNDLICH ADSORPTION ISOTHERM:** Freundlich, in 1909, gave an empirical relationship between the quantity of gas adsorbed by unit mass of solid adsorbent and pressure at a particular temperature.

- The relationship can be expressed by the following equation:  $\frac{x}{m} = k \cdot P^{1/n} \cdot (n > 1)$  .....(i) where

$x$  is the mass of the gas adsorbed on mass  $m$  of the adsorbent at pressure  $P$ ,  $k$  and  $n$  are constants which depend on the nature of the adsorbent and the gas at a particular temperature.

- The relationship is generally represented in the form of a curve where mass of the gas adsorbed per gram of the adsorbent is plotted against pressure (Fig.). These curves indicate that at a fixed pressure, there is a decrease in physical adsorption with increase in temperature. These curves always seem to approach saturation at high pressure.



- Taking logarithm of eq. (i)  $\log \frac{x}{m} = \log k + \frac{1}{n} \log P$  ..... (2)
- The validity of Freundlich isotherm can be verified by plotting  $\log x/m$  on  $y$ -axis (ordinate) and  $\log P$  on  $x$ -axis (abscissa). If it comes to be a straight line, the Freundlich isotherm is valid, otherwise not (Fig.). The slope of the straight line gives the value of  $1/n$ . The intercept on the  $y$ -axis gives the value of  $\log k$ .
- Freundlich isotherm explains the behavior of adsorption in an approximate manner. The factor  $1/n$  can have values between 0 and 1 (probable range 0.1 to 0.5). Thus, equation (2) holds good over a limited range of pressure.
- When  $1/n = 0$ ,  $x/m = \text{constant}$ , the adsorption is independent of pressure.
- When  $1/n = 1$ ,  $x/m = k P$ , i.e.  $x/m \propto P$ , the adsorption varies directly with pressure

- Both the conditions are supported by experimental results. The experimental isotherms always seem to approach saturation at high pressure. This cannot be explained by Freundlich isotherm. Thus, it fails at high pressure.

14. **Adsorption from Solution Phase:** The following observations have been made in the case of adsorption from solution phase:

- The extent of adsorption decreases with an increase in temperature.
- The extent of adsorption increases with an increase of surface area of the adsorbent.
- The extent of adsorption depends on the concentration of the solute in solution.
- The extent of adsorption depends on the nature of the adsorbent and the adsorbate.

The precise mechanism of adsorption from solution is not known. Freundlich's equation approximately describes the behaviour of adsorption from solution with a difference that instead of pressure, concentration of the solution is taken into account, i.e.

$$\frac{x}{m} = k \cdot C^{1/n} \quad (n > 1)$$

(C is the equilibrium concentration, i.e., when adsorption is complete). On taking logarithm of

the above equation, we have  $\log \frac{x}{m} = \log k + \frac{1}{n} \log c$ , Plotting  $\log \frac{x}{m}$  against  $\log C$  a straight line is obtained

which shows the validity of Freundlich isotherm.

#### 15. Applications of Adsorption:

- Production of high vacuum:** The remaining traces of air can be adsorbed by charcoal from a vessel evacuated by a vacuum pump to give a very high vacuum
- Gas masks:** Gas mask (a device which consists of activated charcoal or mixture of adsorbents) is usually used for breathing in coal mines to adsorb poisonous gases.
- Control of humidity:** Silica and aluminium gels are used as adsorbents for removing moisture and controlling humidity.
- Removal of colouring matter from solutions:** Animal charcoal removes colours of solutions by adsorbing coloured impurities.
- Heterogeneous catalysis:** Adsorption of reactants on the solid surface of the catalysts increases the rate of reaction.
- Separation of inert gases:** Due to the difference in degree of adsorption of gases by charcoal, a mixture of noble gases can be separated by adsorption on coconut charcoal at different temperatures.
- In curing diseases:** A number of drugs are used to kill germs by getting adsorbed on them.
- Froth floatation process:** A low grade sulphide ore is concentrated by separating it from silica and other earthy matter by this method using pine oil and frothing agent .
- Adsorption indicators:** Surfaces of certain precipitates such as silver halides have the property of adsorbing some dyes like eosin, fluorescein, etc. and thereby producing a characteristic colour at the end point.
- Chromatographic analysis:** Chromatographic analysis based on the phenomenon of adsorption finds a number of applications in analytical and industrial fields.

**QUESTION BASED ON ADSORPTION , ABSORPTION, DESORPTION ,SORPTION,TYPES OF ADSORPTION,ADSORPTION ISOTHERMS, APPLICATIONS OF ADSORPTION**

1. Distinguish between the meaning of the terms adsorption and absorption. Give one example of each.
2. Define the terms desorption & Sorption.
3. What is the difference between Physisorption and Chemisorption?
4. What is the sign of  $\Delta H$  &  $\Delta S$  when a gas is adsorbed by an adsorbent.
5. Explain the reason for following :
  - a) Powdered substances more effective adsorbents than their crystalline forms.
  - b) Finely divided substance is more effective as an adsorbent.
  - c)  $\text{NH}_3$  gas adsorbs more readily than  $\text{N}_2$  gas on the surface of Charcoal.
  - d) Adsorption is accompanied by decrease in entropy.
  - e) Enthalpy of chemisorption is high .
  - f) Adsorption is always exothermic.
  - g) Physical adsorption is reversible , while chemisorption is irreversible
  - h) Physisorption decrease with the increase of temperature.
  - i) Physical adsorption is multilayered, while chemisorption is monolayered.
  - j) It is important to have clean surface in surface studies.
  - k) We add alum to purify water.
  - l) Adsorption of a gas on the surface of solid is generally accompanied by a decrease in entropy. Still it is spontaneous process.
  - m) White precipitate of silver halide become coloured in the presence of dye eosin.
6. Discuss the effect of pressure and temperature on the adsorption of gases on solids.( Hint:Effect of Temperature and Pressure: The adsorption of gases on solids decreases with increase in temperature at constant pressure Effect of Pressure: The adsorption of gases on solids Increases with increase in pressure at constant Temperature.)
7. Out of  $\text{NH}_3$  &  $\text{CO}_2$  which gas will be adsorbed more readily on the surface of activated Charcoal & why?
8. Arrange  $\text{H}_2$ ,  $\text{CH}_4$ ,  $\text{CO}_2$  and  $\text{NH}_3$  in order of the ease with which the gases are adsorbed on the surface of charcoal.
9. What do you understand by activation of adsorbent? How is it achieved?
10. Why is chemisorption referred to as activated adsorption?
11. What is the effect of temperature on chemisorptions.
12. Explain Adsorption from solution phase.
13. Give applications of adsorption.
14. Explain clearly how the phenomenon of adsorption finds application in : (a) Production of high vacuum (b) Heterogeneous catalysis (c) Froth floatation process (d)Controlling humidity.
15. Why do physisorption and chemisorption behave differently with rise in temperature?
16. What is the role of activated charcoal in gas mask used in coal mines?
17. Give an example where physisorption changes to chemisorption with rise in temperature. Explain the reason for change.
18. What are the factors which influence the adsorption of a gas on a solid? (Hint: (i)Nature of adsorbate (ii) Surface area of adsorbent (iii) Temperature (iv) Pressure)
19. What is an adsorption isotherm?
20. Describe Freundlich adsorption isotherm.

**TOPIC: COLLOIDS, TYPES OF COLLOIDAL SOLUTIONS, PREPARATION OF COLLOIDS, PURIFICATION OF COLLOIDAL SOLUTIONS & PROPERTIES OF COLLOIDAL SOLUTIONS**

1. A **Colloid** is a heterogeneous system in which one substance is dispersed (dispersed phase) as very fine particles in another substance called dispersion medium. Colloidal particles are larger than simple

molecules but small enough to remain suspended. Their range of diameters is between 1 and 1000 nm ( $10^{-9}$  to  $10^{-6}$  m).

## 2. Classification Based on Physical State of Dispersed Phase and Dispersion Medium

Dispersed Phase	Dispersion medium	Type of Colloid	Examples
Solid	Solid	Solid sol	Coloured glasses and gem stones
<b>Solid</b>	<b>Liquid</b>	<b>Sol</b>	Paints, cell fluids
Solid	Gas	Aerosol	Smoke, dust
<b>Liquid</b>	<b>Solid</b>	<b>Gel</b>	<b>Cheese, butter, jellies</b>
<b>Liquid</b>	<b>Liquid</b>	<b>Emulsion</b>	<b>Milk, hair cream</b>
Liquid	Gas	Aerosol	<b>Fog, mist, cloud, insecticide sprays</b>
Gas	Solid	Solid sol	Pumice stone, foam rubber
Gas	Liquid	<b>Foam</b>	<b>Froth, whipped cream, soap lather</b>

If the dispersion medium is water, the sol is called **aquasol** or hydrosol and if the dispersion medium is alcohol, it is called **alcosol**.

## 3. Classification Based on Nature of Interaction between Dispersed Phase and Dispersion Medium

### (a) LYOPHILIC SOL (LIQUID-LOVING)

- Particles of dispersed phase have greater affinity i.e strong interaction for dispersion medium .
- Colloidal sols directly formed by mixing substances like gum, gelatine, starch, rubber, etc., with a suitable liquid (the dispersion medium) are called lyophilic sols. They can be easily prepared by shaking or warming.
- These sols are quite stable and cannot be easily coagulated
- They are reversible because if the dispersion medium is separated from the dispersed phase (say by evaporation), the sol can be reconstituted by simply remixing with the dispersion medium.
- Examples : gum, gelatine, starch, rubber, etc

### (b) LYOPHOBIC SOL (LIQUID-HATING)

- Particles of dispersed phase have no affinity i.e less interaction for dispersion medium.
- They cannot be prepared by directly mixing. It can be prepared only by special methods.
- These sols are readily precipitated (or coagulated) on the addition of small amounts of electrolytes, by heating or by shaking and hence, are not stable.
- They are irreversible because once precipitated, they do not give back the colloidal sol by simple addition of the dispersion medium. Hence, these sols are also called **irreversible sols**. Lyophobic sols need stabilizing agents for their preservation.
- Examples : colloidal solutions of gold, silver,  $\text{Fe}(\text{OH})_3$ ,  $\text{As}_2\text{S}_3$ , etc

LYOPHILIC SOL (LIQUID-LOVING.)	LYOPHOBIC SOL (LIQUID-HATING)
Strong interaction between dispersed phase & dispersion medium	Very Less Interaction between dispersed phase & dispersion medium
It can be prepared by directly mixing	It cannot be prepared by directly mixing
Quite stable	Not stable
cannot be easily coagulated	readily precipitated (or coagulated)
They are reversible	They are irreversible
Mostly of organic nature Ex. Gelatin, Starch, Gum, Albumin & Cellulose Solution	Mostly of Inorganic nature Ex. Transition metal salt in water Gold, As, colloidal solutions of gold, silver, $\text{Fe}(\text{OH})_3$ , $\text{As}_2\text{S}_3$ , etc

## 4. CLASSIFICATION BASED ON TYPE OF PARTICLES OF THE DISPERSED PHASE

MULTIMOLECULAR COLLOIDS	MACRO MOLECULAR COLLOIDS	ASSOCIATED COLLOIDS
A large number of atoms or smaller molecules of	Formation by aggregation of big size molecules.	These are the substances which behave as normal



substance on dissolution aggregate together to form species having size in the colloidal range. (diameter < 1nm) (Aggregation of large number of small atoms or molecules) Ex. → Gold, Sol, Sulphur sol (Au)                          (S <sub>8</sub> ) They are generally lyophobic.	In this type of colloids, colloidal particles are themselves large molecules of colloidal dimensions. These are polymers with high molecular mass Ex. → <b>Starch, Cellulose, Protein etc.</b> They are generally lyophilic.	electrolytes at low concentration but get associated and behave as colloidal solutions. These associated particles are also called <i>micelles</i> . (Aggregation of large number of ions in concentrated solutions) Ex. → <b>Soap &amp; Detergent</b>
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5. **CRITICAL MICELLE CONCENTRATION (CMC) & KRAFT TEMPERATURE (T<sub>k</sub>)** : The formation of micelles takes place only above a particular temperature called **Kraft temperature (T<sub>k</sub>)** and above a particular concentration called **critical micelle concentration (CMC)**.
6. **MECHANISM OF MICELLE FORMATION**: Let us take the example of soap solutions. Soap is sodium or potassium salt of a higher fatty acid and may be represented as RCOO<sup>-</sup>Na<sup>+</sup> (e.g., sodium stearate CH<sub>3</sub>(CH<sub>2</sub>)<sub>16</sub>COO<sup>-</sup>Na<sup>+</sup>, which is a major component of many bar soaps). When dissolved in water, it dissociates into RCOO<sup>-</sup> and Na<sup>+</sup> ions. The RCOO<sup>-</sup> ions, however, consist of two parts — a long hydrocarbon chain R (also called non-polar 'tail') which is hydrophobic (water repelling), and a polar group COO<sup>-</sup> (also called polar-ionic 'head'), which is hydrophilic (water loving). The RCOO<sup>-</sup> ions are, therefore, present on the surface with their COO<sup>-</sup> groups in water and the hydrocarbon chains R staying away from it and remain at the surface. But at critical micelle concentration, the anions are pulled into the bulk of the solution and aggregate to form a spherical shape with their hydrocarbon chains pointing towards the centre of the sphere with COO<sup>-</sup> part remaining outward on the surface of the sphere. An aggregate thus formed is known as '**ionic micelle**'. These micelles may contain as many as 100 such ions. Similarly, in case of detergents, e.g., sodium laurylsulphate, CH<sub>3</sub>(CH<sub>2</sub>)<sub>11</sub>SO<sub>4</sub><sup>-</sup>Na<sup>+</sup>, the polar group is — SO<sub>4</sub><sup>-</sup> along with the long hydrocarbon chain. Hence, the mechanism of micelle formation here also is same as that of soaps.
7. **CLEANSING ACTION OF SOAPS** : It has been mentioned earlier that a micelle consists of a hydrophobic hydrocarbon — like central core. The cleansing action of soap is due to the fact that soap molecules form micelle around the oil droplet in such a way that hydrophobic part of the stearate ions is in the oil droplet and hydrophilic part projects out of the grease droplet like the bristles (Fig. 5.7 NCERT). Since the polar groups can interact with water, the oil droplet surrounded by stearate ions is now pulled in water and removed from the dirty surface. Thus soap helps in emulsification and washing away of oils and fats. The negatively charged sheath around the globules prevents them from coming together and forming aggregates.
8. **PREPARATION OF COLLOIDS : CHEMICAL METHODS**  
**(a) Double decomposition:**  $As_2O_3 + 3H_2S \rightarrow As_2S_3 + 3H_2O$   
**(b) Oxidation:**  $2H_2S + SO_2 \rightarrow 2H_2O + 3S$     **(c) Reduction:**  $2AuCl_3 + 3SnCl_2 \rightarrow 3SnCl_4 + 2Au$   
**(d) Hydrolysis :**  $FeCl_3 + 3H_2O \rightarrow Fe(OH)_3 + 3HCl$
9. **ELECTRICAL DISINTEGRATION OR BREDIG'S ARC METHOD**: This method is suitable for the preparation of colloidal solutions of metals like gold, silver, platinum etc. This Process involves dispersion as well as condensation. An arc is struck between the metal electrodes under the surface of water containing some stabilizing agent such as a trace of KOH. The water is cooled by immersing the container in a ice bath. The intense heat of the arc vapourises some of the metal which condenses under cold water. Ex. Pt, Ag, Cu, Au, Sol are prepared by this method.
10. **PEPTIZATION** : Peptization may be defined as the **process of converting a precipitate into colloidal sol** by shaking it with dispersion medium in the presence of a small amount of electrolyte. The electrolyte used for this purpose is called **peptizing agent**. This method is applied, generally, to convert a freshly prepared precipitate into a colloidal sol. Freshly prepared ferric hydroxide on treatment with a small amount of ferric chloride solution at once forms a dark reddish brown solution. Ferric chloride acts as a

peptizing agent. During peptization, the precipitate adsorbs one of the ions of the electrolyte on its surface. This causes the development of positive or negative charge on precipitates, which ultimately break up into smaller particles of the size of a colloid.

11. **Purification of Colloidal Solutions;** The process used for reducing the amount of impurities to a requisite minimum is known as purification of colloidal solution.
12. **Dialysis:** It is a process of removing a dissolved substance from a colloidal solution by means of diffusion through a suitable membrane. It is a process of purification of sols containing electrolyte by keeping the sol in a bag made of parchment or cellophane and suspending the bag in pure water. Small molecules or ions can pass through the membrane, but the sol is retained. (Fig. 5.9 ,138). The apparatus used for this purpose is called dialyser.
13. **Electro-dialysis:** The process of dialysis is quite slow. It can be made faster by applying an electric field if the dissolved substance in the impure colloidal solution is only an electrolyte. The process is then named electrodialysis. The colloidal solution is placed in a bag of suitable membrane while pure water is taken outside. Electrodes are fitted in the compartment as shown in (Fig. 5.10 page138) . The ions present in the colloidal solution migrate out to the oppositely charged electrodes.

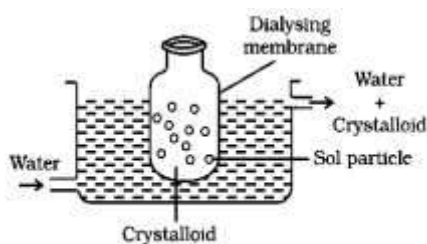


Fig. 5.9: Dialysis

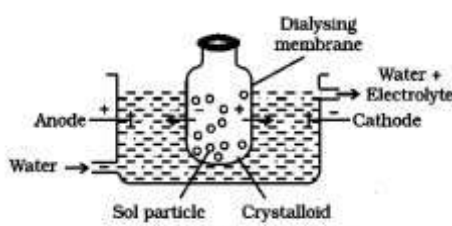


Fig. 5.10: Electro-dialysis

14. **Ultrafiltration:** Ultrafiltration is the process of separating the colloidal particles from the solvent and soluble solutes present in the colloidal solution by specially prepared filters, which are permeable to all substances except the colloidal particles. Colloidal particles can pass through ordinary filter paper because the pores are too large. However, the pores of filter paper can be reduced in size by impregnating with **colloidion** solution to stop the flow of colloidal particles. The usual colloidion is a 4% solution of nitrocellulose in a mixture of alcohol and ether. An ultra-filter paper may be prepared by soaking the filter paper in a colloidion solution, hardening by formaldehyde and then finally drying it. Thus, by using ultra-filter paper, the colloidal particles are separated from rest of the materials. Ultrafiltration is a slow process.

#### PROPERTIES OF COLLOIDAL SOLUTIONS

15. **COLLIGATIVE PROPERTIES:** Colloidal particles being bigger aggregates, the number of particles in a colloidal solution is comparatively small as compared to a true solution. Hence, the values of colligative properties (osmotic pressure, lowering in vapour pressure, depression in freezing point and elevation in boiling point) are of small order as compared to values shown by true solutions at same concentrations.
16. **TYNDALL EFFECT:** When a beam of light is passed through a colloidal solution and viewed perpendicular to the path of incident light, the path of beam is illuminated by a bluish light. The Tyndall effect is due to the fact that colloidal particles scatter light in all directions in space. This scattering of light illuminates the path of beam in the colloidal dispersion. The bright cone of the light is called **Tyndall cone**. Tyndall effect is used to distinguish between a colloidal and true solution.

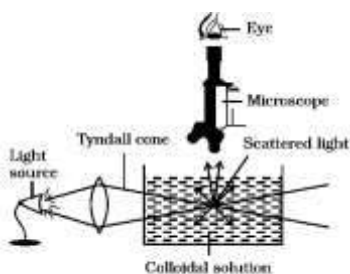


Fig. 5.11: Tyndall effect

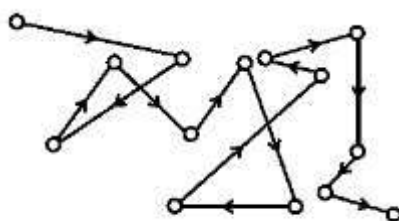


Fig. 5.12: Brownian movement

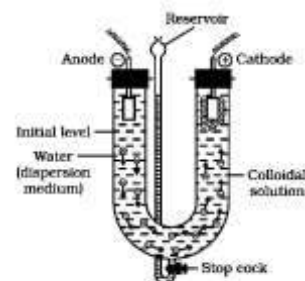


Fig. 5.13: Electrophoresis

17. **BROWNIAN MOVEMENT:** When colloidal solutions are viewed under a powerful ultra microscope, the colloidal particles appear to be in a state of continuous **zig-zag motion** all over the field of view. The Brownian movement has been explained to be **due to the unbalanced bombardment of the particles** by the molecules of the dispersion medium. The Brownian movement has a stirring effect which does not permit the particles to settle and thus, **is responsible for the stability of sols.**
18. **COLOUR:** The colour of colloidal solution depends on the wavelength of light scattered by the dispersed particles. The wavelength of light further depends on the size and nature of the particles. The colour of colloidal solution also changes with the manner in which the observer receives the light. For example, a mixture of milk and water appears blue when viewed by the reflected light and red when viewed by the transmitted light. Finest gold sol is red in colour; as the size of particles increases, it appears purple, then blue and finally golden.
19. **ELECTROPHORESIS:** The movement of colloidal particles towards positive or negative electrode in electric field is called electrophoresis. When electric potential is applied across two platinum electrodes dipping in a colloidal solution, the colloidal particles move towards one or the other electrode. . Positively charged particles move towards the cathode while negatively charged particles move towards the anode. (Fig. 5.13 page 142). **Electrophoresis provides an experimental proof to show that the colloidal particles are charged particles.**
20. **ELECTROOSMOSIS :** When electrophoresis, i.e., movement of particles is prevented by some suitable means, it is observed that the dispersion medium begins to move in an electric field. This phenomenon is termed electroosmosis.
21. **COAGULATION:** The process of changing the colloidal particles in a sol into the insoluble precipitate by addition of some suitable electrolytes is known as coagulation. The process of settling of colloidal particles is called coagulation or precipitation of the sol. The coagulation of the lyophobic sols can be carried out in the following ways:
- By electrophoresis:* The colloidal particles move towards oppositely charged electrodes, get discharged and precipitated.
  - By mixing two oppositely charged sols:* Oppositely charged sols when mixed in almost equal proportions, neutralise their charges and get partially or completely precipitated. Mixing of hydrated ferric oxide (+ve sol) and arsenious sulphide (-ve sol) bring them in the precipitated forms. This type of coagulation is called **mutual coagulation.**
  - By boiling:* When a sol is boiled, the adsorbed layer is disturbed due to increased collisions with the molecules of dispersion medium. This reduces the charge on the particles and ultimately lead to settling down in the form of a precipitate.
  - By persistent dialysis:* On prolonged dialysis, traces of the electrolyte present in the sol are removed almost completely and the colloids become unstable and ultimately coagulate.
  - By addition of electrolytes:* When excess of an electrolyte is added, the colloidal particles are precipitated. The reason is that colloids interact with ions carrying charge opposite to that present on themselves. This causes neutralisation leading to their coagulation. The ion responsible for neutralisation of charge on the particles is called the coagulating ion. A negative ion causes the precipitation of positively charged sol and vice versa.
22. **HARDY SCHULZE RULE** – This rule states that the precipitating effect of an ion on dispersed phase of opposite charge increases with the valency of the ion. The higher the valency of the flocculating ion, the greater is its precipitating power. Thus for the precipitation of  $As_2S_3$  sol (-ve) the precipitating power of  $Al^{3+}$ ,  $Ba^{2+}$ , and  $Na^+$  ions is in the order  $Al^{3+} > Ba^{2+} > Na^+$  Similarly for precipitating  $Fe(OH)_3$  sol (positive) the precipitating power of  $[Fe(CN)_6]^{3-}$ ,  $SO_4^{2-}$  and  $Cl^-$  ions is in the order  $[Fe(CN)_6]^{3-} > SO_4^{2-} > Cl^-$
23. **COAGULATING VALUE :** The minimum concentration of an electrolyte in millimoles per litre required to cause precipitation of a sol in two hours is called coagulating value. The smaller the quantity needed, the higher will be the coagulating power of an ion.
24. **COAGULATION OF LYOPHILIC SOLS :** There are two factors which are responsible for the stability of lyophilic sols. These factors are the **charge and solvation of the colloidal particles.** When these two

factors are removed, a lyophilic sol can be coagulated. This is done (i) by adding an electrolyte and (ii) by adding a suitable solvent. When solvents such as alcohol and acetone are added to hydrophilic sols, the dehydration of dispersed phase occurs. Under this condition, a small quantity of electrolyte can bring about coagulation.

25. **Protection of colloids** : Lyophilic sols are more stable than lyophobic sols. This is due to the fact that lyophilic colloids are extensively solvated, i.e., colloidal particles are covered by a sheath of the liquid in which they are dispersed. Lyophilic colloids have a unique property of protecting lyophobic colloids. When a lyophilic sol is added to the lyophobic sol, the lyophilic particles form a layer around lyophobic particles and thus protect the latter from electrolytes. Lyophilic colloids used for this purpose are called **Protective Colloids**.
26. **CHARGE ON COLLOIDAL PARTICLES**: Colloidal particles always carry an electric charge. The nature of this charge is the same on all the particles in a given colloidal solution and may be either positive or negative. The charge on the sol particles is due to one or more reasons, viz., due to electron capture by sol particles during electrodispersion of metals, due to preferential adsorption of ions from solution and/or due to formulation of electrical double layer. **Preferential adsorption** of ions is the most accepted reason. The sol particles acquire positive or negative charge by preferential adsorption of +ve or -ve ions. When two or more ions are present in the dispersion medium, preferential adsorption of the ion common to the colloidal particle usually takes place. This can be explained by taking the following examples:
- (a) When silver nitrate solution is added to potassium iodide solution, the precipitated silver iodide adsorbs iodide ions from the dispersion medium and negatively charged colloidal solution results. However, when KI solution is added to  $\text{AgNO}_3$  solution, positively charged sol results due to adsorption of  $\text{Ag}^+$  ions from dispersion medium.  $\text{AgI}/\text{I}^-$  (Negatively charged)  $\text{AgI}/\text{Ag}^+$  (Positively charged)
- (b) If  $\text{FeCl}_3$  is added to excess of hot water, a positively charged sol of hydrated ferric oxide is formed due to adsorption of  $\text{Fe}^{3+}$  ions. However, when ferric chloride is added to NaOH a negatively charged sol is obtained with adsorption of  $\text{OH}^-$  ions.  $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}/\text{Fe}^{3+}$  (Positively charged)  $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}/\text{OH}^-$  (Negatively charged)
27. **ELECTRICAL DOUBLE LAYER** :The surface of a colloidal particle acquires a +ve charge by selective adsorption of a layer of positive ions around it. This layer attracts counter ions from the medium which form a second layer of -ve charges. The combination of the two layers of +ve and -ve charges around the sol particle was called **Helmholtz double layer**. According to modern view, the first layer of ions is firmly held and is termed **Fixed layer** while the second layer is mobile which is termed a **Diffused layer**. The combination of the compact and diffused layer is referred as the **Stern double layer**. The diffused layer is only loosely attached to the particle surface and moves in the opposite direction under an applied electric field.
28. **ZETA POTENTIAL** :The potential difference between the fixed layer and the diffused layer of opposite charge is called **Electrokinetic Potential or Zeta Potential**.
29. **DEMULSIFICATION** :The process of breaking emulsion is called Demulsification, e.g., freezing, boiling, centrifugation or chemical methods are used to destroy emulsifying agent.
30. **COLLOIDS AROUND US**
- **Blue colour of the sky**: Dust particles along with water suspended in air scatter blue light which reaches our eyes and the sky looks blue to us.
  - **Artificial Rain** : It is possible to cause artificial rain by throwing electrified sand or spraying a sol carrying charge opposite to the one on clouds from an aeroplane.
  - **Blood**: It is a colloidal solution of an albuminoid substance. The styptic action of alum and ferric chloride solution is due to coagulation of blood forming a clot which stops further bleeding.
  - **Soils**: Fertile soils are colloidal in nature in which humus acts as a protective colloid. On account of colloidal nature, soils adsorb moisture and nourishing materials.

- **Formation of delta:** River water is a colloidal solution of clay. Sea water contains a number of electrolytes. When river water meets the sea water, the electrolytes present in sea water coagulate the colloidal solution of clay resulting in its deposition with the formation of delta.

### 31. APPLICATIONS OF COLLOIDS

- **Electrical precipitation of smoke:** Smoke is a colloidal solution of solid particles such as carbon, arsenic compounds, dust, etc., in air. The smoke, before it comes out from the chimney, is led through a chamber containing plates having a charge opposite to that carried by smoke particles. The particles on coming in contact with these plates lose their charge and get precipitated. The particles thus settle down on the floor of the chamber. The precipitator is called **Cottrell precipitator**.
- **Purification of drinking water:** The water obtained from natural sources often contains suspended impurities. Alum is added to such water to coagulate the suspended impurities and make water fit for drinking purposes.
- **Tanning:** Animal hides are colloidal in nature. When a hide, which has positively charged particles, is soaked in tannin, which contains negatively charged colloidal particles, mutual coagulation takes place. This results in the hardening of leather. This process is termed as tanning. Chromium salts are also used in place of tannin.
- **Medicines:** Most of the medicines are colloidal in nature. For example, argyrol is a silver sol used as an eye lotion. Colloidal antimony is used in curing kalaazar. Colloidal gold is used for intramuscular injection. Milk of magnesia, an emulsion, is used for stomach disorders. Colloidal medicines are more effective because they have large surface area and are therefore easily assimilated.
- **Photographic plates and films:** Photographic plates or films are prepared by coating an emulsion of the light sensitive silver bromide in gelatin over glass plates or celluloid films.
- **Rubber industry:** Latex is a colloidal solution of rubber particles which are negatively charged. Rubber is obtained by coagulation of latex.

### Questions .....

1. Differentiate among a True solution, a suspension and a Colloidal solution give a suitable example of each.
2. How are colloids classified on the basis of (i) Physical states of components (ii) Nature of dispersion medium and (iii) Interaction between dispersed phase and dispersion medium.
3. Write the Dispersed Phase & Dispersion Medium of the following Colloidal Solutions. (a) Smoke (b) Butter (c) Milk (d) Fog (e) Froth (f) dust
4. What type of colloid is formed when (a) Liquid is dispersed in a solid. (b) Gas is dispersed in a liquid. (c) solid is dispersed in a Gas. (d) Liquid is dispersed in a liquid (e) solid is dispersed in a liquid. Give Examples for each case.
5. What are the physical states of dispersed phase and dispersion medium of froth?
6. Explain the terms with suitable examples : (i) Alcosol (ii) Aerosol (iii) Hydrosol.
7. What are Lyophilic and Lyophobic sols? Give one example of each type.
8. Why hydrophobic sols are easily coagulated?
9. What is difference between multimolecular and macromolecular colloids? Give one example of each.
10. Define associated colloids giving an example.
11. Define the terms : (i) Critical Micelle concentration (CMC) (ii) Kraft Temperature ( $T_K$ ) (iii) ionic micelle'
12. What type of solutions are formed on dissolving different concentrations of soap in water?
13. What are micelles? Give an example of a micellers system.
14. Write chemical methods of preparation of colloids.
15. How are following colloidal solutions prepared? (i) Sulphur in water (ii) Gold in water
16. Write physical methods Preparation of Colloids.
17. Write a note on: (i) Bredig's Arc methods (b) Peptization
18. Explain the following with diagrams: (a) Dialysis (b) Electro-dialysis (c) ultrafiltration

19. Explain the following terms (a) Tyndall effect (b) Brownian movement (c) Electrophoresis.(d) Hardy Schulze rule. (e) Zeta Potential
20. What is the reason for Brownian movement in colloidal solution.
21. Explain Coagulation. Describe any three methods by which coagulation of lyophobic sols can be carried out.
22. How can a colloidal solution and true solution of the same colour be distinguished from each other.
23. What happens when electric field is applied to colloidal solution?
24. On the basis of Hardy-Schulze rule explain why the coagulating power of phosphate is higher than chloride.
25. Most effective electrolyte causing the coagulation of  $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}/\text{Fe}^{3+}$  is a)  $\text{MgCl}_2$  b)  $\text{KCl}$  c)  $\text{K}_4[\text{Fe}(\text{CN})_4]$  d)  $\text{AlCl}_3$
26. Which one of the following electrolytes is most effective for the Coagulation of  $\text{Fe}(\text{OH})_3$  sol & why .(a)  $\text{NaCl}$  (b)  $\text{Na}_2\text{SO}_4$  (c)  $\text{Na}_3\text{PO}_4$
27. Out of  $\text{BaCl}_2$  &  $\text{KCl}$  which one is more most effective for the Coagulation of negatively charged sol & why .
28. A colloidal solution of  $\text{AgI}$  is prepared by two different methods. (A)  $\text{AgNO}_3$  solution is added to excess  $\text{KI}$  solution. (B)  $\text{KI}$  solution is added to excess  $\text{AgNO}_3$  solution. What is the charge on the  $\text{AgI}$  colloidal particles in the two cases. Explain.
29. Why is  $\text{Fe}(\text{OH})_3$  colloid positively charged, when prepared by adding  $\text{FeCl}_3$  to hot water?
30. How does it become possible to cause artificial rain by spraying silver iodide on the clouds?
31. What are emulsions? What are their different types? Give example of each type. Give four uses of emulsions.
32. What is Demulsification? Name two demulsifiers.
33. How do emulsifying agents (emulsifier) stabilise the emulsion?
34. What happens when gelatin is mixed with gold sol?
35. How does the precipitation of colloidal smoke take place in Cottrell precipitator?
36. What is the reason for stability of colloidal solution.
37. Give reason for the following :
  - (a) Leather gets hardened after Tanning.
  - (b) Delta is formed at the meeting point of sea water and river water.
  - (c) Bleeding stop by rubbing moist alum.
  - (d) some medicines more effective in the colloidal form
  - (e) Sky looks blue to us.
  - (f) ferric chloride preferred over potassium chloride in case of a cut Leading to bleeding
  - (g) Lyophilic sols are more stable than lyophobic sols
  - (h) Lyophilic sols are also called as reversible sols.
  - (i) Artificial Rain is caused by spraying salt over clouds.
  - (j) Gelatin which is a peptide is added in icecreams
  - (k) Same substance can act as both colloids & crystalloids.
38. Explain what is observed:
  - (i) When a beam of light is passed through a colloidal sol.
  - (ii) An electrolyte,  $\text{NaCl}$  is added to hydrated ferric oxide sol or ferric hydroxide.
  - (iii) Electric current is passed through a colloidal sol.
  - (iv) Ferric hydroxide sol gets coagulated on addition of sodium chloride solution
  - (v) Cottrell's smoke precipitator is fitted at the mouth of the chimney used in factories.
  - (vi) Persistent dialysis of a colloidal solution is carried out.
  - (vii) An emulsion is centrifuged.

# THE d- AND f-BLOCK ELEMENTS

**1. d-block elements :** The elements of periodic table belonging to **group 3 to 12** are known as d-Block elements. Because in these elements last electron enters in d sub shell or d orbital .

**2. Transition Series:** There are four series of the transition metals, **3d series** (Sc to Zn), **4d series** (Y to Cd) and **5d series** (La to Hg, omitting Ce to Lu). The fourth **6d series** which begins with Ac is still incomplete

**3.** d- Block elements are collectively known as Transition Elements because properties of these elements vary in between s-Block and p-Block elements.

**4.** The general electronic configuration of these elements is  $(n-1)d^{1-10} ns^{1-2}$

**5. Transition element: A transition element is defined as the one which has incompletely filled d orbitals in its ground state or in any one of its oxidation states. i.e.** A transition element should have partially filled (n-1) d orbital.

**6. Zinc, cadmium and mercury of group 12 have full  $d^{10}$  configuration in their ground state as well as in their common oxidation states and hence, are not regarded as transition metals**

**Melting points & Boiling points of transition elements:** Transition metals have high melting and boiling points because they have strong **metallic bonding** due to involvement of greater number of electrons from (n-1)d in addition to the ns electrons. In any row the melting points of these metals rise to a maximum at  $d^5$  except for **anomalous values of Mn.**

**7. Enthalpy of atomization:** The transition elements exhibit higher enthalpies of atomization Because of large number of unpaired electrons in their atoms they have stronger interatomic interaction and hence stronger Metallic bonding between atoms resulting in higher enthalpies of atomization.

**8** In the series Sc(Z = 21) to Zn (Z = 30), the enthalpy of atomisation of zinc is the lowest, i.e.,  $126 \text{ kJ mol}^{-1}$ . because in the formation of metallic bonds, no electrons from 3d-orbitals are involved in case of zinc, while in all other metals of the 3d series, electrons from the d-orbitals are always involved in the formation of metallic bonds.

**9. Variation in Atomic Size of Transition Metals along 3d transition series:** The atomic radii decreases from group 3 to 6 (i.e. Sc to Cr) because of increase in effective nuclear charge gradually, The atomic radii of group 7, 8, 9 & 10 elements (i.e. Fe, Co, Ni) is almost same because Screening effect counter balances increased effective nuclear charge, Group 11 & 12 elements i.e. Cu & Zn have bigger size due to increase in inter-electronic repulsion as result electron cloud expands and size increases.

**10.** Members of second(4d) and the third (5d) series in each group of transition elements have similar radii and shows similar properties because **lanthanoid contraction** essentially compensates for the expected increase in atomic size with increasing atomic number.

**11.** Zr (160 pm) & Hf (159 pm) and have very similar physical and chemical properties because Zr & Hf belongs to same group of second(4d) and the third (5d) series, as a result they have similar radii due to **lanthanoid contraction.**

**12. Variation in density of Transition Metals along 3d transition series** The decrease in metallic radius coupled with increase in atomic mass results in a general increase in the density of these elements. Thus, from titanium (22) to copper (29) the significant increase in the density may be noted.

**13. Variation in Ionisation Enthalpies of Transition Metals along 3d transition series**

There is an increase in ionisation enthalpy along each series of the transition elements from left to right due to an increase in nuclear charge which accompanies the filling of the inner d orbitals,. However, many small variations occur. Irregular variation of ionisation enthalpies is mainly attributed to varying degree of stability of different 3d-configurations (e.g.,  $d^0$ ,  $d^5$ ,  $d^{10}$  are exceptionally stable).

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
$\Delta_i H / \text{kJ mol}^{-1}$	631	656	650	653	717	762	758	736	745	906

**14. Oxidation States:** The transition elements show variable oxidation state due to small energy difference between (n-1)d & ns orbital as a result both (n-1)d & ns electrons take part in bond formation. The highest oxidation state of an element is equal to number of unpaired e<sup>-</sup> present in (n-1) d & ns orbital.

- The highest oxidation state of an element is equal to number of unpaired electrons present in (n-1)d & ns orbital..
- The largest number of oxidation states are exhibited by the elements in the middle of first row of the transition elements due to maximum unpaired electrons present in (n-1) d & ns orbital. for example Manganese, , exhibits all the oxidation states from +2 to +7.
- The lesser number of oxidation states at the extreme ends stems from either too few electrons to lose or share (Sc, Ti) or too many d electrons (hence fewer orbitals available in which to share electrons with others) for higher valence (Cu, Zn). Thus, early in the series scandium(II) is virtually unknown and titanium (IV) is more stable than Ti(III) or Ti(II). At the other end, the only oxidation state of zinc is +2 (**no d electrons are involved**).

**15. Formation of Coloured Ions:** Most of the transition metal ions in solution as well as in solid states are coloured. This is due to the presence of unpaired electrons in d-orbitals of the transition metal ions. It is because of these **d – d transitions** occurring in a transition metal ions by absorption of visible light that they appear coloured.

**16. Magnetic Properties:** Diamagnetic substances are repelled by the applied field while the paramagnetic substances are attracted. Substances which are attracted very strongly are said to be *ferromagnetic*. In fact, ferromagnetism is an extreme form of paramagnetism.

**a) Most of the transition metal ions are paramagnetic. Because transition elements contain unpaired electrons in their (n-1) d sub shells.**

**b)** The magnetic moment is determined by the number of unpaired electrons and is calculated by using the 'spin-only' formula, i.e.  $\mu = \sqrt{n(n+2)}$  where n is the number of unpaired electrons and  $\mu$  is the magnetic moment in units of Bohr magneton (BM).

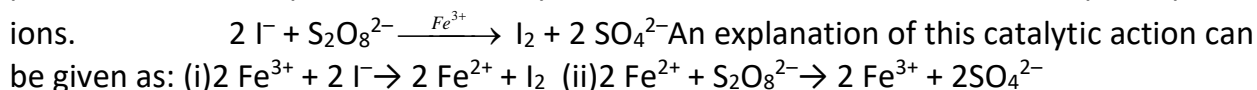
**c)** The magnetic moment increases with the increasing number of unpaired electrons.

**d)** Variation in magnetic behaviour of Transition Metals along 3d transition series.: In the 3d-transition series as we move from Sc (21) to Mn (25) the number of unpaired electrons increases and hence paramagnetic character increases. After Mn, the pairing of electrons in the d-orbital starts and the number of unpaired electrons decreases and hence, paramagnetic character decreases.

**17. Formation of Complex Compounds:** The transition metals form a large number of complex compounds. This is due to **smaller sizes of the metal ions, their high ionic charges and the availability of d orbitals for bond formation**. A few examples are:  $[\text{Fe}(\text{CN})_6]^{3-}$ ,  $[\text{Fe}(\text{CN})_6]^{4-}$ ,  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  and  $[\text{PtCl}_4]^{2-}$

**18. Catalytic Properties:** The catalytic activity of transition metal ions is attributed to the following two reasons:

a) **Variable oxidation states** due to which they can form a variety of unstable intermediate products. For example, iron(III) catalyses the reaction between iodide and persulphate ions.





- a) **Large surface area** so that the reactants are absorbed on the surface and come closer to each other facilitating the reaction process.

**19. Formation of Interstitial Compounds:** Interstitial compounds are those which are formed when small atoms like H, C or N are trapped inside the crystal lattices of metals. Transition elements form interstitial compounds because size of C, N, O, and B is similar to size of interstitial voids of transition metal

**20. Alloy Formation:** Alloys may be homogeneous solid solutions in which the atoms of one metal are distributed randomly among the atoms of the other. **Because of similar radii** and other characteristics of transition metals, alloys are readily formed by these metals. Example: brass (copper-zinc) and bronze (copper-tin).

**21. Standard Electrode Potentials:** Transition elements have lower value of **Standard Electrode Potentials** due to high ionization potential, high heat of sublimation & low enthalpy of hydration.

**22. Trends in the  $M^{2+}/M$  Electrode Potentials:** For the first row transition metals the  $E^{\circ}$  values are:

$E^{\circ}$	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
$(M^{2+}/M)$	-1.63	-	-	-	-	-	-	+0.34	-0.76
		1.18	0.91	1.18	0.44	0.28	0.25		

- a) The  $E^{\circ} (M^{2+}/M)$  values are not regular which can be explained from the irregular variation of ionization energy and sublimation energy of Mn due to half-filled orbitals.
- b) The general trend towards less negative  $E^{\circ}$  values across the series is related to the general increase in the sum of the first and second ionisation enthalpies.
- c) It is interesting to note that the value of  $E^{\circ}$  for Mn, Ni and Zn are more negative than expected from the trend. The stability of the half-filled  $d$  sub-shell in  $Mn^{2+}$  and the completely filled  $d^{10}$  configuration in  $Zn^{2+}$  are related to their  $E^{\circ}$  values, whereas  $E^{\circ}$  for Ni is related to the highest negative  $\Delta_{hyd}H^{\circ}$

**23. Trends in the  $(M^{3+}/M^{2+})$  Standard Electrode Potentials**

Element	Sc	Ti	V	Cr	Mn	Fe	Co
$E^{\circ}(M^{3+}/M^{2+})$	-	-	-	-	+1.57	+0.77	<b>+1.97</b>
		0.37	0.26	0.41			

- a) The low value for Sc reflects the stability of  $Sc^{3+}$  which has a noble gas configuration
- b) The highest value for Zn is due to the removal of an electron from the stable  $d^{10}$  configuration of  $Zn^{2+}$ .
- c) The comparatively high value for Mn shows that  $Mn^{2+}(d^5)$  is particularly stable,

**24. The oxide of transition metals** in lower oxidation states are generally basic while those in the higher oxidation states are acidic. Acidic character increases with increase in oxidation state is due to decrease in size of metal ion and increase in effective nuclear charge .e.g.  $MnO$  (basic),  $Mn_3O_4$  (amphoteric),  $Mn_2O_7$  (acidic).

**Questions.....**

- How are d - Block Elements & Transition elements different?
- Write the Electronic Configuration of elements with atomic number 21 to 30.
- Write down the electronic configuration of : (i)  $Cr^{3+}$  (iii)  $Cu^+$  (v)  $Co^{2+}$  (vii)  $Mn^{2+}$
- Write down the number of 3d electrons in each of the following ions:  $Ti^{2+}$ ,  $V^{2+}$ ,  $Cr^{2+}$ ,  $Mn^{2+}$ ,  $Fe^{2+}$ ,  $Fe^{3+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ , and  $Cu^{2+}$ .
- Zn, Cd and Hg are not considered as transition elements. Why
- Which of the d-block elements may not be regarded as the transition elements?

7. Scandium is a transition element but Zinc is not. Why [Ans: Scandium is a transition element because it has incompletely filled  $d$  orbitals in its ground state but Zinc has full  $d^{10}$  configuration in their ground state as well as in their common oxidation state.]
8. Copper atom has completely filled  $d$  orbital ( $3d^{10}$ ) in its ground state, yet it is a transition element. Why [Ans: Copper ( $Z = 29$ ) can exhibit +2 oxidation state wherein it will have incompletely filled  $d$ -orbitals ( $3d$ ), hence a transition element.]
9. Silver atom has completely filled  $d$  orbital ( $4d^{10}$ ) in its ground state, yet it is a transition element. Why [Ans: Silver ( $Z = 47$ ) can exhibit +2 oxidation state wherein it will have incompletely filled  $d$ -orbitals ( $4d$ ), hence a transition element.]
10. What are the characteristics of the transition elements and why are they called transition elements? [Ans: Characteristics of the transition elements: . variety of oxidation states, formation of coloured ions and entering into complex formation with a variety of ligands. The transition metals and their compounds also exhibit catalytic property and paramagnetic behaviour. The very name 'transition' given to the elements of  $d$ -block is only because of their position between  $s$ - and  $p$ - block elements]
11. All  $d$  block elements are not transition elements but all transition elements are  $d$ -block elements. Explain. [ Ans: All  $d$  block elements are not transition elements because  $d$  block elements like Zinc have full  $d^{10}$  configuration in their ground state as well as in their common oxidation state. which is not according to definition of transition elements. but all transition elements are  $d$ -block elements because transition elements are defined as  $d$  block elements which are having incompletely filled  $d$  orbitals in its ground state or in any one of its oxidation states]
12. Why do the transition elements exhibit higher enthalpies of atomization?
13. In the series Sc ( $Z = 21$ ) to Zn ( $Z = 30$ ), the enthalpy of atomisation of zinc is the lowest
14. Why do the Transition metals have high melting and boiling points?
15. Chromium group elements have highest melting points.
16. Fe has higher melting point than Cu.
17. Zinc is soft whereas Cr is hard
18. Explain Variation in Atomic Size of Transition Metals along 3d transition series.
19. In general the atomic radii of transition elements decrease with atomic number in the given series.
20. Members of second ( $4d$ ) and the third ( $5d$ ) series in each group of transition elements have similar radii.
21. Zr and Hf exhibit similar properties.
22. How would you account for the irregular variation of ionization enthalpies (I & II) in the first series of the transition elements?
23. The third ionization enthalpy of Mn is exceptionally high. [Ans: Because  $Mn^{2+}$  has half filled  $d$ -orbital.
24. Transition elements show variable oxidation states. Give reason
25. Name a transition element which does not exhibit variable oxidation states. [Scandium]
26. Which of the 3d transition series metals exhibits the largest number of oxidation states and why?

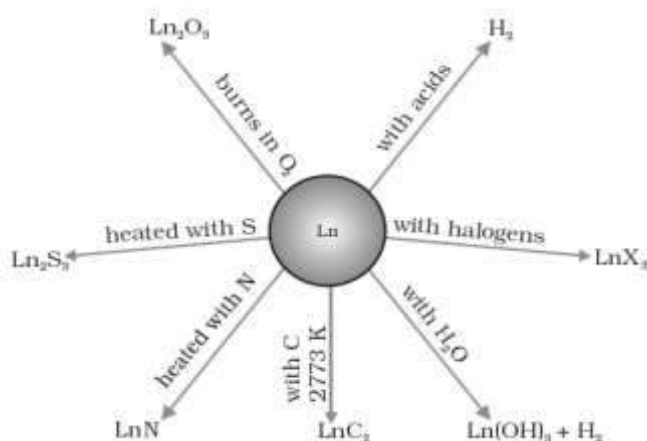
27. Why are  $\text{Mn}^{2+}$  compounds more stable than  $\text{Fe}^{2+}$  towards oxidation to their +3 state. [Ans: It is because  $\text{Mn}^{2+}$  has  $3d^5$  configuration which has extra stability, further loss of electron requires high energy.]
28. Explain briefly how +2 state becomes more and more stable in the first half of the first row transition elements with increasing atomic number? [Ans: In the first half more and more of d orbitals are half filled imparting greater stability to +2 state. In the second half electrons in 3d orbital pair up and the number of half filled orbital decreases. hence the stability +2 state decreases ].
29. To what extent do the electronic configurations decide the stability of oxidation states in the first series of the transition elements? Illustrate answer with examples. [Ans: In a transition series the oxidation states which lead to noble gas ( $\text{Sc}^{3+}$ )/ exactly half filled ( $\text{Mn}^{2+}$ )/ completely filled ( $\text{Zn}^{2+}$ ) d orbitals are more stable.]
30. What may be the stable oxidation state of the transition element with the following d electron configurations in the ground state of their atoms:  $3d^3$ ,  $3d^5$ ,  $3d^8$  and  $3d^4$ ? [Ans: Stable oxidation states.  $3d^3$  (Vanadium): (+2), +3, +4, and +5,  $3d^5$  (Chromium): +3, +4, +6,  $3d^5$  (Manganese): +2, +4, +6, +7,  $3d^8$  (Cobalt): +2, +3 (in complexes),  $3d^4$  There is no  $d^4$  configuration in the ground state.]
31. Compare the stability of +2 oxidation state for the elements of the first transition series. [Ans: In general the stability +2 oxidation state decreases from left to right (the exceptions being Mn (exactly half filled d orbital in d +2 state) and Zn (completely filled d orbital in d +2 state)]
32. Calculate the number of unpaired electrons in the following gaseous ions:  $\text{Mn}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{V}^{3+}$  and  $\text{Ti}^{3+}$ . Which one of these is the most stable in aqueous solution. [Ans:  $\text{Mn}^{3+}$  (4),  $\text{Cr}^{3+}$  (3),  $\text{V}^{3+}$  (2),  $\text{Ti}^{3+}$  (1). Stable  $\text{Cr}^{3+}$ ].
33. Which metal in the first series of transition metals exhibits +1 oxidation state most frequently and why? [Ans: Copper due to  $3d^{10}$  configuration]
34. There occurs much more frequent metal-metal bonding in compounds of heavy transition elements (3<sup>rd</sup> series).
35. There is in general increase in density of element from titanium to copper.
36. In transition series with an increase in atomic number the atomic radii does not change very much.
37. Radius of  $\text{Fe}^{+2}$  is less than  $\text{Mn}^{+2}$ .
38. Although Zr belongs to 4d and Hf belongs to 5d transition series but it is quite difficult to separate them.
39. Mn Shows the highest oxidation state of +7 with oxygen but with fluorine it shows the highest oxidation state of +4.
40. Highest fluoride of Mn is  $\text{MnF}_4$  whereas the highest oxide is  $\text{Mn}_2\text{O}_7$ .
41.  $\text{Cu}^+$  salts are colourless while  $\text{Cu}^{2+}$  salts are Coloured
42. The Transition metals ions such as  $\text{Cu}^+$ ,  $\text{Ag}^+$ ,  $\text{Sc}^{3+}$  are colourless
43. Unlike  $\text{Cr}^{3+}$ ,  $\text{Mn}^{+2}$ ,  $\text{Fe}^{+3}$  and the subsequent other  $\text{M}^{2+}$  ions of the 3d series of elements, the 4d and the 5d series metals generally do not form stable cationic species

44. Metal –metal bonding is more frequent for the 4d & 5d series of transition metals than that for the series.
45. Chromium is a typical hard metal while mercury is a liquid.
46. Cobalt (II) is stable in aqueous solution but in the presence of complexing reagents it is easily oxidized.
47. Cobalt (II) is easily oxidized in the presence of strong ligands.
48. Transition elements tend to be unreactive with increasing atomic number in the series.
49. +3 state of Mn is of little importance.
50.  $Mn^{+3}$  undergoes disproportionation reaction easily.
51. First Ionization enthalpy of Cr is lower than that of Zinc.
52. Give reason (a) Transition element form generally coloured compounds. (b)  $Cu^+$  salts are colourless while  $Cu^{2+}$  salts are Coloured (c) The Transition metals ions such as  $Cu^+$   $Ag^+$   $Sc^{+3}$  are colourless..
53.  $Zn^{+2}$  salts are white ,but  $Cu^{+2}$  are coloured. Why
54. Out of  $Ag_2SO_4$ ,  $CuF_2$ ,  $MgF_2$  and  $CuCl$  which compound will be coloured and why?
55. Predict which of the following will be coloured in aqueous solution?  $Ti^{3+}$ ,  $V^{3+}$ ,  $Cu^+$ ,  $Sc^{3+}$ ,  $Mn^{2+}$ ,  $Fe^{3+}$  &  $Co^{2+}$ .
56. Give reason (a) Transition metals show paramagnetic behaviour. (b)  $Mn^{2+}$  exhibits maximum paramagnetism
57. Explain Variation in magnetic behaviour of Transition Metals along 3d transition series.
58. Calculate the magnetic moment of a divalent ion in aqueous solution if its at.no is 25. [ **Ans:**  $\mu = \sqrt{5(5+2)} = 5.92BM$  ]
59. Calculate the 'spin only' magnetic moment of  $M^{2+}$  ion ( $Z = 27$ ). [ **Ans:**  $\mu = \sqrt{3(3+2)} = 4.9 BM$  ]
60. Give reason (i) Transition metal ions form complex ions (ii) Most of the transition metals and their compounds possess catalytic properties. (iii) Transition metals form interstitial compounds. (iv) Most of the transition metals form alloys.
61. What are interstitial compounds? Why are such compounds well known for transition metals.
62. Give reason
- The greatest number of oxidation states are exhibited by the elements in the middle of transition series.
  - A transition metal exhibit higher oxidation state in oxides and fluorides. [**Ans:** *Because of small size and high electronegativity oxygen or fluorine can oxidise the metal to its highest oxidation state*]
  - The highest oxidation state is exhibited in oxoanions of a metal. [**Ans:** *This is due to the high electronegativity of oxygen*]
  - The lowest oxide of transition metal is basic, the highest is amphoteric/acidic. [**Ans: Point-10**]
  - Of the  $d^4$  species,  $Cr^{2+}$  is strongly reducing while manganese(III) is strongly oxidising. [**Ans:**  *$Cr^{2+}$  is reducing as its configuration changes from  $3d^4$  to  $3d^3$ , the latter having a stable configuration ,half-filled  $t_{2g}$  level (see Unit 9) . On the other hand, the change from  $Mn^{2+}$  to  $Mn^{3+}$  results in the half-filled ( $3d^5$ ) configuration which is an extra stable configuration.*]
  - $Cr^{2+}$  is reducing and  $Mn^{3+}$  oxidising when both have  $d^4$  configuration. [**Ans: same as d**]
  - $Cr^{2+}$  is a stronger reducing agent  $Fe^{2+}$ . [**Ans:** *because change in  $3d^4 \rightarrow 3d^3$  occurs in case of  $Cr^{2+}$  to  $Cr^{3+}$  But  $3d^6 \rightarrow 3d^5$  occurs in case of  $Fe^{2+}$  to  $Fe^{3+}$  .In a medium (like water)  $d^3$  is more stable as compared to  $d^5$* ]

- h)  $\text{Cu}^+$  ion is not stable in aqueous solutions. [Ans:  $\text{Cu}^+$  in aqueous solution undergoes disproportionation, i.e.,  $2\text{Cu}^+(\text{aq}) \rightarrow \text{Cu}^{2+}(\text{aq}) + \text{Cu}(\text{s})$ . The  $E^0$  value for this is favourable.]
- i) Cobalt (II) is stable in aqueous solution but in the presence of complexing reagents it is easily oxidized. [Ans: Because  $\text{Co}^{3+}$  is more stable than  $\text{Co}^{2+}$ . OR Due to CFSE, which more than compensates the 3rd IE.]
- j)  $E^0$  value for the  $\text{Mn}^{3+}/\text{Mn}^{2+}$  couple much more positive than that for  $\text{Cr}^{3+}/\text{Cr}^{2+}$  or  $\text{Fe}^{3+}/\text{Fe}^{2+}$  [Ans: Much larger third ionisation energy of Mn (where the required change is  $d^5$  to  $d^4$ ) is mainly responsible for this. This also explains why the +3 state of Mn is of little importance.]
- k)  $\text{K}_2[\text{PtCl}_6]$  is well known compound whereas the corresponding Ni compound is not known. [Ans: The oxidation state of Pt in is +4 which is stable for Pt. The +4 oxidation state for Ni is very difficult to achieve because the sum of first four ionization energies is very high. Hence, the corresponding Ni(II) compound is known.]
- l) Transition elements tend to be unreactive with increasing atomic number in the series. [Ans: Due to increase ionization enthalpy in the series]
- m) The  $d^1$  configuration is very unstable in ions. [Ans: The ion with  $d^1$  configuration try to lose the only electron in order to acquire inert gas configuration]
63. How would you account for the irregular variation of ionization enthalpies (first and second) in the first series of the transition elements? [Ans: Irregular variation of ionisation enthalpies is mainly attributed to varying degree of stability of different 3d-configurations (e.g.,  $d^0$ ,  $d^5$ ,  $d^{10}$  are exceptionally stable).]
64. For the first row transition metals the  $E^0$  ( $\text{M}^{2+}/\text{M}$ ), explain the irregularities in the values. [Ans: The  $E^0$  ( $\text{M}^{2+}/\text{M}$ ) values are not regular which can be explained from the irregular variation of ionisation enthalpies ( $\Delta_i H_1 + \Delta_i H_2$ ) and also the sublimation enthalpies]
65. How would you account for the increasing oxidising power in the  $\text{VO}_2^+ < \text{Cr}_2\text{O}_7^{2-} < \text{MnO}_4^-$  [Ans: This is due to the increasing stability of the lower species to which they are reduced].
66. Which is a stronger reducing agent  $\text{Cr}^{2+}$  or  $\text{Fe}^{2+}$  and why? [Ans: Same as f]
67. Name the oxometal anions of the first series of the transition metals in which the metal exhibits the oxidation state equal to its group number. [Ans:  $\text{MnO}_4^-$ ,  $\text{Cr}_2\text{O}_7^{2-}$ ]
68.  $\text{CrO}_4^{2-}$  is a strong oxidizing agent while  $\text{MnO}_4^-$  is not
69.  $\text{Cu}^+$  ion has  $d^{10}$  configuration while  $\text{Cu}^{+2}$  has  $d^9$  configuration, still  $\text{Cu}^{+2}$  is stable in aqueous solutions.
70.  $E^0$  value for the  $\text{Mn}^{2+}/\text{Mn}$  much more than expected
71.  $E^0$  value for the  $\text{Cu}^{2+}/\text{Cu}$  is positive.
72. Although  $\text{Co}^{2+}$  ion appears to be stable, it is easily oxidized to  $\text{Co}^{3+}$  ion in the presence of a strong ligand.
73. Cobalt (II) is stable in aqueous solution but in the presence of complexing reagents it is easily oxidized
74. MnO is basic while  $\text{Mn}_2\text{O}_7$  is acidic in nature.
75. Unlike  $\text{Cr}^{3+}$ ,  $\text{Mn}^{+2}$ ,  $\text{Fe}^{+3}$  and the subsequent other  $\text{M}^{2+}$  ions of the 3d series of elements, the 4d and the 5d series metals generally do not form stable cationic species
76. Metal-metal bonding is more frequent for the 4d & 5d series of transition metals than that for the series
77. Chromium is a typical hard metal while mercury is a liquid

## LANTHANOIDS

1. The 14 elements after Lanthanum having atomic number 58 to 71 are collectively known as Lanthanoids.
2. **Electronic Configurations:** The general electronic configuration of these elements is  $[\text{Xe}] 4f^{1-14}, 5d^{0-1}, 6s^2$ .
3. **Atomic and Ionic Sizes (lanthanoid contraction):** The overall decrease in atomic and ionic radii from lanthanum to lutetium is due to poor shielding of 4f electrons is known as **lanthanoid contraction**.
  - **Consequence of the lanthanoid contraction :** (i) Members of second (4d) and the third (5d) series in each group of transition elements have similar radii. The almost identical radii of Zr(160 pm) and Hf (159 pm), a consequence of the lanthanoid contraction,
  - It is difficult to separate lanthanoid elements in pure state.
4. **Oxidation States:** Most common oxidation state of these elements is +3, However, occasionally +2 and +4 ions in solution or in solid compounds are also obtained. This irregularity arises mainly from the extra stability of empty, half-filled or filled *f* subshell.
  - The formation of Ce(IV) is favoured by its noble gas configuration, but it is a strong oxidant reverting to the common +3 state.
  - $\text{Eu}^{2+}$  is a strong reducing agent changing to the common +3 state.
  - $\text{Yb}^{2+}$  which has  $f^{14}$  configuration is a reductant. Tb(IV) has half-filled *f*-orbitals and is an oxidant.
5. **Colour Formation :** Many trivalent lanthanoid ions are coloured both in the solid state and in aqueous solutions. Colour of these ions may be attributed to the presence of *unpaired* electrons in *f* subshell. Neither  $\text{La}^{3+}(f^0)$  nor  $\text{Lu}^{3+}(f^{14})$  ion shows any colour due to absence of *unpaired* electrons in *f* subshell.
6. **Magnetic Behaviour:** The lanthanoid ions other than the  $f^0$  type ( $\text{La}^{3+}$  and  $\text{Ce}^{4+}$ ) and the  $f^{14}$  type ( $\text{Yb}^{2+}$  and  $\text{Lu}^{3+}$ ) are all paramagnetic. The paramagnetism rises to maximum in neodymium.
7. The first **ionisation enthalpies** of the lanthanoids are around  $600 \text{ kJ mol}^{-1}$ , the second about  $1200 \text{ kJ mol}^{-1}$  comparable with those of calcium.
8. In their **Chemical behaviour**, in general, the earlier members of the series are quite reactive similar to calcium but, with increasing atomic number, they behave more like aluminium.
9. **Chemical reactions of the lanthanoids.**



## 10. Uses of Lanthanoids:

- Production of alloy steels for plates and pipes.
- A well known alloy is *mischmetal* which consists of a lanthanoid metal (~ 95%) and iron (~ 5%) and traces of S, C, Ca and Al. A good deal of *mischmetal* is used in Mg-based alloy to produce bullets, shell and lighter flint.
- Mixed oxides of lanthanoids are employed as catalysts in petroleum cracking. Some individual Ln oxides are used as phosphors in television screens and similar fluorescing surfaces.

## ACTINOIDS

1. The 14 elements after Actinium having atomic number 90 to 113 are collectively known as Actinoids

2. The actinoids are radioactive elements. These facts render their study more difficult.

**3. Electronic Configurations:** The general electronic configuration of these elements is  $[\text{Rn}] 5f^{1-14}, 6d^{0-1}, 7s^2$

**4. Ionic Sizes (Actinoid contraction):** The overall decrease in atomic and ionic radii across the series due to poor shielding of 5f electrons is known as **Actinoid contraction**

5. The actinoid contraction is, however, greater from element to element in this series resulting from poor shielding by 5f electrons.

**6. Oxidation States:** The actinoids show in general +3 oxidation state. The actinoids exhibit a larger number of oxidation states, which is in part attributed to the fact that the 5f, 6d and 7s levels are of comparable energies. The elements, in the first half of the series frequently exhibit higher oxidation states. For example, the maximum oxidation state increases from +4 in Th to +5, +6 and +7 respectively in Pa, U and Np but decreases in succeeding elements. The actinoids are highly reactive metals, especially when finely divided. The magnetic properties of the actinoids are more complex than those of the lanthanoids. Although the variation in the magnetic susceptibility of the actinoids with the number of unpaired 5f electrons is roughly parallel to the corresponding results for the lanthanoids

## QUESTIONS .....

1. Write the electronic configurations of the elements with the atomic numbers 61, 91, 101, and 109.
2. Compare the chemistry of lanthanoids with that of the actinoids with reference to (i) electronic configuration (ii) Oxidation state (iii) atomic size and ionic size (iv) chemical reactivity
3. What is Lanthanoid contraction? Give its cause. What are its consequences?
4. Name the members of the lanthanoid series which exhibit +4 oxidation states and those which exhibit +2 oxidation states.
5. The chemistry of the actinoid elements is not so smooth as that of the lanthanoids. Justify this statement by giving some examples from the oxidation state of these elements.
6. Use Hund's rule to derive the electronic configuration of  $\text{Ce}^{3+}$  ion, and calculate its magnetic moment on the basis of 'spin-only' formula.
7. Which is the last element in the series of the actinoids? Write the electronic configuration of this element. Comment on the possible oxidation state of this element.
8. What are alloys? Name an important alloy which contains some of the lanthanoid metals. Mention its uses.
9. **Give Reasons for the following**
  - i. Chemistry of all the lanthanoids are quite similar.

- ii. Size of trivalent lanthanoid cations decreases with increase in the atomic number
- iii. It is difficult to separate lanthanoid elements in pure state..
- iv.  $\text{Ce}^{4+}$  in aqueous solution is a good oxidising agent.
- v.  $\text{Ce}^{3+}$  can be easily oxidized to  $\text{Ce}^{4+}$ .
- vi. d-block elements exhibit more oxidation states than f block elements.
- vii. Actinoids contraction is greater from element to element than lanthanoid contraction.
- viii. The actinoids exhibit a larger number of oxidation states than the corresponding lanthanoids
- ix.  $\text{La}^{3+}$  and  $\text{Lu}^{3+}$  do not show any colour in solutions..

### **IMPORTANT QUESTIONS OF D-BLOCK ELEMENTS**

1. **What are transition elements? Write two characteristics of the transition elements.**
2. Calculate the number of unpaired electrons in the following gaseous ions:  $\text{Mn}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{V}^{3+}$  and  $\text{Fe}^{2+}$ . Which one of these is the most stable in aqueous solution.
3. **How would you account for the following :**
  - a) Zn, Cd and Hg are not considered as transition elements. Why
  - b) Scandium is a transition element but Zinc is not.
  - c) Copper atom has completely filled d orbital ( $3d^{10}$ ) in its ground state, yet it is transition element.
  - d) Silver atom has completely filled d orbital ( $4d^{10}$ ) in its ground state, yet it is transition element.
4. **Explain giving a suitable reason for each of the following**
  - a) Transition elements exhibit higher enthalpies of atomization.
  - b) In the series Sc(Z = 21) to Zn (Z = 30), the enthalpy of atomisation of zinc is the lowest
  - c) Transition metals have high melting and boiling points.
  - d) Fe has higher melting point than Cu.
  - e) Chromium group elements have highest melting points.
  - f) Transition elements are much harder than alkali metals.
  - g) Zinc is soft whereas Cr is hard.
  - h) Chromium is a typical hard metal while mercury is a liquid.
  - i) There occurs much more frequent metal –metal bonding in compounds of heavy transition elements( $3^{\text{rd}}$  series).
  - j) Metal –metal bonding is more frequent for the 4d & 5d series of transition metals than that for the 3d series.
5. **Assign reasons for the following :**
  - a) Transition element form generally coloured compounds.
  - b)  $\text{Sc}^{3+}$  is colourless, while  $\text{Ti}^{3+}$  is Coloured
  - c)  $\text{Zn}^{2+}$  salts are white ,but  $\text{Cu}^{+2}$  are blue.
  - d)  $\text{Cu}^+$  salts are colourless while  $\text{Cu}^{2+}$  salts are Coloured
  - e) The Transition metals ions such as  $\text{Cu}^+$   $\text{Ag}^+$   $\text{Sc}^{3+}$  are colourless.
6. Predict which of the following will be colored in aqueous solution?  $\text{Ti}^{3+}$ ,  $\text{V}^{3+}$ ,  $\text{Cu}^+$ ,  $\text{Sc}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{3+}$  &  $\text{Co}^{2+}$ .
7. Out of  $\text{Ag}_2\text{SO}_4$ ,  $\text{CuF}_2$ ,  $\text{MgF}_2$  and  $\text{CuCl}$  which compound will be coloured and why?
8. **Explain the following observations.**
  - a) Transition metals show paramagnetic behavior.
  - b)  $\text{Mn}^{2+}$  exhibits maximum paramagnetism
9. (a) Explain Variation in magnetic behaviour of Transition Metals along 3d transition series.



- (b) Calculate the magnetic moment of a divalent ion in aqueous solution if its at.no is 25.
- (c) Calculate the 'spin only' magnetic moment of  $M^{2+}$  ion ( $Z = 27$ )
10. Explain Variation in Atomic Size of Transition Metals along 3d transition series.
11. **Account for the following :**
- Members of second (4d) and the third (5d) series in each group of transition elements have similar radii.
  - Zr and Hf exhibit similar properties.
  - Although Zr belongs to 4d and Hf belongs to 5d transition series but it is quite difficult to separate them.
  - Radius of  $Fe^{+2}$  is less than  $Mn^{+2}$ .
12. **Assign reasons for the following**
- There is in general increase in density of element from titanium to copper
  - Transition metal ions form complex ions.
  - Most of the transition metals and their compounds possess catalytic properties.
  - Transition metals form interstitial compounds.
  - Most of the transition metals form alloys.
13. Explain briefly how +2 state becomes more and more stable in the first half of the first row transition elements with increasing atomic number?
14. **Explain the following observations.**
- Transition element show variable oxidation state.
  - Mn Shows the highest oxidation state of +7 among 3d series elements.
  - The greatest number of oxidation states are exhibited by the elements in the middle of transition series.
  - Mn Shows the highest oxidation state of +7 with oxygen but with fluorine it shows the highest oxidation state of +4.
  - Highest fluoride of Mn is  $MnF_4$  whereas the highest oxide is  $Mn_2O_7$ .
  - $Mn^{2+}$  compounds more stable than  $Fe^{2+}$  towards oxidation to their +3 state.
15. **Account for the following :**
- Of the  $3d^4$  species,  $Cr^{2+}$  is strongly reducing while  $Mn^{3+}$  is strongly oxidising.
  - $Cr^{2+}$  is strong reducing agent.
  - $Cr^{2+}$  is a stronger reducing agent  $Fe^{2+}$ .
  - The lowest oxide of transition metal is basic, the highest is amphoteric/acidic.
  - MnO is basic while  $Mn_2O_7$  is acidic in nature.
  - $CrO_4^{2-}$  is a strong oxidizing agent while  $MnO_4^{2-}$  is not
  - The increasing oxidising power of oxoanions are in the  $VO_2^+ < Cr_2O_7^{2-} < MnO_4^-$
16. **Explain the following observations:**
- The  $E^0(M^{2+}/M)$  values are not regular for the first row transition metals.
  - $E^0$  value for the  $Mn^{3+}/Mn^{2+}$  couple much more positive than that for  $Cr^{3+}/Cr^{2+}$  or  $Fe^{3+}/Fe^{2+}$
  - $E^0$  value for the  $Mn^{2+}/Mn$  much more than expected.
  - $E^0$  value for the  $Cu^{2+}/Cu$  is positive .
17. **Assign reasons for the following**
- Transition metal exhibit higher oxidation state in oxides and fluorides.
  - Highest fluoride of Mn is  $MnF_4$  whereas the highest oxide is  $Mn_2O_7$
  - The highest oxidation state is exhibited in oxoanions of a metal.
18. **Account for the following**
- Irregular variation of ionization enthalpies (first and second) in the first series of the transition elements.

- b) +3 state of Mn is of little importance.
- c) The Third ionization enthalpy of manganese is exceptionally high,
- d) First Ionization enthalpy of Cr is lower than that of Zinc.
- e)  $Mn^{+3}$  undergoes disproportionation reaction easily.
- f)  $d^1$  configuration is very unstable in ions.

19. Account for the following :

- a)  $Cu^+$  ion is not stable in aqueous solutions.
- b)  $Cu^+$  ion has  $d^{10}$  configuration while  $Cu^{+2}$  has  $d^9$  configuration, still  $Cu^{+2}$  is stable in aqueous solutions
- c) Cobalt (II) is stable in aqueous solution but in the presence of complexing reagents it is easily oxidized.
- d) Cobalt (II) is easily oxidized in the presence of strong ligands.
- e) Although  $Co^{2+}$  ion appears to be stable, it is easily oxidized to  $Co^{3+}$  ion in the presence of a strong ligand.
- f) Unlike  $Cr^{3+}, Mn^{+2}, Fe^{+3}$  and the subsequent other  $M^{2+}$  ions of the 3d series of elements, the 4d and the 5d series metals generally do not form stable cationic species.
- g) Transition elements tend to be unreactive with increasing atomic number in the series.

**ANSWER THE FOLLOWING:-**

1. Name a transition element which does not exhibit variable oxidation states
2. Which of the 3d transition series metals exhibits the largest number of oxidation states and why
3. What may be the stable oxidation state of the transition element with the following d electron configurations in the ground state of their atoms:  $3d^3, 3d^5, 3d^8$  and  $3d^4$ ?
4. Which metal in the first series of transition metals exhibits +1 oxidation state most frequently and why?
5. Name the oxometal anions of the first series of the transition metals in which the metal exhibits the oxidation state equal to its group number.
6. What may be the possible oxidation states of transition metals with the following electronic configuration in the ground states in their atoms? (i)  $3d^3 4s^2$  (ii)  $3d^5 4s^2$  (iii)  $3d^6 4s^2$
7. Which is a stronger reducing agent  $Cr^{2+}$  or  $Fe^{2+}$  and why?
8. Among Elements of 3d transition series are given as :

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
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**Answer the following:**

- a) Write the element which is not regarded as transition element. why
- b) Write the element which can show an oxidation state of +1.
- c) Which element is soft and why?
- d) Write the element which shows maximum number of oxidation states.
- e) Which element has the highest melting point?
- f) Which element shows only +3 state?
- g) Which element is a strong oxidizing agent in + 3 oxidation state and why.
- h) Which element is a strong reducing agent in + 2 oxidation state and why.

**Topic: LANTHANOIDS**

10. Give Reasons for the following

- (a) Chemistry of all the lanthanoids are quite similar.
- (b) Size of trivalent lanthanoid cations decreases with increase in the atomic number
- (c) It is difficult to separate lanthanoid elements in pure state..
- (d)  $Ce^{4+}$  in aqueous solution is a good oxidising agent.
- (e)  $Ce^{4+}$  is used oxidising agent in volumetric analysis.

- (f)  $\text{Ce}^{3+}$  can be easily oxidized to  $\text{Ce}^{4+}$ .
- (g) d-block elements exhibit more oxidation states than f block elements.
- (h)  $\text{Eu}^{2+}$  is a strong reducing agent.
- (i)  $\text{La}^{3+}$  and  $\text{Lu}^{3+}$  do not show any colour in solutions.
- (j) Although Zr belongs to 4d and Hf belongs to 5d transition series but it is quite difficult to separate them.
11. What is Lanthanoid contraction? Give its cause. What are its Consequences?
12. Name an important alloy which contains some of the lanthanoid metals. Mention its uses.
13. Explain the chemistry of lanthanoids with reference to (i) electronic configuration (ii) Oxidation state (iii) atomic size and ionic size (iv) chemical reactivity
14. Name the members of the lanthanoid series which exhibit +4 oxidation states and those which exhibit +2 oxidation states.
15. Use Hund's rule to derive the electronic configuration of  $\text{Ce}^{3+}$  ion, and calculate its magnetic moment on the basis of 'spin-only' formula.

**KEEP ENJOYING CHEMISTRY.....**

## Unit: 9:- COORDINATION COMPOUNDS

- Double salt** : Double salts are formed by the combination of two or more stable compounds that dissociate into simple ions completely when dissolved in water. for example: **Mohr's salt,  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$**  gives  $\text{Fe}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$  ions when dissolved in water, & potash alum,  $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  dissociate into simple ions  $\text{K}^+$ ,  $\text{Al}^{3+}$ , gives  $\text{Fe}^{2+}$ ,  $\text{SO}_4^{2-}$ , ions when dissolved in water completely when dissolved in water.
- Coordination compound**: are formed by the combination of two or more stable compounds that does not dissociate in to constituent ions. i.e. A complex always retains its identity even in solution e.g.  $[\text{Fe}(\text{CN})_6]^{4-}$  of  $\text{K}_4[\text{Fe}(\text{CN})_6]$ , do not dissociate into  $\text{Fe}^{2+}$  and  $\text{CN}^-$  ions.
- Coordination entity**: A coordination entity constitutes a central metal atom or ion bonded to a fixed number of ions or molecules. For example,  $[\text{CoCl}_3(\text{NH}_3)_3]$  is a coordination entity in which the cobalt ion is surrounded by three ammonia molecules and three chloride ions. Other examples are  $[\text{PtCl}_2(\text{NH}_3)_2]$ ,  $[\text{Fe}(\text{CN})_6]^{4-}$ ,  $[\text{Co}(\text{NH}_3)_6]^{3+}$ .
- Central atom or ion**: In a coordination entity, the atom/ion to which a fixed number of ions/groups are bound in a definite geometrical arrangement around it, is called the central atom or ion. E.g.: in  $\text{K}_4[\text{Fe}(\text{CN})_6]$ ,  $\text{Fe}^{2+}$  is the central metal ion. These central atoms/ions are also referred to as Lewis acids.
- Ligands**: A molecule, ion or group that is bonded to the metal atom or ion in a complex or coordination compound by a coordinate bond is called ligand. A ligand is a lewis base .It may be neutral, positively or negatively charged. These may be simple ions such as  $\text{Cl}^-$ , small molecules such as  $\text{H}_2\text{O}$  or  $\text{NH}_3$ , larger molecules such as  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$  or even macromolecules, such as proteins.

- Unidentate** ligand: When a ligand is bound to a metal ion through a single donor atom, as with  $\text{Cl}^-$ ,  $\text{H}_2\text{O}$  or  $\text{NH}_3$ , the ligand is said to be **unidentate**.
- Didentate**: When a ligand can bind through two donor atoms as in  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$  (ethane-1,2-diamine)(en)
 

$\begin{array}{c} \text{H}_2\text{C} \quad \ddot{\text{N}}\text{H}_2 \\ | \quad \quad | \\ \text{H}_2\text{C} \quad \quad \ddot{\text{N}}\text{H}_2 \end{array}$

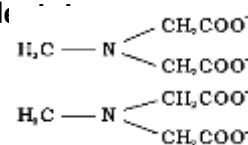
$\begin{array}{c} \text{COO}^- \\ | \\ \text{COO}^- \end{array}$

or  $\text{C}_2\text{O}_4^{2-}$  (oxalate),
 

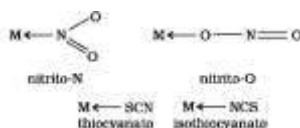
$\begin{array}{c} \text{COO}^- \\ | \\ \text{COO}^- \end{array}$

 the ligand is said to be **Didentate**

- Polydentate** :when several donor atoms are present in a single ligand is said to be **polydentate**. Ethylenediaminetetraacetate ion ( $\text{EDTA}^{4-}$ ) is an important hexadentate ligand. It can bind through two nitrogen and four oxygen atoms to a central metal ion.


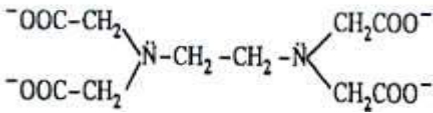
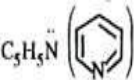


- Chelate** ligand When a di- or polydentate ligand uses its two or more donor atoms to bind a single metal ion, it is said to be a **chelate** ligand. An example is the complex ion formed between ethylene diamine and cupric ion,  $[\text{Cu}(\text{NH}_2\text{CH}_2\text{NH}_2)_2]^{2+}$ .
- The number of such ligating groups is called the **denticity** of the ligand. Such complexes, called chelate complexes tend to be more stable than similar complexes containing unidentate ligands.
- Ambidentate ligand**: Ligand which can ligate through two different atoms is called **ambidentate ligand**. Examples of such ligands are the  $\text{NO}_2^-$  and  $\text{SCN}^-$  ions.  $\text{NO}_2^-$  ion can coordinate either through nitrogen or through oxygen to a central metal atom/ion. Similarly,  $\text{SCN}^-$  ion can coordinate through the sulphur or nitrogen atom.



### SOME COMMON LIGANDS AND THEIR NAMES

Actual Name (Symbol used)	Formula	Charge	Donor Atom/Atoms	Name Given In the Complex
<b>NEGATIVE LIGANDS</b>				
(a) <b>monodentate</b> cyanide ion	: $\text{CN}^-$	-1	C	Cyano or Cyanido
Halide ion	$\text{X}^-$ ( $\text{F}^-$ , $\text{Cl}^-$ , $\text{Br}^-$ , $\text{I}^-$ )	-1	X	(fluorido, chlorido, bromido, iodido)
Hydride ion	$\text{H}^-$	-1	H	hydrido

Nitro	$\text{NO}_2^-$	-1	N	nitrito-N
Nitrite ion	$\text{ONO}^-$	-1	O	nitrito-O
Nitrate ion	$\text{NO}_3^-$	-1	N	Nitrato
Hydroxide ion	$\text{OH}^-$	-1	O	Hydroxo
Amide ion	$\text{NH}_2^-$	-1	N	Amido
Thiocyanate ion	$\text{SCN}^-$	-1	S	Thiocyanato
Isothiocyanate ion	$\text{NCS}^-$	-1	N	isothio-cyanato
Acetate ion	$\text{CH}_3\text{COO}^-$	-1	O	Acetato
Oxide ion	$\text{O}^{2-}$	-2	O	Oxo
Peroxide ion	$\text{O}_2^{2-}$	-2	O	Peroxo
Sulphide ion	$\text{S}^{2-}$	-2	S	sulphido
Sulphite ion	$\text{SO}_3^{2-}$	-2	S	Sulphito
Sulphate ion	$\text{SO}_4^{2-}$	-2	S	Sulphato
Thiosulphate ion	$\text{S}_2\text{O}_3^{2-}$	-2	S	Thiosulphato
Carbonate ion	$\text{CO}_3^{2-}$	-2	O	Carbonato
Imide ion	$\text{NH}^{2-}$	-2	N	Imido
<b>(b) Bidentate</b>				
Oxalate ion (ox)		-2	Two O <sup>-</sup> Atoms	Oxalato
<b>(c) Hexadentate</b> Ethylenediamine tetra-acetate ion (edta <sup>4-</sup> )		-4	Two N and four O <sup>-</sup> Atoms	Ethylenediamine tetraacetato
<b>NEUTRAL LIGANDS</b>				
<b>(a) Monodentate</b>				
Ammonia	$\text{NH}_3$	Zero	N	Ammine
Water	$\text{N}_2\text{O}$	Zero	O	Aqua or aquo
Nitric oxide	$\text{NO}$	Zero	N	Nitrosyl
Carbon Monoxide	$\text{CO}$	Zero	O	Carbonyl
Phosphine	$\text{PH}_3$	Zero	P	Phosphine
Triphenyl Phosphine	$(\text{C}_6\text{H}_5)_3\text{P}$	Zero	P	Triphenyl phosphine
Pyridine (py)		Zero	N	Pyridine
<b>(b) Bidentate</b> Ethylenediamine (en)	$\begin{array}{l} \text{CH}_2 - \text{NH}_2 \\   \\ \text{CH}_2 - \text{NH}_2 \end{array}$	Zero	Two N atoms	ethane-1,2-diamine or ethylene diamine

**6. Coordination number:** The coordination number (CN) of a metal ion in a complex can be defined as the number of ligand donor atoms to which the metal is directly bonded. For example, in the complex ions,  $[\text{PtCl}_6]^{2-}$  and  $[\text{Ni}(\text{NH}_3)_4]^{2+}$ , the coordination number of Pt and Ni are 6 and 4 respectively. Similarly, in the complex ions,  $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$  and  $[\text{Co}(\text{en})_3]^{3+}$ , the coordination number of both, Fe and Co, is 6 because  $\text{C}_2\text{O}_4^{2-}$  and en (ethane-1,2-diamine) are didentate ligands.

7. **Coordination sphere:** The central atom/ion and the ligands attached to it are enclosed in square bracket and is collectively termed as the coordination sphere. For example: in the complex  $K_4[Fe(CN)_6]$ ,  $[Fe(CN)_6]^{4-}$  is the coordination sphere.
8. **Counter ions:** The ions present outside the coordination sphere are called counter ions. For example: in the complex  $K_4[Fe(CN)_6]$ ,  $K^+$  is the counter ion.
9. **Coordination polyhedron:** The spatial arrangement of the ligand atoms which are directly attached to the central atom/ ion defines a coordination polyhedron about the central atom. The most common coordination polyhedra are octahedral, square planar and tetrahedral. For example:  $[PtCl_4]^{2-}$  is square planar,  $[Ni(CO)_4]$  is tetrahedral while  $[Cu(NH_3)_6]^{3+}$  is octahedral.
10. **Oxidation number of central atom:** The oxidation number of the central atom in a complex is defined as the charge it would carry if all the ligands are removed along with the electron pairs that are shared with the central atom. The oxidation number is represented by a Roman numeral in parenthesis following the name of the coordination entity. For example, oxidation number of copper in  $[Cu(CN)_4]^{3-}$  is +1 and it is written as Cu(I).
11. **Homoleptic complexes:** Those complexes in which metal or ion is coordinate bonded to only one kind of donor atoms. For example:  $[Co(NH_3)_6]^{3+}$
12. **Heteroleptic complexes:** Those complexes in which metal or ion is coordinate bonded to more than one kind of donor atoms. For example:  $[CoCl_2(NH_3)_4]^+$ ,  $[Co(NH_3)_5Br]^{2+}$
13. **Naming of Mononuclear Coordination Compounds:** The following rules are used when naming coordination compounds:
  - a. The cation is named first in both positively and negatively charged coordination entities.
  - b. The ligands are named in an alphabetical order before the name of the central atom/ion.
  - c. Names of the anionic ligands end in  $-o$ , those of neutral and cationic ligands are the same except aqua for  $H_2O$ , ammine for  $NH_3$ , carbonyl for  $CO$  and nitrosyl for  $NO$ . These are placed within enclosing marks ( ).
  - d. Prefixes mono, di, tri, etc., are used to indicate the number of the individual ligands in the coordination entity. When the names of the ligands include a numerical prefix, then the terms, *bis*, *tris*, *tetrakis* are used, the ligand to which they refer being placed in parentheses.
  - e. Oxidation state of the metal in cation, anion or neutral coordination entity is indicated by Roman numeral in parenthesis.
  - f. If the complex ion is a cation, the metal is named same as the element. For example, Co in a complex cation is called cobalt and Pt is called platinum.
  - g. If the complex ion is an anion, the name of the metal ends with the suffix  $-ate$ .

<b>Co</b>	<b>cobaltate</b>
<b>Fe</b>	<b>Ferrate</b>
<b>Ag</b>	<b>Argentite</b>
<b>Zn</b>	<b>Zincate</b>
<b>Al</b>	<b>Aluminate</b>
<b>Pt</b>	<b>Platinate</b>

<b>Ni</b>	<b>Nickelate</b>
<b>Pd</b>	<b>Palladate</b>
<b>Cr</b>	<b>Chromate</b>
<b>Cu</b>	<b>Cuprate</b>
<b>Au</b>	<b>Aurate</b>

- h. The neutral complex molecule is named similar to that of the complex cation.

#### 14. Writing the Formulas of Mononuclear Coordination Entities:

- a. The central atom is listed first.
- b. The ligands are then listed in alphabetical order. The placement of a ligand in the list does not depend on its charge.
- c. Polydentate ligands are also listed alphabetically. In case of abbreviated ligand, the first letter of the abbreviation is used to determine the position of the ligand in the alphabetical order.
- d. The formula for the entire coordination entity, whether charged or not, is enclosed in square brackets. When ligands are polyatomic, their formulas are enclosed in parentheses. Ligand abbreviations are also enclosed in parentheses.
- e. There should be no space between the ligands and the metal within a coordination sphere.

- f. When the formula of a charged coordination entity is to be written without that of the counter ion, the charge is indicated outside the square brackets as a right superscript with the number before the sign. For example,  $[\text{Co}(\text{CN})_6]^{3-}$ ,  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ , etc.
- g. The charge of the cation(s) is balanced by the charge of the anion(s).

#### EXAMPLES [Cationic & Neutral complexes]

1	$[\text{Cr}(\text{NH}_3)_3(\text{H}_2\text{O})_3]\text{Cl}_3$	triamminetriaquachromium(III) chloride
2	$[\text{Co}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_2(\text{SO}_4)_3]$	tris(ethane-1,2-diammine)cobalt(III) sulphate
3	$[\text{Co}(\text{NH}_3)_5(\text{CO}_3)]\text{Cl}$	pentaamminecarbonatocobalt(III) chloride
4	$[\text{CoCl}_2(\text{en})_2]\text{Cl}$	dichloridobis(ethane-1,2-diamine)cobalt(III) chloride
5	$[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]\text{Cl}_2$	tetraamineaquachloridocobalt(III) chloride
6	$[\text{CoCl}_2(\text{en})_2]^+$	dichloridobis(ethane-1,2-diamine)cobalt(III) ion
7	$[\text{Ni}(\text{CO})_4]$	tetracarbonylnickel(0)
8	$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$	hexaamminecobalt(III) chloride
9	$[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$	pentaamminechloridocobalt(III) chloride
10	$[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]\text{Cl}_3$	tetraamminediaquacobalt(III) chloride
11	$[\text{Cr}(\text{en})_3]\text{Cl}_3$	tris(ethane-1,2-diamine) chromium(III) chloride
12	$[\text{PtCl}_2(\text{en})_2](\text{NO}_3)_2$	dichloridobis(ethane-1,2-diamine)platinum(IV) nitrate
13	$[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$	diamminedichloridoplatinum(II)
14	$[\text{Co}(\text{NH}_3)_5(\text{ONO})]^{2+}$	pentaamminenitrito-O-cobalt(III) ion
15	$[\text{Co}(\text{NH}_3)_6]_2(\text{SO}_4)_3$	hexaamminecobalt(III) sulphate
16	$[\text{Pt}(\text{NH}_3)_6]^{4+}$	hexaammineplatinum(IV) ion
17	$[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]^{2+}$	pentaamminenitrito-N-cobalt(III) ion
18	$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$	hexaaquatitanium(III)ion
19	$[\text{Co}(\text{NH}_3)_4\text{Cl}(\text{NO}_2)]\text{Cl}$	tetraamminechloridonitrito-N-cobalt(III)chloride
20	$[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$	hexaamminenickel(II)chloride
21	$[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{NH}_2\text{CH}_3)]\text{Cl}$	diamminechloridomethylamineplatinum(II)chloride
22	$[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$	hexaaquamanganese(II)ion
23	$[\text{Co}(\text{en})_3]^{3+}$	tris(ethane-1,2-diamine) cobalt(III)ion
24	$[\text{NiCl}_2(\text{PPh}_3)_2]$	dichlorobis(triphenylphosphine)nickel(II)
25	$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$	hexaaquairon(III)ion

#### EXAMPLES [Anionic complexes]

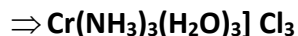
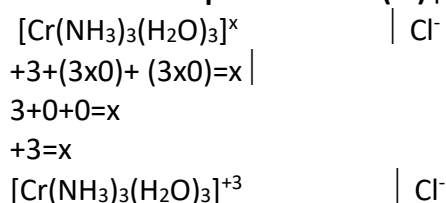
1	$\text{K}_2[\text{Zn}(\text{OH})_4]$	potassium tetrahydroxozincate(II)
2	$\text{K}_3[\text{Al}(\text{C}_2\text{O}_4)_3]$	potassium trioxalatoaluminate(III)
3	$\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]$	potassium trioxalatochromate(III)
4	$\text{Hg}[\text{Co}(\text{SCN})_4]$	mercury tetrathiocyanatocobaltate(III)
5	$\text{K}_2[\text{Ni}(\text{CN})_4]$	potassium tetracyanonickelate(II)
6	$[\text{Pt}(\text{NH}_3)\text{BrCl}(\text{NO}_2)]^-$	amminebromidochloridonitrito-N-platinate(II)
7	$\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$	iron(III) hexacyanoferrate(II)
8	$\text{K}_3[\text{Fe}(\text{CN})_6]$	potassium hexacyanoferrate(III)
9	$\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$	potassium trioxalatoferrate(III)
10	$\text{K}_2[\text{PdCl}_4]$	potassium tetrachloridopalladate(II)
11	$[\text{Zn}(\text{OH})_4]^{2-}$	tetrahydroxozincate(II) ion
12	$[\text{CuBr}_4]^{2-}$	tetrabromidocuprate(II) ion
13	$[\text{NiCl}_4]^{2-}$	tetrachloridonickelate(II)ion

#### EXAMPLES OF POLYNUCLEAR COORDINATION COMPOUND:

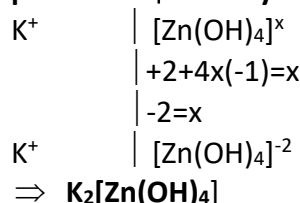
- (a)  $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$  =hexaammineplatinum(II) hexachloridoplatinate(II)
- (b)  $[\text{Co}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$  =hexaamminecobalt(III) hexacyanocobaltate(III)
- (c)  $[\text{Ag}(\text{NH}_3)_2][\text{Ag}(\text{CN})_2]$  =diamminesilver(I) dicyanoargentate(I)

## How to Write the Formulas of Coordination Compounds

1. **triamminetriaquachromium(III) | chloride**



2. **potassium | tetrahydrozincate(II)**



## Questions.....

- What is a Difference between a double salt and a complex.
- Explain with two examples each of the following: coordination entity, ligand, coordination number, coordination polyhedron, homoleptic complexes and heteroleptic complexes.?
- What is meant by unidentate, didentate denticity [Chelating and ambidentate ligands Give two examples for each.?
- Specify the oxidation numbers & coordination number of the metals in the following coordination entities: (i)  $[\text{Co}(\text{H}_2\text{O})(\text{CN})(\text{en})_2]^{2+}$  (iii)  $[\text{PtCl}_4]^{2-}$  (v)  $[\text{Cr}(\text{NH}_3)_3\text{Cl}_3]$  (ii)  $[\text{CoBr}_2(\text{en})_2]^+$  (iv)  $\text{K}_3[\text{Fe}(\text{CN})_6]$  (vi)  $\text{K}[\text{Co}(\text{CO})_4]$
- Using IUPAC norms write the formulae for the following:
  - tetrahydrozincate(II) ion
  - pentaamminenitrito-N-cobalt (III)
  - potassiumtri(oxalato) chromate (III)
  - diamminedichloridoplatinum (II)
  - hexaammine cobalt (III) sulphate
  - potassiumtetrachloridopalladate (II)
  - hexaammineplatinum (IV)
  - potassiumtetracyanonickelate (II)
  - tetrabromido cuprate (II)
  - pentaamminenitrito-O-cobalt (III)
  - iron(III) hexacyanoferrate(II)
  - tetraammineaquachloridocobalt (III) chloride
  - potassiumtetrahydrozincate (II)
  - potassiumtrioxalatoaluminate (III)
  - tetracarbonylnickel (0)
  - tetraamminediaquacobalt(III) chloride
  - potassium tetracyanonickelate(II)
  - tris(ethane-1,2-diamine) chromium(III) chloride
  - amminebromidochloridonitrito-N-platinate(II)
  - dichloridobis(ethane-1,2-diamine)platinum(IV) nitrate
  - dichloride bis (ethane-1, 2-diamine) cobalt (III)
- $\text{FeSO}_4$  solution mixed with  $(\text{NH}_4)_2\text{SO}_4$  solution in 1:1 molar ratio gives the test of  $\text{Fe}^{2+}$  ion but  $\text{CuSO}_4$  solution mixed with aqueous ammonia in 1:4 molar ratio does not give the test of  $\text{Cu}^{2+}$  ion. Explain why?
- Write the IUPAC names, Specify the coordination number of the central Atom of the following:
  - $\text{Na}_3[\text{Cr}(\text{OH})_2\text{F}_4]$
  - $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2$
  - $[\text{Cr}(\text{H}_2\text{O})_3(\text{NH}_3)_3]\text{Cl}_3$
  - $[\text{CrCl}_3(\text{py})_3]$
  - $\text{K}_4[\text{Mn}(\text{CN})_6]$
  - $\text{Cs}[\text{FeCl}_4]$
  - $[\text{Pt}(\text{NH}_3)_4\text{Cl}(\text{NO}_2)]^+$
  - $\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]$
  - $[\text{Fe}(\text{en})_2\text{Cl}_2]\text{Cl}$
  - $[\text{Co}(\text{NH}_3)_5(\text{CO}_3)]\text{Cl}$
  - $\text{Hg}[\text{Co}(\text{SCN})_4]$
  - $[\text{CoCl}_4]^{2-}$
  - $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$
  - $\text{K}[\text{Cr}(\text{H}_2\text{O})_2(\text{C}_2\text{O}_4)_2] \cdot 3\text{H}_2\text{O}$
  - $[\text{Cr}(\text{H}_2\text{O})_2(\text{C}_2\text{O}_4)_2]^-$
  - $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$
  - $\text{K}_2[\text{PdCl}_4]$
  - $[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{NH}_2)]\text{Cl}$
  - $[\text{Ni}(\text{CN})_4]^{2-}$
  - $[\text{Ni}(\text{CO})_4]$
  - $[\text{CoCl}(\text{NO}_2)(\text{NH}_3)_4]\text{Cl}$  [2008]
  - $[\text{Co}(\text{en})_3]^{3+}$
  - $[\text{Co}(\text{H}_2\text{O})(\text{CN})(\text{en})_2]^{2+}$
  - $[\text{Cr}(\text{NH}_3)_3\text{Cl}_3]$
  - $[\text{CoBr}_2(\text{en})_2]^+$
  - $\text{K}_3[\text{Fe}(\text{CN})_6]$
  - $\text{K}[\text{Co}(\text{CO})_4]$
  - $[\text{Fe}(\text{NH}_3)_2(\text{CN})_4]^-$
  - $[\text{Co}(\text{en})_2(\text{ONO})\text{Cl}]\text{Cl}$
  - $(\text{NH}_4)_3[\text{Co}(\text{ONO})_6]$
  - $[\text{Co}(\text{NH}_3)_5\text{SCN}]\text{Cl}_2$
  - $[\text{Ni}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$
  - $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$



### VALENCE BOND THEORY(VBT)

- According to this theory, the metal atom or ion under the influence of ligands can use its  $(n-1)d$ ,  $ns$ ,  $np$  or  $ns$ ,  $np$ ,  $nd$  orbitals for hybridization to yield a set of equivalent orbitals of definite geometry .

Coordination number	Type of hybridization	Distribution of hybrid orbitals in space
2	$Sp$	Linear
4	$Sp^3$	Tetrahedral
4	$dsp^2$	Square planar
5	$sp^3d$	Trigonal bipyramidal
6	$sp^3d^2$ [nd orbitals are involved – outer orbital complex or high spin complex]	Octahedral
6	$d^2sp^3$ [(n-1) d orbitals are involved – inner orbital or low spin or spin paired complex]	Octahedral

- These hybridised orbitals are allowed to overlap with ligand orbitals that can donate electron pairs for bonding.
- The **inner orbital (low spin)** or the **outer orbital (high spin)** complexes are formed depending upon whether the  $d$  –orbitals of inner shell or  $d$  –orbitals of outer shell are used in hybridization.
- The complex will be **diamagnetic** if all electrons are paired.If unpaired electrons are present then the complex will be **paramagnetic**.
- Applications of valence Bond treatment to some complexes.** :It is usually possible to predict the geometry of a complex from the knowledge of its magnetic behaviour on the basis valence bond Theory.

#### Note:

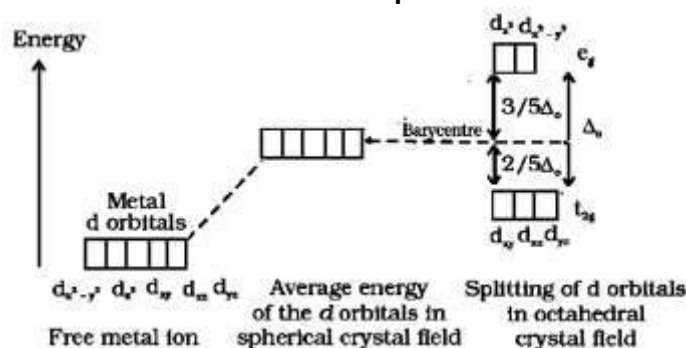
- In Presence of ligands like  $CO, CN^-, C_2O_4^{2-}, NH_3(d^5- d^6)$ ,  $n$  electrons of central atom/ions gets paired. In Presence of ligands like  $F^-, Cl^-, I^-, Br^-, H_2O$  electrons  $NH_3(d^1- d^4)$  of central atom/ions remains as it is.

Complex	Central metal ion	Configuration of metal ion	Type of hybridisation	Geometry of the complex	Unpaired $e^-$	Magnetic Behavior
$[Ag(NH_3)_2]^+$	$Ag^+$	$4d^{10}$	$Sp$	Linear	0	Diamagnetic
$[CoF_6]^{3-}$	$Co^{3+}$	$3d^6$	$sp^3d^2$	Octahedral	4	Paramagnetic
$[Cr(H_2O)_6]^{3+}$	$Cr^{3+}$	$3d^3$	$d^2sp^3$	Octahedral	3	Paramagnetic
$[Cr(NH_3)_6]^{3+}$	$Cr^{3+}$	$3d^3$	$d^2sp^3$	Octahedral	3	Paramagnetic
$[FeF_6]^{3-}$	$Fe^{3+}$	$3d^5$	$sp^3 d^2$	Octahedral	5	Paramagnetic
$[Fe(H_2O)_6]^{3+}$	$Fe^{3+}$	$3d^5$	$sp^3 d^2$	Octahedral	5	Paramagnetic
$[Fe(CN)_6]^{3-}$	$Fe^{3+}$	$3d^5$	$d^2sp^3$	Octahedral	1	Paramagnetic
$[Fe(CN)_6]^{4-}$	$Fe^{3+}$	$3d^6$	$d^2sp^3$	Octahedral	0	Diamagnetic
$[Co(NH_3)_6]^{3+}$	$Co^{3+}$	$3d^6$	$d^2sp^3$	Octahedral	0	Diamagnetic
$[Ni(H_2O)_6]^{2+}$	$Ni^{2+}$	$3d^8$	$sp^3 d^2$	Octahedral	2	Paramagnetic
$[NiCl_4]^{2-}$	$Ni^{2+}$	$3d^8$	$sp^3$	Tetrahedral	2	Paramagnetic
$[Ni(CN)_4]^{2-}$	$Ni^{2+}$	$3d^8$	$dsp^2$	Square planar	0	Diamagnetic
$[Ni(CO)_4]$	$Ni$	$3d^8 4s^2$	$sp^3$	Tetrahedral	0	Diamagnetic
$[CoF_4]^{2-}$	$Co^{2+}$	$3d^7$	$sp^3$	Tetrahedral	3	Paramagnetic
$[Co(C_2O_4)_3]^{3-}$	$Co^{3+}$	$3d^6$	$d^2sp^3$	Octahedral	0	Diamagnetic
$[Cr(H_2O)_2(C_2O_4)_2]^-$	$Cr^{3+}$	$3d^3$	$d^2sp^3$	Octahedral	3	Paramagnetic
$[CuCl_4]^{2-}$	$Cu^{2+}$	$3d^9$	$sp^3$	Tetrahedral	1	Paramagnetic
$[Fe(en)_2Cl_2]$	$Fe^{3+}$	$3d^5$	$d^2sp^3$	Octahedral	1	Paramagnetic
$[Zn(H_2O)_6]^{2+}$	$Zn^{2+}$	$3d^{10}$	$d^2sp^3$	Octahedral	0	Diamagnetic

## 6. CRYSTAL FIELD THEORY: (CFT)

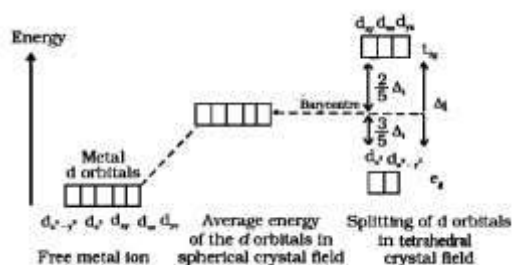
- The metal-ligand bond is ionic arising purely from electrostatic interactions between the metal ion and the ligand.
- Ligands are treated as point charges or dipoles in case of anions and neutral molecules.
- In an isolated gaseous metal atom or ion the five d-orbitals are degenerate.
- Degeneracy is maintained if a spherically symmetrical field of negative charges surrounds the metal /ion.
- In a complex the negative field becomes asymmetrical and results in splitting of the d-orbitals.

## 7. Crystal field splitting in octahedral coordination complexes

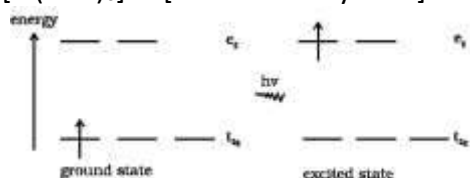


- In an octahedral coordination **complexes** with six ligands surrounding the metal atom/ion, there will be repulsion between the electrons in metal *d* orbitals and the electrons (or negative charges) of the ligands.
  - Such a repulsion is more when the metal *d* orbital is directed towards the ligand than when it is away from the ligand.
  - The  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals which point towards the axes along the direction of the ligand will experience more repulsion and will be raised in energy.
  - The  $d_{xy}$ ,  $d_{yz}$  and  $d_{zx}$  orbitals which are directed between the axes will be lowered in energy relative to the average energy in the spherical crystal field.
  - The degeneracy of the *d* orbitals has been removed due to ligand electron-metal electron repulsions in the octahedral complex to yield three orbitals of lower energy,  $t_{2g}$  set and two orbitals of higher energy,  $e_g$  set.
  - This splitting of the degenerate levels due to the presence of ligands in a definite geometry is termed as **crystal field splitting** and the energy separation is denoted by  $\Delta_o$  (the subscript o is for octahedral). Thus, the energy of the two  $e_g$  orbitals will increase by  $(3/5) \Delta_o$  and that of the three  $t_{2g}$  will decrease by  $(2/5) \Delta_o$ .
  - The crystal field splitting,  $\Delta_o$ , depends upon the field produced by the ligand and charge on the metal ion. Some ligands are able to produce strong fields in which case, the splitting will be large whereas others produce weak fields and consequently result in small splitting of *d* orbitals.
8. **Spectrochemical series:** In general, ligands can be arranged in a series in the order of increasing field strength as given below:  $I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < edta^{4-} < NH_3 < en < CN^- < CO$  Such a series is termed as **Spectrochemical series**.
9. **Assigning electrons in the *d*-orbitals of metal ion in octahedral coordination entities**
- $d^1 = t_{2g}^1$   $d^2 = t_{2g}^2$   $d^3 = t_{2g}^3$ , the *d* electrons occupy the orbitals singly in accordance with the Hund's rule.
  - For  **$d^4$  ions**, two possible patterns of electron distribution arise:
    - (i) If  $\Delta_o < P$ , the fourth electron enters one of the  $e_g$  orbitals giving the configuration  $t_{2g}^3 e_g^1$ . Ligands for which  $\Delta_o < P$  are known as **weak field ligands and form high spin complexes**.
    - (ii) If  $\Delta_o > P$ , it becomes more energetically favourable for the 4<sup>th</sup> electron to occupy a  $t_{2g}$  orbital with configuration  $t_{2g}^4 e_g^0$ . Ligands which produce this effect are known as **strong field ligands and form low spin complexes**

## 10. Crystal field splitting in tetrahedral coordination complexes:



11. **Colour in Coordination Compounds:** Consider, for example, the complex  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ , which is violet in colour  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ .  $[\text{Ti}^{3+}$  is a  $3d^1$  system]



Transition of an electron in  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$

**Note:** It is important to note that in the absence of ligand, crystal field splitting does not occur and hence the

substance is colourless. For example, removal of water from  $[\text{Ti}(\text{H}_2\text{O})_6]\text{Cl}_3$  on heating renders it colourless.

12. **Limitations of Crystal Field Theory:** From the assumptions that the ligands are point charges, it follows that anionic ligands should exert the greatest splitting effect. The anionic ligands actually are found at the low end of the spectrochemical series. Further, it does not take into account the covalent character of bonding between the ligand and the central atom. These are some of the weaknesses of CFT.

13. **BONDING IN METAL CARBONYLS** The metal-carbon bond in metal carbonyls possess both  $\sigma$  and  $\pi$  character. The  $\text{M}-\text{C}$   $\sigma$  bond is formed by the donation of lone pair of electrons on the carbonyl carbon into a vacant orbital of the metal. The  $\text{M}-\text{C}$   $\pi$  bond is formed by the donation of a pair of electrons from a filled d orbital of metal into the vacant antibonding  $\pi^*$  orbital of carbon monoxide. The metal to ligand bonding creates a synergic effect which strengthens the bond between CO and the metal

14. **Stability of Coordination Compounds:** The stability of a complex in solution refers to the degree of association between the two species involved in the state of equilibrium. The stability of a complex,  $\text{ML}_n$  is measured in terms of magnitude of (stability or formation) equilibrium constant for the association. quantitatively expresses the stability. if we have a reaction of the type:  $\text{M} + n\text{L} \rightleftharpoons \text{ML}_n$  we can write stability constants as follows:

- $\text{M} + \text{L} \rightleftharpoons \text{ML} \quad K_1 = [\text{ML}]/[\text{M}][\text{L}]$
- $\text{ML} + \text{L} \rightleftharpoons \text{ML}_2 \quad K_2 = [\text{ML}_2]/[\text{ML}][\text{L}]$
- $\text{ML}_2 + \text{L} \rightleftharpoons \text{ML}_3 \quad K_3 = [\text{ML}_3]/[\text{ML}_2][\text{L}]$
- .....
- $\text{ML}_{n-1} + \text{L} \rightleftharpoons \text{ML}_n \quad K_n = [\text{ML}_n]/[\text{ML}_{n-1}][\text{L}]$
- where  $K_1, K_2, K_3, \dots, K_n$  etc., are referred to as **stepwise stability constants**.

Alternatively, we can write the **overall stability constant** thus:  $\text{M} + n\text{L} \rightleftharpoons \text{ML}_n, \beta_n = [\text{ML}_n]/[\text{M}][\text{L}]^n$

The stepwise and overall stability constant are therefore related as follows  $\beta_n = K_1 \times K_2 \times K_3 \dots \times K_n$

- The **instability constant or the dissociation constant** of coordination compounds is defined as the reciprocal of the formation constant.

## 15. Factors affecting the stability of Complexes:

- a) **Nature of the central ion:** Greater the charge density (charge/radius ratio) on the central ion, greater is the stability of the complex. For example complexes of  $\text{Fe}^{3+}$  are more stable than  $\text{Fe}^{2+}$ .
- b) **Chelate effect:** The presence of chelate rings in the complex increases its stability increases. When chelation occurs entropy increases therefore the formation of the complex becomes more favourable. For example chelate  $[\text{Cd}(\text{en})_2]^{2+}$  is 10000 times stable than  $[\text{Cd}(\text{CH}_3\text{-NH}_2)_4]^{2+}$ .

16. **WERNER'S THEORY** : Alfred Werner in 1898 proposed Werner's theory explaining the structure of coordination compounds.

**Werner's Experiment:** By mixing  $\text{AgNO}_3$  (silver nitrate) with  $\text{CoCl}_3 \cdot 6\text{NH}_3$ , all three chloride ions got converted to  $\text{AgCl}$  (silver chloride). However, when  $\text{AgNO}_3$  was mixed with  $\text{CoCl}_3 \cdot 5\text{NH}_3$ , two moles of  $\text{AgCl}$  were formed.

Further, on mixing  $\text{CoCl}_3 \cdot 4\text{NH}_3$  with  $\text{AgNO}_3$ , one mole of  $\text{AgCl}$  was formed. Based on this observation, the following Werner's theory was postulated:

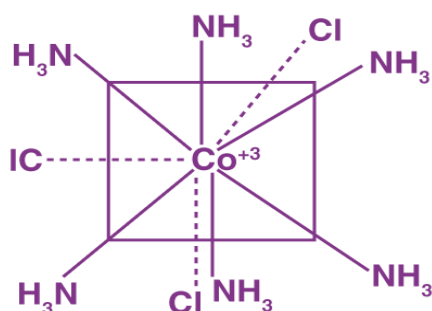
Postulates of Werner's Theory

- The central metal atom in the coordination compound exhibits two types of valency, namely, primary and secondary linkages or valencies.
- Primary linkages are ionizable and are satisfied by the negative ions.
- Secondary linkages are non-ionizable. These are satisfied by negative ions. Also, the secondary valence is fixed for any metal and is equal to its coordination number.
- The ions bounded by the secondary linkages to the metal exhibit characteristic spatial arrangements corresponding to different coordination numbers.

Difference between Primary and Secondary Valency in Coordination Compounds

Werner's Theory	
Primary valency	Secondary valency
These are ionizable	These are Non-ionizable
Satisfied by charged ions	Satisfied by ligands
<b>Primary valency</b> does not help in the structure of complex	<b>Secondary valency</b> helps in structure
It can also function as a secondary valence	It can not function as a primary valency

**Example:**  $\text{CoCl}_3 \cdot 6\text{NH}_3$  is Werner complex.



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Such spatial arrangement is termed as coordination polyhedra. The terms inside the square brackets are coordination complexes and the ions outside the square brackets are counter-ions.

Limitations of Werner's Theory

1. It fails to explain the magnetic, colour and optical properties shown by coordination compounds.
2. It failed to explain the reason why all elements don't form coordination compounds.
3. It failed to explain the directional properties of bonds in coordination compounds.
4. This theory does not explain the stability of the complex
5. This theory could not explain the nature of complexes

## Questions.....

1. Write the main points of VBT. Give its limitations.
2. Write the name & Using **VBT** Predict the Magnetic behaviour, Hybridization, Shape of following. Also predict whether it is inner or outer orbital complex in case of octahedral complexes.:  $[\text{Ag}(\text{NH}_3)_2]^+$ ,  $[\text{CoF}_6]^{3-}$ ,  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ ,  $[\text{Cr}(\text{NH}_3)_6]^{3+}$ ,  $[\text{FeF}_6]^{3-}$ ,  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ ,  $[\text{Fe}(\text{CN})_6]^{3-}$ ,  $[\text{Fe}(\text{CN})_6]^{4-}$ ,  $[\text{Co}(\text{NH}_3)_6]^{3+}$ ,  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ ,  $[\text{NiCl}_4]^{2-}$ ,  $[\text{Ni}(\text{CN})_4]^{2-}$ ,  $[\text{Ni}(\text{CO})_4]$ ,  $[\text{CoF}_4]^{2-}$ ,  $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$ ,  $[\text{Cr}(\text{H}_2\text{O})_2(\text{C}_2\text{O}_4)_2]^-$ ,  $[\text{CuCl}_4]^{2-}$ ,  $[\text{Fe}(\text{en})_2\text{Cl}_2]$ ,  $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$ ,  $[\text{CoF}_6]^{3-}$ ,  $[\text{CoCl}_4]^{2-}$ ,  $[\text{Cr}(\text{CO})_6]$
3. Amongst the following ions which one has the highest magnetic moment value? (i)  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  (ii)  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  (iii)  $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$
4. Write down the IUPAC name for each of the following complexes and indicate the oxidation state, electronic configuration and coordination number. Also give stereochemistry and magnetic moment of the complex: (i)  $\text{K}[\text{Cr}(\text{H}_2\text{O})_2(\text{C}_2\text{O}_4)_2] \cdot 3\text{H}_2\text{O}$  (iii)  $[\text{CrCl}_3(\text{py})_3]$  (v)  $\text{K}_4[\text{Mn}(\text{CN})_6]$  (ii)  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  (iv)  $\text{Cs}[\text{FeCl}_4]$  (v)  $\text{K}_2[\text{Ni}(\text{CN})_6]$  (vi)  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$  (vii)  $[\text{Cr}(\text{en})_3]\text{Cl}_3$
5. The spin only magnetic moment of  $[\text{MnBr}_4]^{2-}$  is 5.9 BM. Predict the geometry of the complex
6. Predict the number of unpaired electrons in the square planar  $[\text{Pt}(\text{CN})_4]^{2-}$  ion.
7. Account for the Following:
  - (a)  $[\text{Ni}(\text{CN})_4]^{2-}$  ion with square planar structure is diamagnetic and the  $[\text{NiCl}_4]^{2-}$  ion with tetrahedral structure is paramagnetic .
  - (b)  $[\text{NiCl}_4]^{2-}$  is paramagnetic while  $[\text{Ni}(\text{CO})_4]$  is diamagnetic though both are tetrahedral.
  - (c)  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  is strongly paramagnetic while  $[\text{Fe}(\text{CN})_6]^{3-}$  is weakly paramagnetic.
  - (d)  $[\text{Co}(\text{NH}_3)_6]^{+3}$  is an inner orbital complex whereas  $[\text{Ni}(\text{NH}_3)_6]^{+2}$  is an outer complex.
  - (e)  $[\text{Cr}(\text{NH}_3)_6]^{+3}$  is paramagnetic while  $[\text{Ni}(\text{CN})_4]^{2-}$  is diamagnetic.
  - (f) A solution of  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  is green but a solution of  $[\text{Ni}(\text{CN})_4]^{2-}$  is colourless.
  - (g)  $[\text{Fe}(\text{CN})_6]^{3-}$  and  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  are of different colours in dilute solutions.
  - (h) Nickel does not form low spin octahedral complexes. [**Ans:**because Ni has E.C.  $3d^8 4s^2$ , in which two inner d –orbitals are not available which are required to form  $d^2sp^3$  hybridisation]
  - (i) The  $\pi$ -complexes are known for the transition metal only. [**Ans:**because Transition metals have d orbitals in their atoms or ions in to which the electron pair donated can be donated by ligands containing  $\pi$  electrons]
  - (j)  $\text{Co}^{+2}$  is easily oxidised to  $\text{Co}^{+3}$  in the presence of a strong ligand. [**Ans:**because in the presence of strong ligand ,the 3d electrons pair up leaving two orbitals empty to be involved in  $d^2sp^3$  hybridisation]
  - (k) CO is a stronger ligand than  $\text{NH}_3$  for many metals. [**Ans:**because in case of CO back bonding takes place in which central atom uses its filled d orbital with empty  $\pi^*$  molecular orbital of CO]
8. Draw diagram to show splitting of d – orbital in octahedral crystal field. Explain the two patterns of filling  $d^4$  in octahedral crystal field.
9. What is crystal field splitting energy? What are the various factors affecting CFSE. How does the magnitude of  $\Delta_0$  decide the actual configuration of d-orbital in a coordination entity?
10. Draw diagram to show splitting of d – orbital in a tetrahedral crystal field.
11. Among octahedral & tetrahedral crystal field ,in which case the magnitude of crystal field splitting is larger? [**Ans:**octahedral crystal field]
12. Explain why  $[\text{Ti}(\text{H}_2\text{O})_6]\text{Cl}_3$  is coloured. What happens to the colour of  $[\text{Ti}(\text{H}_2\text{O})_6]\text{Cl}_3$  when heated gradually?
13. The Hexaaquamanganese (II) ion contains five unpaired electrons, while the Hexacyano manganese (II) ion contains only one unpaired electron. Explain using CFT.
14. What is spectrochemical series? Explain the difference between a weak field ligand and a strong field ligand.
15. Give the oxidation state, d orbital occupation and coordination number of the central metal ion in the following complexes: (i)  $\text{K}_3[\text{Co}(\text{C}_2\text{O}_4)_3]$  (iii)  $(\text{NH}_4)_2[\text{CoF}_4]$  (ii) cis- $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$  (iv)  $[\text{Mn}(\text{H}_2\text{O})_6]\text{SO}_4$
16. What is meant by stability of a coordination compound in solution? State the factors which govern stability of complexes.

17. Which are of the two is more stable & why?  $K_4[Fe(CN)_6]$  &  $K_3[Fe(CN)_6]$  {Ans:  $Fe^{3+}$  are more stable than  $Fe^{2+}$ }
18. What do you understand by stepwise stability constants.& overall stability constant of a coordination compound. How are stepwise and overall stability constant related
19. What is meant the chelate effect? Give an example.
20. Amongst the following, the most stable complex is (i)  $[Fe(H_2O)_6]^{3+}$  (ii)  $[Fe(NH_3)_6]^{3+}$  (iii)  $[Fe(C_2O_4)_3]^{3-}$  (iv)  $[FeCl_6]^{3-}$
21. Discuss the nature of Bonding in metal carbonyls.
22. What is the coordination entity formed when excess of aqueous KCN is added to an aqueous solution of Copper sulphate? Why is it that no precipitates of Copper sulphide is obtained when  $H_2S$  (g) is passed through this solution
23. A coordination compound has the formula  $CoCl_3.4NH_3$ . It does not liberate ammonia but forms a precipitate with  $AgNO_3$ . Write the structure and IUPAC name of the complex compound.
24. The Values of dissociation constant of  $[Cu(NH_3)_4]^{2+}$  and  $[Co(NH_3)_6]^{2+}$  are  $1.0 \times 10^{-12}$  and  $6.2 \times 10^{-36}$  respectively. which complex is more stable and why?
25. How many ions are produced from the complex  $[Co(NH_3)_6]Cl_2$  in solution?
26. What will be the correct order for the wavelengths of absorption in the visible region for the following:  $[Ni(NO_2)_6]^{4-}$ ,  $[Ni(NH_3)_6]^{2+}$ ,  $[Ni(H_2O)_6]^{2+}$ ?
27. Explain the bonding in coordination compounds in terms of Werner's postulates.

### IMPORTANT QUESTIONS FOR TERM -2 (PYQ CBSE papers)

1. **Explain giving examples:**

a) Chelating ligands	d) Polydentate ligand
b) ambidentate ligands	e) Homoleptic complexes
c) bidentate or Didentate ligand	f) Heteroleptic complexes
2. **A chelating agent has two or more than two donor atoms to bind to a single metal ion. Which of the following is not a chelating agent? (i) thiosulphate (ii) oxalate (iii) glycinato (iv) ethane-1,2-diamine**
3. **Which of the following species is not expected to be a ligand? (i) NO (ii)  $NH_4^+$  (iii)  $NH_2CH_2CH_2NH_2$  (iv) CO**
4. **Using IUPAC norms write the formulae for the following:**
  - a. potassiumtri(oxalato) chromate (III)
  - b. pentaamminenitrito-O-cobalt (III) ion
  - c. pentaamminenitrito-N-cobalt(III) ion
  - d. iron(III) hexacyanoferrate(II)
  - e. mercury tetrathiocyanatocobaltate(III)
  - f. tetraammineaquachloridocobalt (III) chloride
  - g. tris(ethane-1,2-diamine) chromium(III) chloride
  - h. amminebromidochloridonitrito-N-platinate(II)
  - i. dichloridobis(ethane-1,2-diamine)platinum(IV) nitrate
5. **Give the formula** of each of the following coordination entities:
  - (i)  $Co^{3+}$  ion is bound to one  $Cl^-$  one  $NH_3$  molecule and two bidentate ligands ethylenediamine(en) molecules
  - (ii)  $Ni^{2+}$  ion is bound to two water molecule and two oxalate ions
6. When a coordination compound  $CrCl_3.6H_2O$  is mixed with  $AgNO_3$ , 2 moles of  $AgCl$  are precipitated per mole of the compound. **Write structural formula & IUPAC name of the complex.**

7. When a coordination compound  $\text{PtCl}_4 \cdot 6\text{NH}_3$  is mixed with  $\text{AgNO}_3$ , 4 moles of  $\text{AgCl}$  are precipitated per mole of the compound. **Write structural formula & IUPAC name of the complex.**
8. **When 1 mol  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  is treated with an excess of  $\text{AgNO}_3$ , 3 mol of  $\text{AgCl}$  are obtained. Write structural formula & IUPAC name of the complex.**
9. Write the **IUPAC names, Specify the coordination number** of the central Atom of the following:
- |   |  |
|---|--|
| a. $[\text{Fe}(\text{en})_2\text{Cl}_2]\text{Cl}$                       | e. $[\text{Cr}(\text{H}_2\text{O})_2(\text{C}_2\text{O}_4)_2]^-$ |
| b. $[\text{CoCl}_4]^{2-}$   | f. $\text{K}_2[\text{PdCl}_4]$                                   |
| c. $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]\text{Cl}_2$ | g. $[\text{Ni}(\text{CN})_4]^{2-}$                               |
| d. $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$                     |  |
10. Write the name & Using **VBT** Predict the Magnetic behaviour, Hybridization, Shape of following. Also predict whether it is inner or outer orbital complex in case of octahedral complexes.
- |   |  |   |
|---|--|---|
| a) $[\text{CoF}_6]^{3-}$                    | i) $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$                      | q) $[\text{Fe}(\text{en})_2\text{Cl}_2]$    |
| b) $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ | j) $[\text{NiCl}_4]^{2-}$  | r) $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$ |
| c) $[\text{Cr}(\text{NH}_3)_6]^{3+}$        | k) $[\text{Ni}(\text{CN})_4]^{2-}$                               | s) $[\text{CoCl}_4]^{2-}$                   |
| d) $[\text{FeF}_6]^{3-}$                    | l) $[\text{Ni}(\text{CO})_4]$                                    | t) $[\text{Cr}(\text{CO})_6]$               |
| e) $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ | m) $[\text{CoF}_4]^{2-}$   | u) $[\text{Fe}(\text{CO})_5]$               |
| f) $[\text{Fe}(\text{CN})_6]^{3-}$          | n) $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$                    | v) $[\text{MnF}_6]^{4-}$                    |
| g) $[\text{Fe}(\text{CN})_6]^{4-}$          | o) $[\text{Cr}(\text{H}_2\text{O})_2(\text{C}_2\text{O}_4)_2]^-$ |   |
| h) $[\text{Co}(\text{NH}_3)_6]^{3+}$        | p) $[\text{CuCl}_4]^{2-}$  |   |
11. Explain inner & outer orbital complex using suitable examples.
12. Draw diagram to show splitting of d – orbital in octahedral crystal field. Explain the two patterns of filling  $d^4$  in octahedral crystal Field.
13. On the basis of crystal field theory, write the electronic configuration for  $d^4$  ion if  $\Delta_o < P$
14. On the basis of crystal field theory, write the electronic configuration for  $d^4$  ion if  $\Delta_o > P$
15. On the basis of crystal field theory, write the electronic configuration for  $d^6$  ion if  $\Delta_o < P$
16. On the basis of crystal field theory, write the electronic configuration for  $d^7$  ion if  $\Delta_o > P$
17. What is crystal field splitting energy? What are the various factors affecting CFSE. How does the magnitude of  $\Delta_o$  decide the actual configuration of d-orbital in a coordination entity?
18. **Based on crystal field theory explain why  $\text{Co}(\text{III})$  forms a paramagnetic octahedral complex with weak field ligands whereas it forms a diamagnetic octahedral complex with strong field ligands.**
19. Explain why  $[\text{Ti}(\text{H}_2\text{O})_6]_3\text{Cl}_3$  is coloured. What happens to the colour of  $[\text{Ti}(\text{H}_2\text{O})_6]_3\text{Cl}_3$  when heated gradually?
20. What is **spectrochemical series**? Explain the difference between a weak field ligand and a strong field ligand.
21. **Arrange following complex ions in increasing order of crystal field splitting energy ( $\Delta_o$ ):  $[\text{Cr}(\text{Cl})_6]^{3-}$ ,  $[\text{Cr}(\text{CN})_6]^{3-}$ ,  $[\text{Cr}(\text{NH}_3)_6]^{3+}$ .**
22. Using CFT, draw the energy level diagram, write electronic configuration of the central atom/ion and determine the magnetic moment value in the following:
- |   |                                    |
|---|------------------------------------|
| a) $[\text{FeF}_6]^{3-}$                    | c) $[\text{Fe}(\text{CN})_6]^{4-}$ |
| b) $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ |                                    |
23. **Account for the Following:**

- a)  $[\text{Ni}(\text{CN})_4]^{2-}$  ion with square planar structure is diamagnetic and the  $[\text{NiCl}_4]^{2-}$  ion with tetrahedral structure is paramagnetic.
- b)  $[\text{NiCl}_4]^{2-}$  is paramagnetic while  $[\text{Ni}(\text{CO})_4]$  is diamagnetic though both are tetrahedral.
- c)  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  is strongly paramagnetic while  $[\text{Fe}(\text{CN})_6]^{3-}$  is weakly paramagnetic.
- d)  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  has a magnetic moment value of 5.92 BM whereas  $[\text{Fe}(\text{CN})_6]^{3-}$  has a value of only 1.74 BM.
- e)  $[\text{Co}(\text{NH}_3)_6]^{+3}$  is an inner orbital complex whereas  $[\text{Ni}(\text{NH}_3)_6]^{+2}$  is an outer complex.
- f)  $[\text{Cr}(\text{NH}_3)_6]^{+3}$  is paramagnetic while  $[\text{Ni}(\text{CN})_4]^{2-}$  is diamagnetic.
- g) A solution of  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  is green but a solution of  $[\text{Ni}(\text{CN})_4]^{2-}$  is colourless
- h)  $[\text{Fe}(\text{CN})_6]^{3-}$  and  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  are of different colours in dilute solutions

**24. Give reason for the Following:**

- a) Nickel does not form low spin octahedral complexes. [Ans: because Ni has E.C.  $3d^8 4s^2$ , in which two inner d-orbitals are not available which are required to form  $d^2sp^3$  hybridisation]
- b) The  $\pi$ -complexes are known for the transition metal only. [Ans: because Transition metals have d orbitals in their atoms or ions in to which the electron pair donated can be donated by ligands containing  $\pi$  electrons]
- c)  $\text{Co}^{+2}$  is easily oxidised to  $\text{Co}^{+3}$  in the presence of a strong ligand. [Ans: because in the presence of strong ligand, the 3d electrons pair up leaving two orbitals empty to be involved in  $d^2sp^3$  hybridisation]
- d) CO is a stronger ligand than  $\text{NH}_3$  for many metals. [Ans: because in case of CO back bonding takes place in which central atom uses its filled d orbital with empty  $\pi^*$  molecular orbital of CO]
- e) **Low spin tetrahedral complexes not formed.** [Ans: For tetrahedral complexes, the crystal field splitting energy is too low. It is lower than pairing energy so, the pairing of electrons is not favoured and therefore the complexes cannot form low spin complexes.]

25. What is meant by stability of a coordination compound in solution? State the factors which govern stability of complexes.

26. Which of the following is the most stable complex species? (i)  $[\text{Fe}(\text{CO})_5]$  (ii)  $[\text{Fe}(\text{CN})_6]^{3-}$  (iii)  $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$  (iv)  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$

27. What do you understand by stepwise stability constants & overall stability constant of a coordination compound. How are stepwise and overall stability constant related.

28. Discuss the nature of Bonding in metal carbonyls.



# ALDEHYDES KETONES AND CARBOXYLIC ACIDS

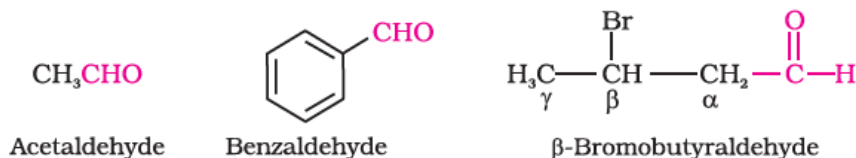
## Nomenclature and Structure of Carbonyl Group

**I. Aldehydes and ketones** - Aldehydes and ketones are the simplest and most important carbonyl compounds.

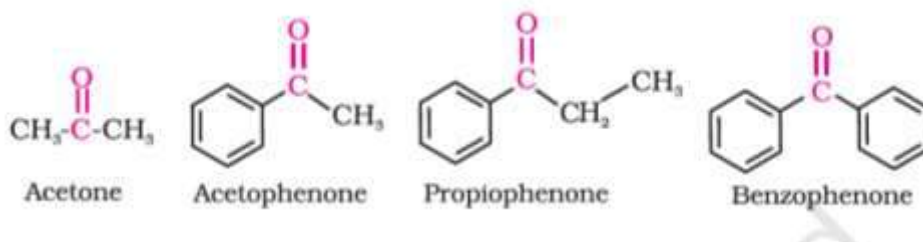
There are two systems of nomenclature of aldehydes and ketones.

### (a) Common names

Aldehydes and ketones are often called by their common names instead of IUPAC names. The common names of most aldehydes are derived from the common names of the corresponding carboxylic acids by replacing the ending *-ic* of acid with aldehyde.

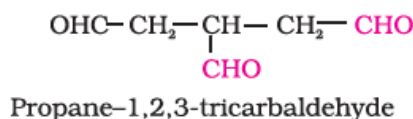
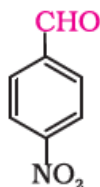
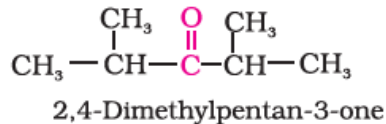
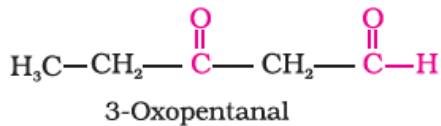
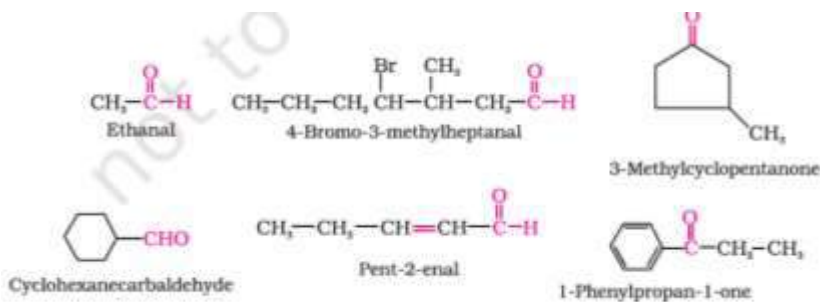


The common names of ketones are derived by naming two alkyl or aryl groups bonded to the carbonyl group. Some ketones have historical common names, the simplest dimethyl ketone is called acetone. Alkyl phenyl ketones are usually named by adding the acyl group as prefix to phenone. For example



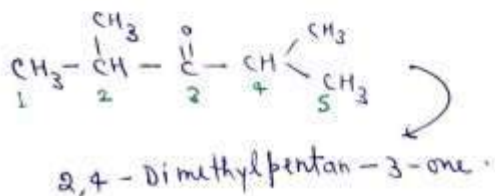
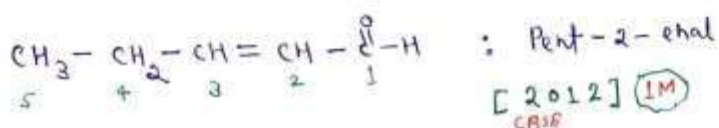
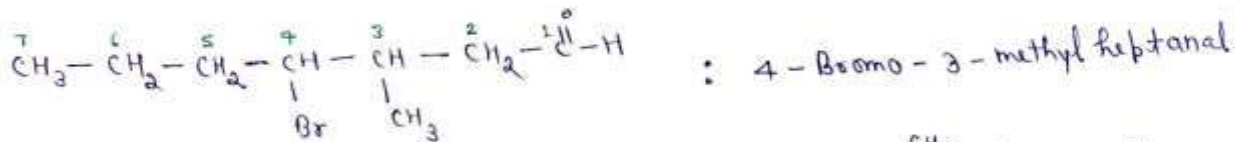
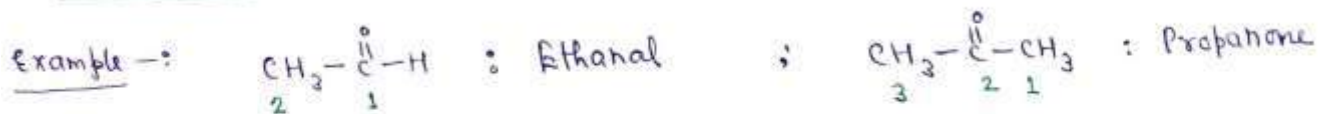
### IUPAC names :-

The IUPAC names of open chain aliphatic aldehydes and ketones are derived from the names of the corresponding alkanes by replacing the ending *-e* with *-al* and *-one* respectively. In case of aldehydes the longest carbon chain is numbered starting from the carbon of the aldehyde group while in case of ketones the numbering begins from the end nearer to the carbonyl group. The substituents are prefixed in alphabetical order along with numerals indicating their positions in the carbon chain. The same applies to cyclic ketones, where the carbonyl carbon is numbered one. When the aldehyde group is attached to a ring, the suffix carbaldehyde is added after the full name of the cycloalkane. The numbering of the ring carbon atoms start from the carbon atom attached to the aldehyde group. The name of the simplest aromatic aldehyde carrying the aldehyde group on a benzene ring is benzenecarbaldehyde. However, the common name benzaldehyde is also accepted by IUPAC. Other aromatic aldehydes are hence named as substituted benzaldehydes.

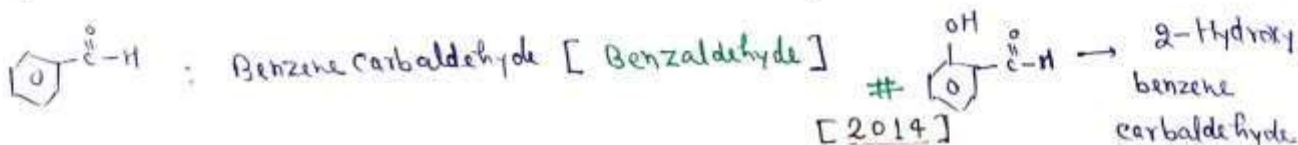
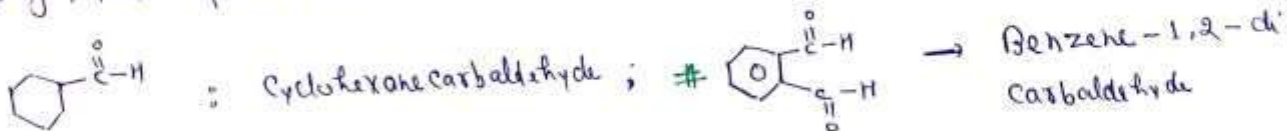


[Note: To give identical treatment to all aldehydic groups, the compound is named as shown above.]

→ In case of ketones -: Numbering begin from the end near to carbonyl group



→ When aldehyde group is attached to cyclic ring, then special suffix is used -: [Carbaldehyde]



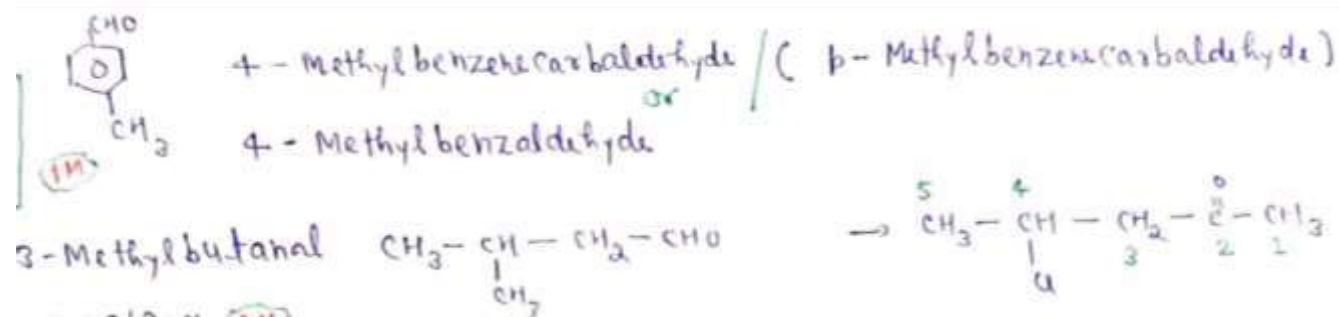
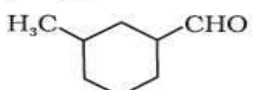
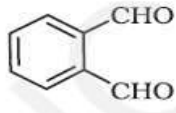
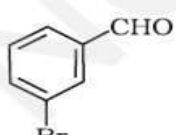
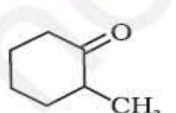
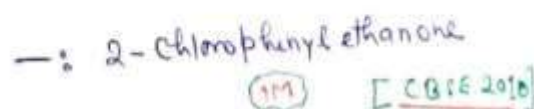
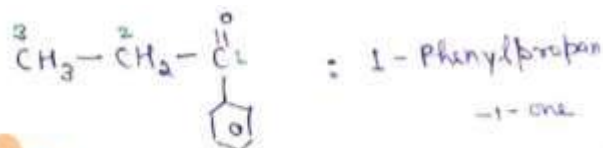
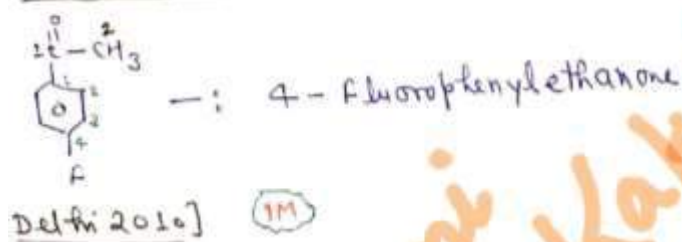
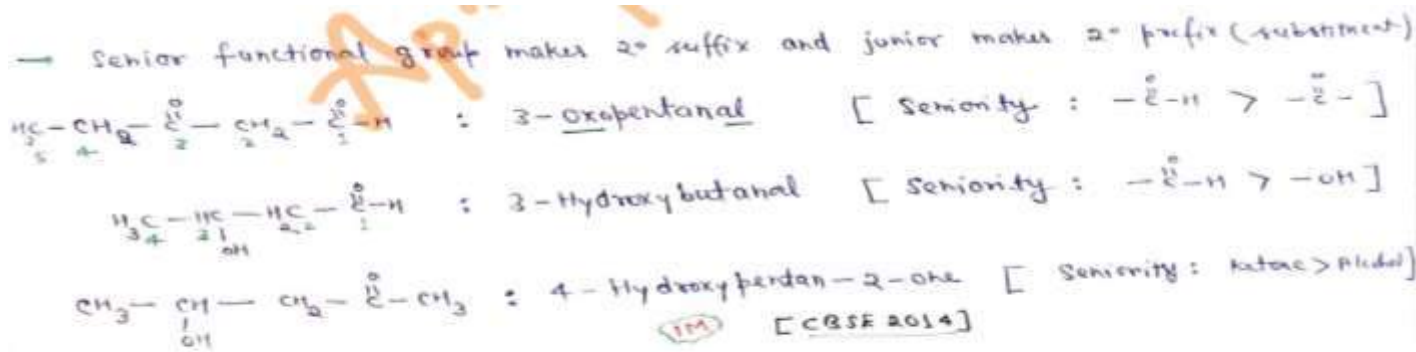


Table 12.1: Common and IUPAC Names of Some Aldehydes and Ketones

Structure	Common name	IUPAC name
<b>Aldehydes</b>		
HCHO	Formaldehyde	Methanal
CH <sub>3</sub> CHO	Acetaldehyde	Ethanal
(CH <sub>3</sub> ) <sub>2</sub> CHCHO	Isobutyraldehyde	2-Methylpropanal
	γ-Methylcyclohexanecarbaldehyde	3-Methylcyclohexanecarbaldehyde
CH <sub>3</sub> CH(OCH <sub>3</sub> )CHO	α-Methoxypropionaldehyde	2-Methoxypropanal
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CHO	Valeraldehyde	Pentanal
CH <sub>2</sub> =CHCHO	Acrolein	Prop-2-enal
	Phthalaldehyde	Benzene-1,2-dicarbaldehyde
	m-Bromobenzaldehyde	3-Bromobenzenecarbaldehyde or 3-Bromobenzaldehyde
<b>Ketones</b>		
CH <sub>3</sub> COCH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	Methyl n-propyl ketone	Pentan-2-one
(CH <sub>3</sub> ) <sub>2</sub> CHCOCH(CH <sub>3</sub> ) <sub>2</sub>	Diisopropyl ketone	2,4-Dimethylpentan-3-one
	α-Methylcyclohexanone	2-Methylcyclohexanone
(CH <sub>3</sub> ) <sub>2</sub> C=CHCOCH <sub>3</sub>	Mesityl oxide	4-Methylpent-3-en-2-one

Benzene as substituent —: Phenyl





## Preparation of aldehydes and ketones

### PREPARATION OF ALDEHYDES AND KETONES

#### 1. By oxidation of alcohols :-

Aldehydes and ketones are generally prepared by oxidation of primary and secondary alcohols, respectively (SEE CHAPTER ALCOHOLS)

#### 2. By dehydrogenation of alcohols

This method is suitable for volatile alcohols and is of industrial application. In this method alcohol vapours are passed over heavy metal catalysts (Ag or Cu). Primary and secondary alcohols give aldehydes and ketones, respectively (SEE CHAPTER ALCOHOLS)

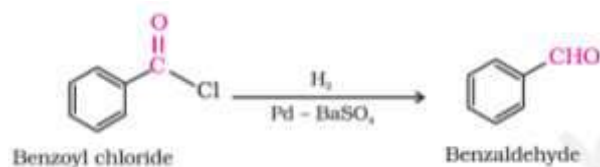
#### 3. From hydrocarbons :-

(i) **By ozonolysis of alkenes:** As we know, ozonolysis of alkenes followed by reaction with zinc dust and water gives aldehydes ketones or a mixture of both depending on the substitution pattern of the alkene

(ii) **By hydration of alkynes:** Addition of water to ethyne in the presence of  $\text{H}_2\text{SO}_4$  and  $\text{HgSO}_4$  gives acetaldehyde. All other alkynes give ketones in this reaction

#### PREPARATION OF ALDEHYDES :-

1. **From acyl chloride (acid chloride) :-** Acyl chloride (acid chloride) is hydrogenated over catalyst, palladium on barium sulphate. This reaction is called **Rosenmund reduction**



#### 2. From nitriles and esters :-

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

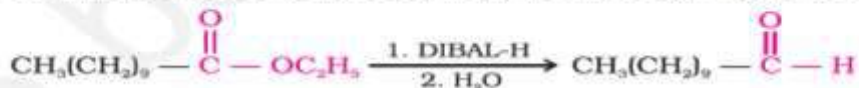
(i). This reaction is called **Stephen reaction**.



(ii). Alternatively, nitriles are selectively reduced by diisobutylaluminium hydride, (DIBAL-H) to imines followed by hydrolysis to aldehydes:



Similarly, esters are also reduced to aldehydes with DIBAL-H.



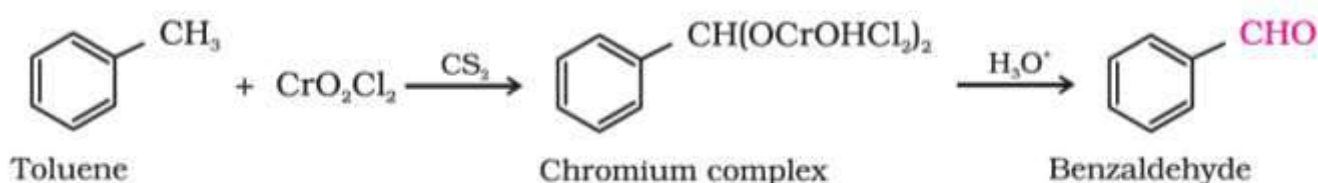
### 3. From hydrocarbons :-

Aromatic aldehydes (benzaldehyde and its derivatives) are prepared from aromatic hydrocarbons by the following methods:

#### (i) By oxidation of methylbenzene :-

Strong oxidising agents oxidise toluene and its derivatives to benzoic acids. However, it is possible to stop the oxidation at the aldehyde stage with suitable reagents that convert the methyl group to an intermediate that is difficult to oxidise further. The following methods are used for this purpose.

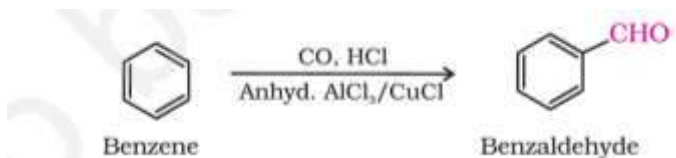
(a) Use of chromyl chloride ( $CrO_2Cl_2$ ): Chromyl chloride oxidises methyl group to a chromium complex, which on hydrolysis gives corresponding benzaldehyde.



This reaction is called **Etard reaction**

#### (ii) By Gatterman – Koch reaction

When benzene or its derivative is treated with carbon monoxide and hydrogen chloride in the presence of anhydrous aluminium chloride or cuprous chloride, it gives benzaldehyde or substituted benzaldehyde.

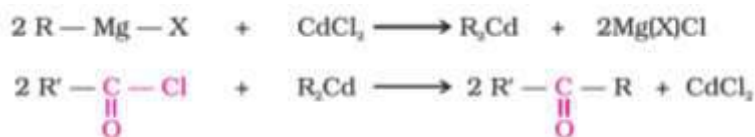


This reaction is known as **Gatterman-Koch reaction**.

### Preparation of ketones:-

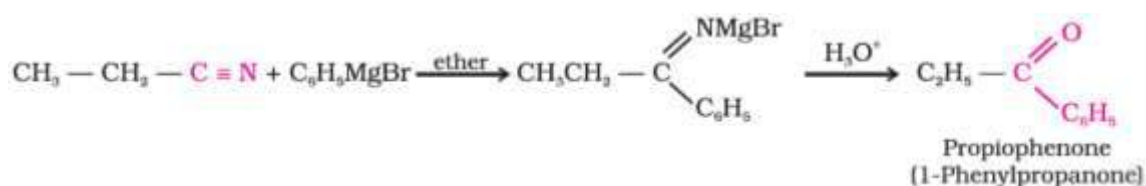
#### 1. From acyl chlorides:-

Treatment of acyl chlorides with dialkylcadmium, prepared by the reaction of cadmium chloride with Grignard reagent, gives ketones.



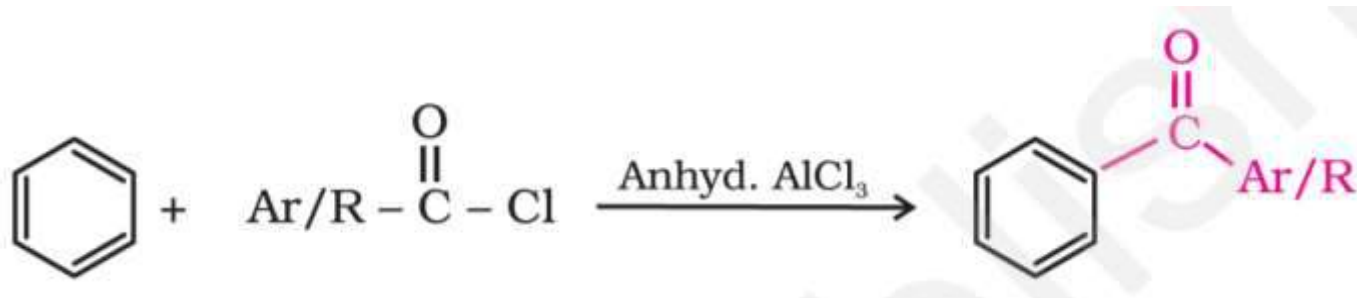
#### 2. From nitriles:-

Treating a nitrile with Grignard reagent followed by hydrolysis yields a ketone.



### 3. From benzene or substituted benzenes :-

When benzene or substituted benzene is treated with acid chloride in the presence of anhydrous aluminium chloride, it affords the corresponding ketone. This reaction is known as **Friedel-Crafts acylation reaction**.

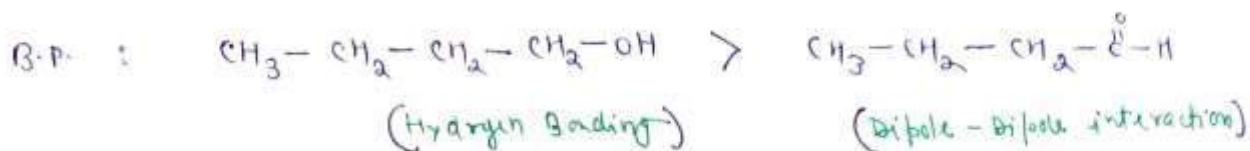


### Physical Properties :-

#### 1. Boiling point:-

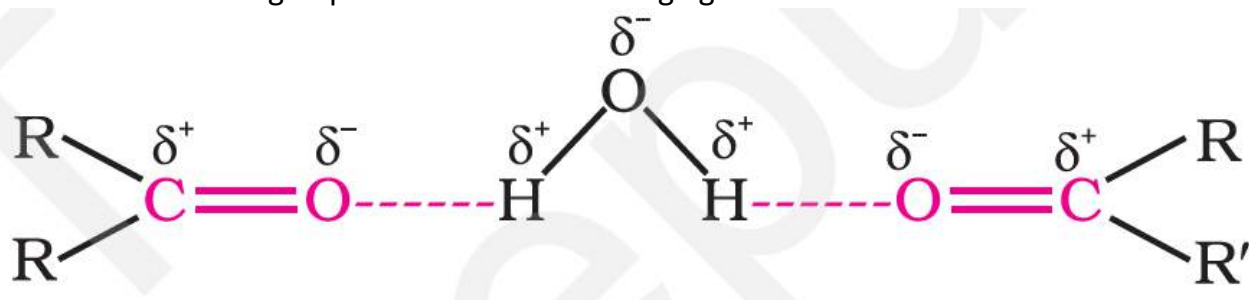
The boiling points of aldehydes and ketones are higher than hydrocarbons and ethers of comparable molecular masses. It is due to weak molecular association in aldehydes and ketones arising out of the dipole-dipole interactions. Also, their boiling points are lower than those of alcohols of similar molecular masses due to absence of intermolecular hydrogen bonding. The following compounds of molecular masses 58

and 60 are ranked in order of increasing boiling points.



#### 2. Solubility:-

However, the solubility of aldehydes and ketones decreases rapidly on increasing the length of alkyl chain. All aldehydes and ketones are fairly soluble in organic solvents like benzene, ether, methanol, chloroform, etc. The lower aldehydes have sharp pungent odours. As the size of the molecule increases, the odour becomes less pungent and more fragrant. In fact, many naturally occurring aldehydes and ketones are used in the blending of perfumes and flavouring agents.



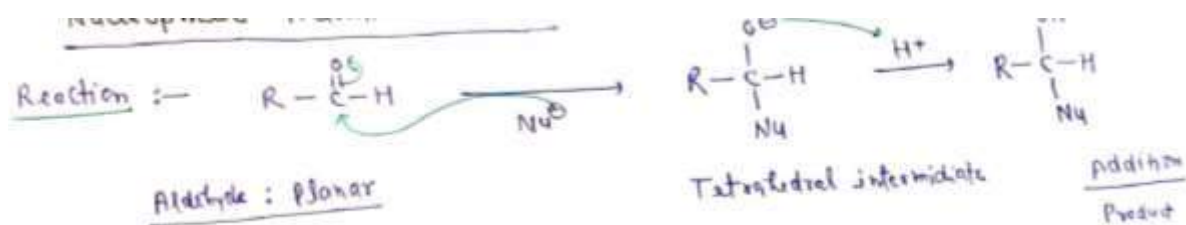
### Chemical Reactions :-

**1. Nucleophilic addition reactions:-** Contrary to electrophilic addition reactions observed in alkenes the aldehydes and ketones undergo nucleophilic addition reactions

#### (i) Mechanism of nucleophilic addition reactions:-

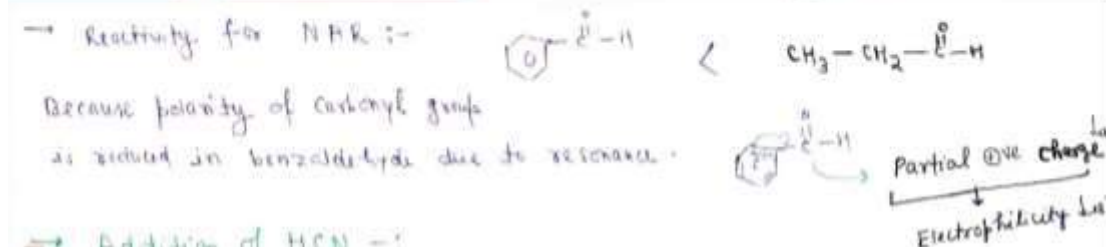
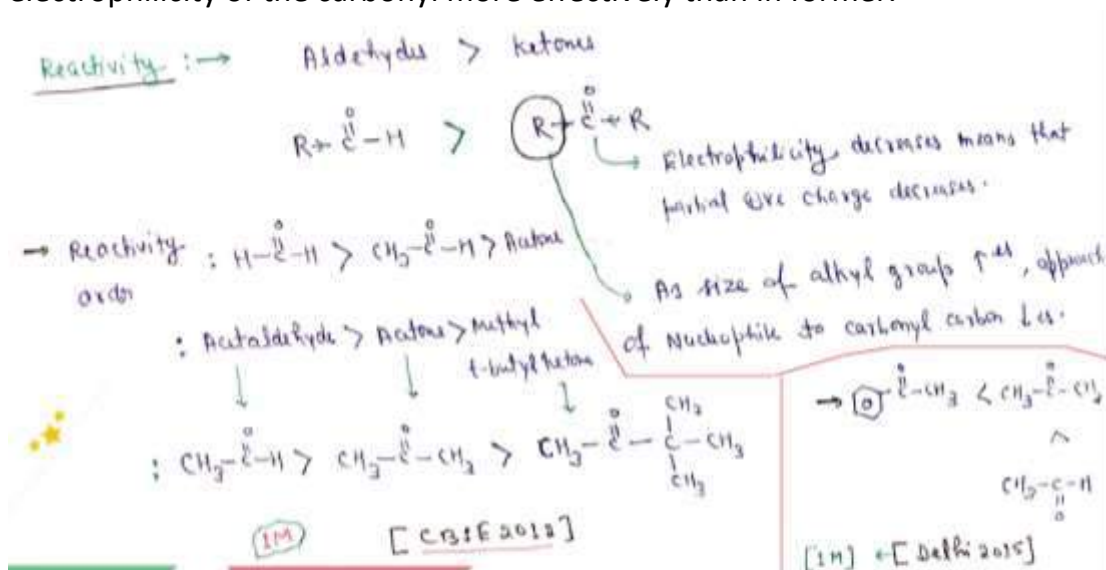
A nucleophile attacks the electrophilic carbon atom of the polar carbonyl group from a direction approximately perpendicular to the plane of  $sp^2$  hybridised orbitals of carbonyl carbon. The hybridisation of carbon changes from  $sp^2$  to  $sp^3$  in this process, and a tetrahedral alkoxide intermediate is produced. This intermediate captures a proton from the reaction medium to give the electrically neutral product. The net

result is addition of  $\text{Nu}^-$  and  $\text{H}^+$  across the carbon oxygen double bond as shown in Arrange the following compounds in increasing order of their boiling points.

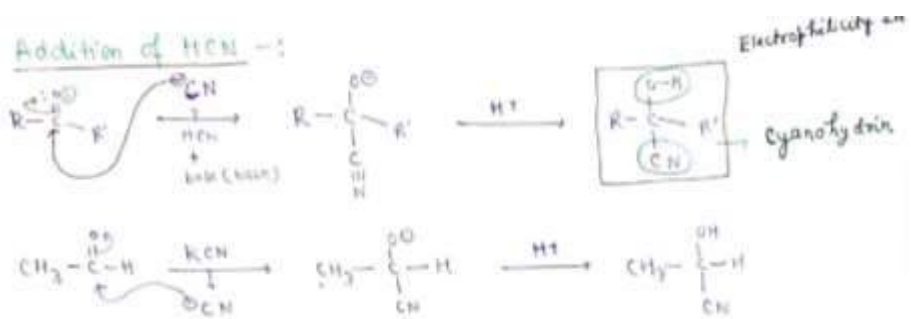


**(ii) Reactivity:-**

Aldehydes are generally more reactive than ketones in nucleophilic addition reactions due to steric and electronic reasons. Sterically, the presence of two relatively large substituents in ketones hinders the approach of nucleophile to carbonyl carbon than in aldehydes having only one such substituent. Electronically, aldehydes are more reactive than ketones because two alkyl groups reduce the electrophilicity of the carbonyl more effectively than in former.



**(a) Addition of hydrogen cyanide (HCN):** Aldehydes and ketones react with hydrogen cyanide (HCN) to yield cyanohydrins. This reaction occurs very slowly with pure HCN. Therefore, it is catalyzed by a base and the generated cyanide ion ( $\text{CN}^-$ ) being a stronger nucleophile readily adds to carbonyl compounds to yield corresponding cyanohydrin. Cyanohydrins are useful synthetic intermediates.

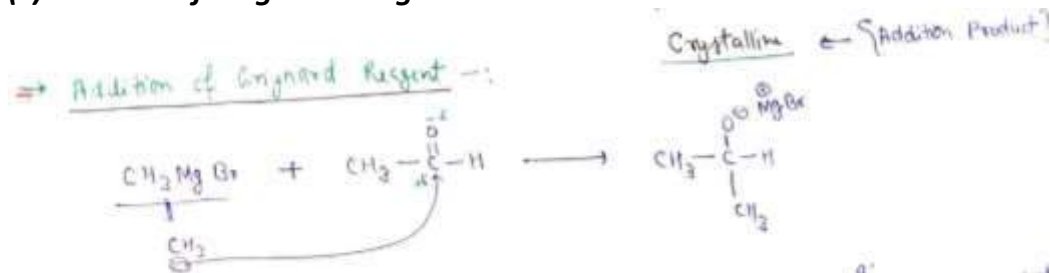


**(b) Addition of sodium hydrogensulphite:** Sodium hydrogensulphite adds to aldehydes and ketones to form the addition products. The position of the equilibrium lies largely to the right hand side for most aldehydes and to the left for most ketones due to steric reasons. The hydrogensulphite addition compound is water soluble and can be converted back to the original carbonyl compound by treating it with dilute mineral acid or alkali. Therefore, these are useful for separation and purification of aldehydes.

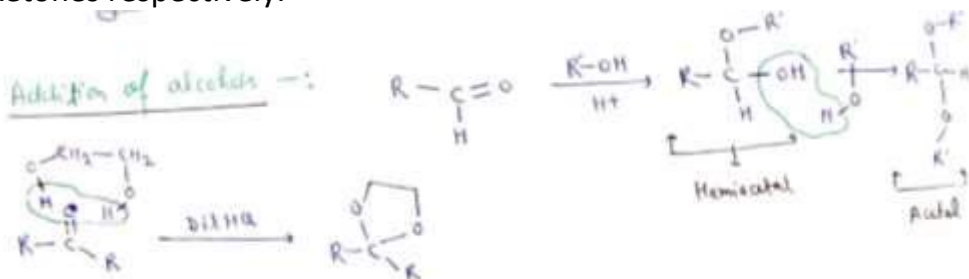
Addition of sodium hydrogen sulphite :-  $[\text{NaHSO}_3]$



**(c) Addition of Grignard reagents:-**

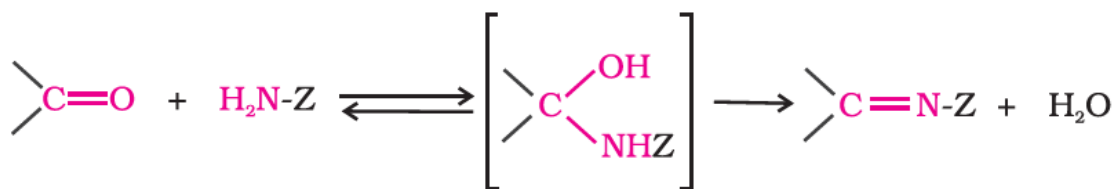


**(d) Addition of alcohols:** Aldehydes react with one equivalent of monohydric alcohol in the presence of dry hydrogen chloride to yield alkoxyalcohol intermediate, known as hemiacetals, which further react with one more molecule of alcohol to give a *gem*-dialkoxy compound known as acetal as shown in the reaction. Ketones react with ethylene glycol under similar conditions to form cyclic products known as ethylene glycol ketals. Dry hydrogen chloride protonates the oxygen of the carbonyl compounds and therefore, increases the electrophilicity of the carbonyl carbon facilitating the nucleophilic attack of ethylene glycol. Acetals and ketals are hydrolysed with aqueous mineral acids to yield corresponding aldehydes and ketones respectively.



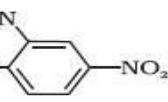
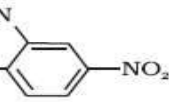
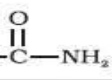


**(e) Addition of ammonia and its derivatives:** Nucleophiles, such as ammonia and its derivatives  $\text{H}_2\text{N-Z}$  add to the carbonyl group of aldehydes and ketones. The reaction is reversible and catalysed by acid. The equilibrium favours the product formation due to rapid dehydration of the intermediate to form  $>\text{C=N-Z}$ . Z = Alkyl, aryl, OH,  $\text{NH}_2$ ,  $\text{C}_6\text{H}_5\text{NH}$ ,  $\text{NHCONH}_2$ , etc.





**Table 12.2: Some N-Substituted Derivatives of Aldehydes and Ketones (>C=N-Z)**

Z	Reagent name	Carbonyl derivative	Product name
-H	Ammonia	$\text{>C=NH}$	Imine
-R	Amine	$\text{>C=NR}$	Substituted imine (Schiff's base)
-OH	Hydroxylamine	$\text{>C=N-OH}$	Oxime
-NH <sub>2</sub>	Hydrazine	$\text{>C=N-NH}_2$	Hydrazone
-HN- 	Phenylhydrazine	$\text{>C=N-NH-}$ 	Phenylhydrazone
-HN- 	2,4-Dinitrophenylhydrazine	$\text{>C=N-NH-}$ 	2,4 Dinitrophenylhydrazone
-NH- 	Semicarbazide	$\text{>C=N-NH-C(=O)-NH}_2$	Semicarbazone

2,4-DNP-derivatives are yellow, orange or red solids, useful for characterisation of aldehydes and ketones.

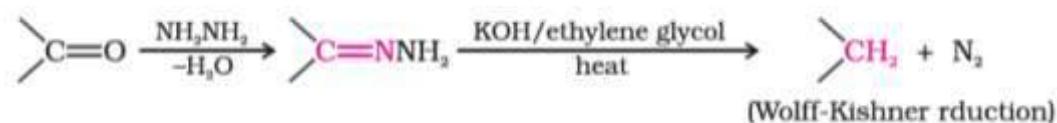
## 2. Reduction:-

**(i) Reduction to alcohols:** Aldehydes and ketones are reduced to primary and secondary alcohols respectively by sodium borohydride (NaBH<sub>4</sub>) or lithium aluminium hydride (LiAlH<sub>4</sub>) as well as by catalytic hydrogenation

**(ii) Reduction to hydrocarbons:** The carbonyl group of aldehydes and ketones is reduced to CH<sub>2</sub> group on treatment with zinc amalgam and concentrated hydrochloric acid [**Clemmensen reduction**]

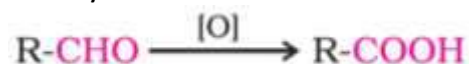


with hydrazine followed by heating with sodium or potassium hydroxide in high boiling solvent such as ethylene glycol (**Wolff-Kishner reduction**).

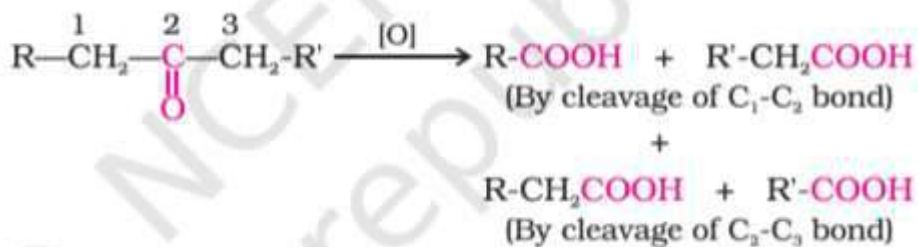


## 3. Oxidation:-

Aldehydes differ from ketones in their oxidation reactions. Aldehydes are easily oxidised to carboxylic acids on treatment with common oxidising agents like nitric acid, potassium permanganate, potassium dichromate, etc. Even mild oxidising agents, mainly Tollens' reagent and Fehlings' reagent also oxidise aldehydes



Ketones are generally oxidised under vigorous conditions, i.e., strong oxidising agents and at elevated temperatures. Their oxidation involves carbon-carbon bond cleavage to afford a mixture of carboxylic acids having lesser number of carbon atoms than the parent ketone.



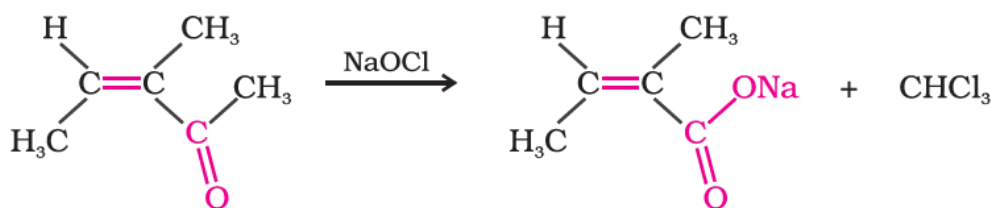
The mild oxidising agents given below are used to distinguish aldehydes from ketones:

**(i) Tollens' test:-** On warming an aldehyde with freshly prepared ammoniacal silver nitrate solution (Tollens' reagent), a bright silver mirror is produced due to the formation of silver metal. The aldehydes are oxidised to corresponding carboxylate anion. The reaction occurs in alkaline medium.



**(ii) Fehling's test:** Fehling reagent comprises of two solutions, Fehling solution A and Fehling solution B. Fehling solution A is aqueous copper sulphate and Fehling solution B is alkaline sodium potassium tartarate (Rochelle salt). These two solutions are mixed in equal amounts before test. On heating an aldehyde with Fehling's reagent, a reddish brown precipitate is obtained. Aldehydes are oxidised to corresponding carboxylate anion. Aromatic aldehydes do not respond to this test.

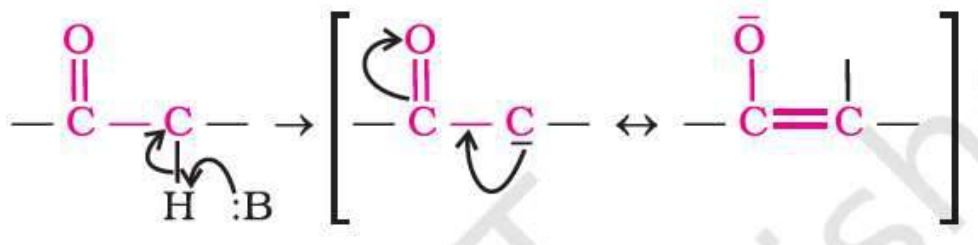
**(iii) Oxidation of methyl ketones by haloform reaction:** Aldehydes and ketones having at least one methyl group linked to the carbonyl carbon atom (methyl ketones) are oxidised by sodium hypohalite to sodium salts of corresponding carboxylic acids having one carbon atom less than that of carbonyl compound. The methyl group is converted to haloform. This oxidation does not affect a carbon-carbon double bond, if present in the molecule. Iodoform reaction with sodium hypoiodite is also used for detection of  $\text{CH}_3\text{CO}$  group or  $\text{CH}_3\text{CH}(\text{OH})$  group which produces  $\text{CH}_3\text{CO}$  group on oxidation.



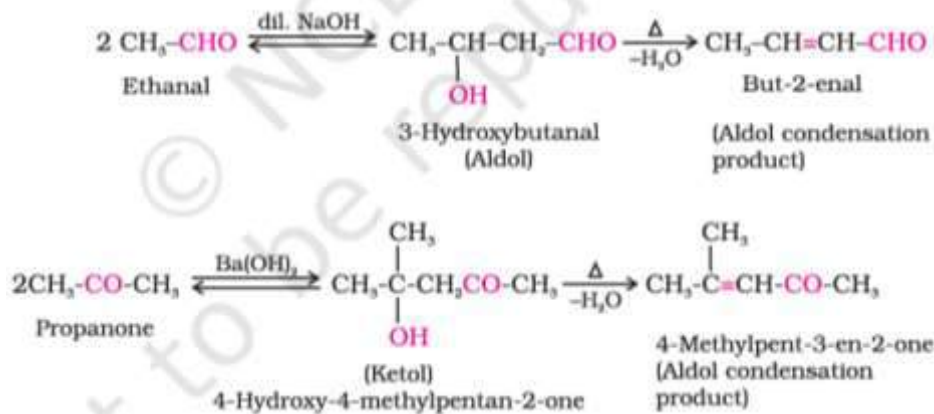
### Reactions due to $\alpha$ -hydrogen:-

**Acidity of  $\alpha$ -hydrogens of aldehydes and ketones:** The aldehydes and ketones undergo a number of reactions due to the acidic nature of  $\alpha$ -hydrogen.

The acidity of  $\alpha$ -hydrogen atoms of carbonyl compounds is due to the strong electron withdrawing effect of the carbonyl group and resonance stabilisation of the conjugate base.

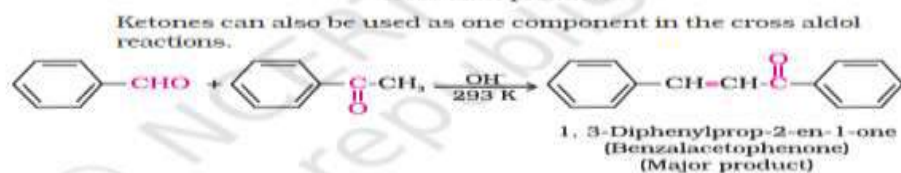
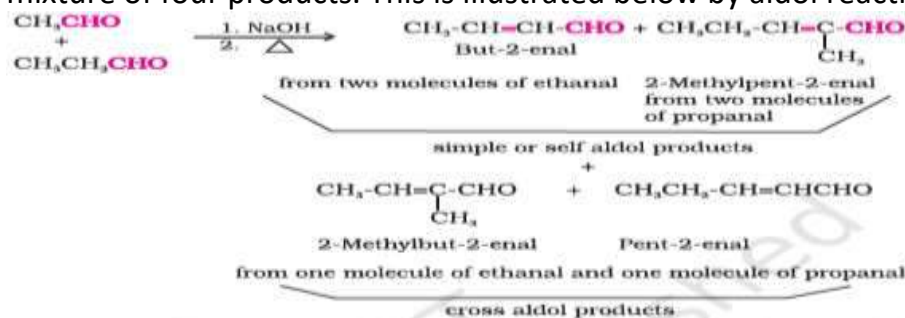


(i) **Aldol condensation:** Aldehydes and ketones having at least one  $\alpha$ -hydrogen undergo a reaction in the presence of dilute alkali as catalyst to form  $\beta$ -hydroxy aldehydes (aldol) or  $\beta$ -hydroxy ketones (ketol), respectively. This is known as **Aldol reaction**.



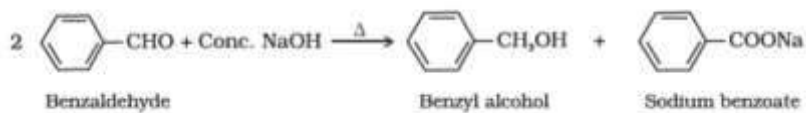
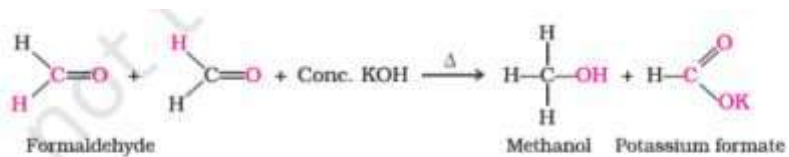
The name aldol is derived from the names of the two functional groups, aldehyde and alcohol, present in the products. The aldol and ketol readily lose water to give  $\alpha,\beta$ -unsaturated carbonyl compounds which are aldol condensation products and the reaction is called **Aldol condensation**. Though ketones give ketols (compounds containing a keto and alcohol groups), the general name aldol condensation still applies to the reactions of ketones due to their similarity with aldehydes.

(ii) **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  $\alpha$ -hydrogen atoms, it gives a mixture of four products. This is illustrated below by aldol reaction of a mixture of ethanal and propanal.

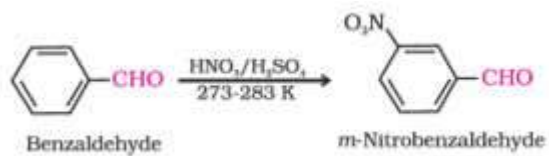


**Other reactions:-**

(i) **Cannizzaro reaction:** Aldehydes which do not have an  $\alpha$ -hydrogen atom, undergo self oxidation and reduction (disproportionation) reaction on heating with concentrated alkali. In this reaction, one molecule of the aldehyde is reduced to alcohol while another is oxidised to carboxylic acid salt.



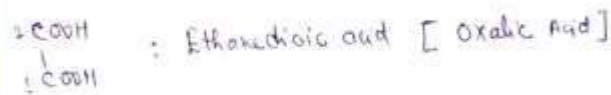
(ii) **Electrophilic substitution reaction:** Aromatic aldehydes and ketones undergo electrophilic substitution at the ring in which the carbonyl group acts as a deactivating and *meta*-directing group.



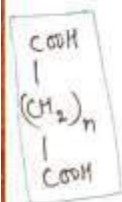


Nomenclature - Alkane - e + oic acid = Alkanoic acid

$\rightarrow$  In numbering the carbon chain, the carboxylic carbon is numbered one.



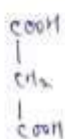
$\rightarrow$  **OMSGAP**



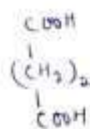
Oxalic Acid (n=0)



Malic Acid (n=1)



Succinic Acid (n=2)



Glutonic Acid (n=3)

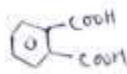
Adipic Acid (n=4)

Pimelic Acid (n=5)

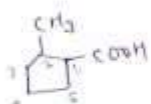
$\rightarrow$  If  $-\overset{\overset{O}{\parallel}}{C}-OH$  group is present on ring then suffix : Carboxylic acid.



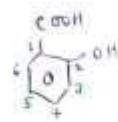
: Benzenecarboxylic acid



: (Phthalic acid) Benzen-1,2-dicarboxylic acid

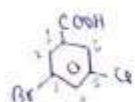


: 2-Methylcyclohexane-1-carboxylic acid



: 3-Hydroxybenzoic acid

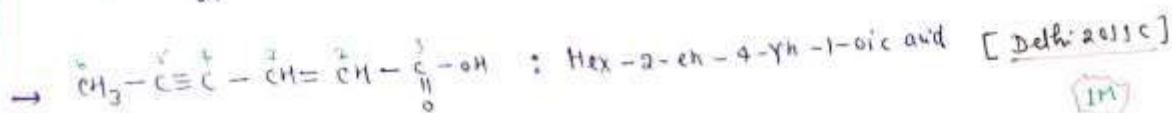
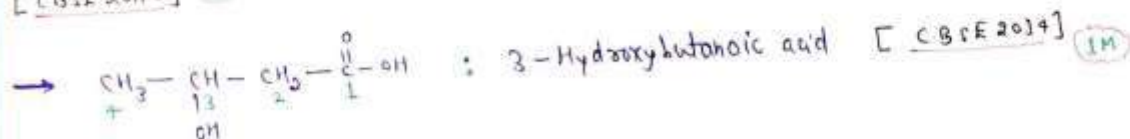
or 2-Hydroxybenzenecarboxylic acid.



: 3-Bromo-5-chlorobenzoic acid

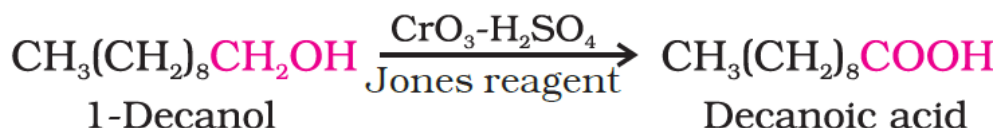
[CBSE 2011C] (IM)

(IM) [Delhi 2019]



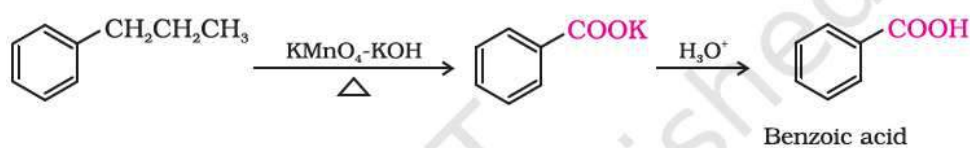
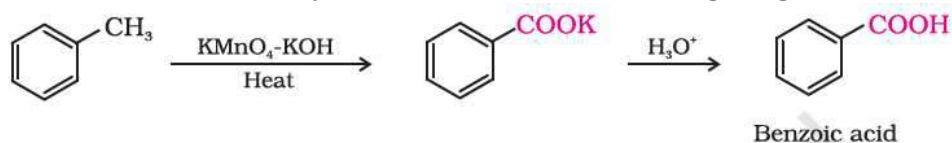
## METHODS OF PREPARATION OF CARBOXYLIC ACIDS :-

**1. From primary alcohols and aldehydes:-** Primary alcohols are readily oxidised to carboxylic acids with common oxidising agents such as potassium permanganate (KMnO<sub>4</sub>) in neutral, acidic or alkaline media or by potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) and chromium trioxide (CrO<sub>3</sub>) in acidic media (Jones reagent).

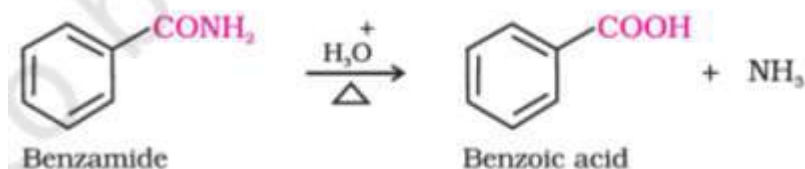
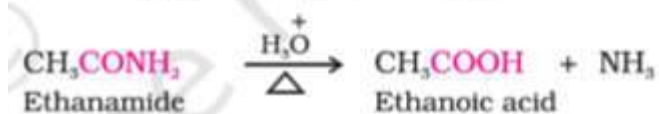


Carboxylic acids are also prepared from aldehydes by the use of mild oxidising agents.

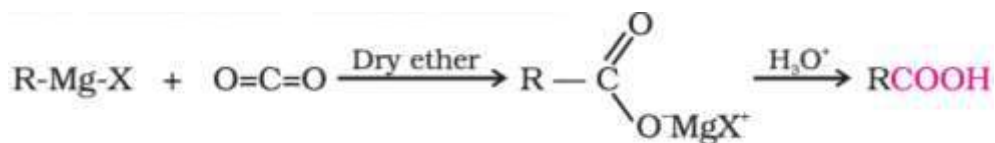
**2. From alkylbenzenes:-** Aromatic carboxylic acids can be prepared by vigorous oxidation of alkyl benzenes with chromic acid or acidic or alkaline potassium permanganate. The entire side chain is oxidised to the carboxyl group irrespective of length of the side chain. Primary and secondary alkyl groups are oxidised in this manner while tertiary group is not affected. Suitably substituted alkenes are also oxidised to carboxylic acids with these oxidising reagents



**3. From nitriles and amides:-** Nitriles are hydrolysed to amides and then to acids in the presence of H<sup>+</sup> or OH<sup>-</sup> as catalyst. Mild reaction conditions are used to stop the reaction at the amide stage.

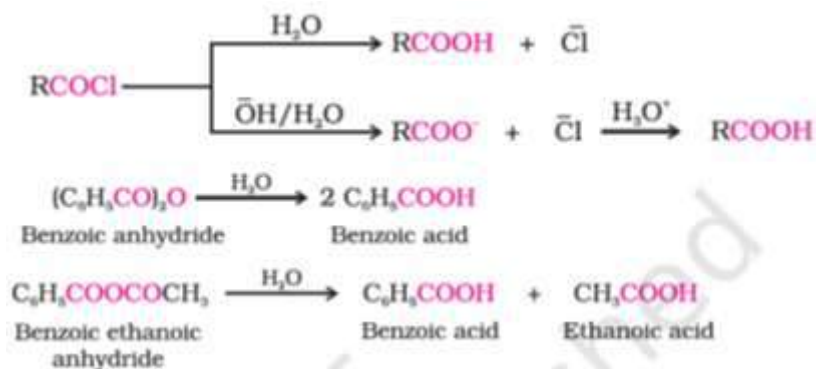


**4. From Grignard reagents :-** Grignard reagents react with carbon dioxide (dry ice) to form salts of carboxylic acids which in turn give corresponding carboxylic acids after acidification with mineral acid.



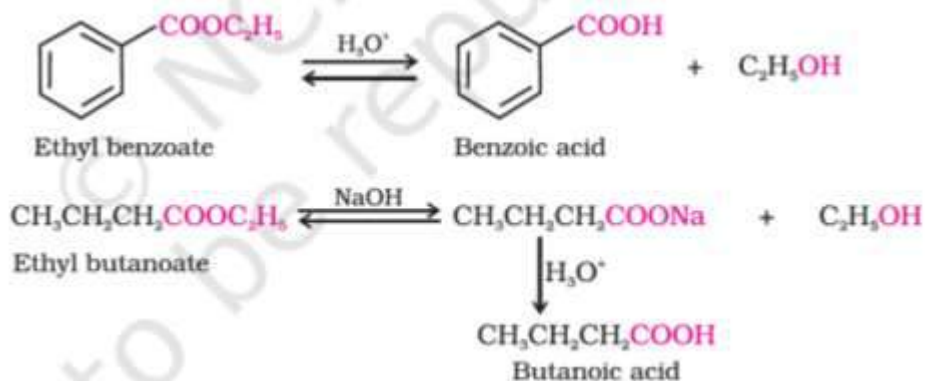
As we know, the Grignard reagents and nitriles can be prepared from alkyl halides. The above methods (3 and 4) are useful for converting alkyl halides into corresponding carboxylic acids having one carbon atom more than that present in alkyl halides (ascending the series).

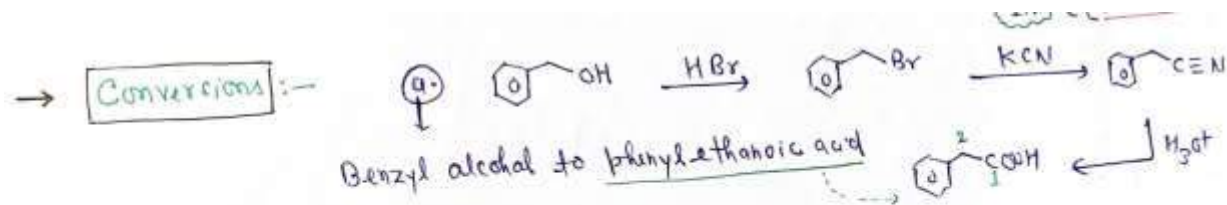
**5. From acyl halides and anhydrides:-** Acid chlorides when hydrolysed with water give carboxylic acids or more readily hydrolysed with aqueous base to give carboxylate ions which on acidification provide corresponding carboxylic acids. Anhydrides on the other hand are hydrolysed to corresponding acid(s) with water.



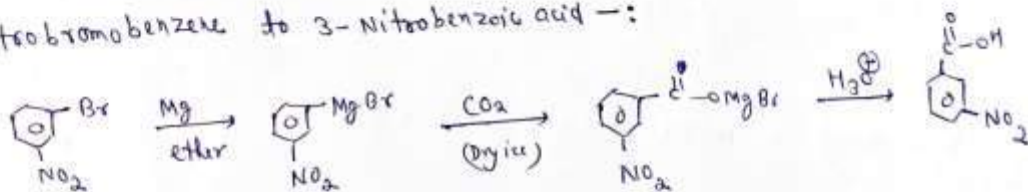
### 6. From esters

Acidic hydrolysis of esters gives directly carboxylic acids while basic hydrolysis gives carboxylates, which on acidification give corresponding carboxylic acids



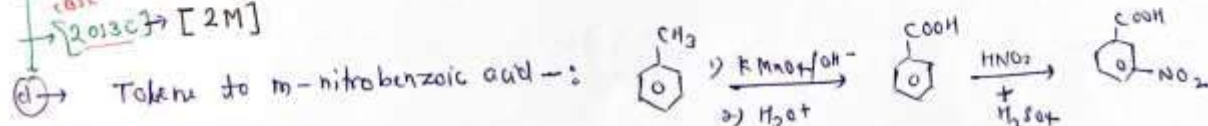


(b) 3-Nitrobromobenzene to 3-Nitrobenzoic acid :-

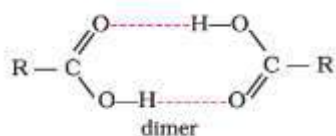


(c) Acetylene to acetic acid :- H-C#C-H  $\xrightarrow[Hg^{2+}]{dil\ H_2SO_4}$  CH\_3-C(=O)-H  $\xrightarrow[H_2SO_4]{K_2Cr_2O_7}$  CH\_3-C(=O)OH

case  
2013C [2M]

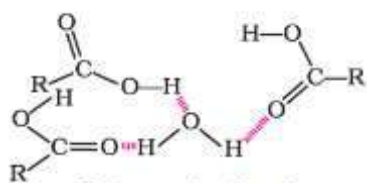


**PHYSICAL PROPERTIES**:- Aliphatic carboxylic acids upto nine carbon atoms are colourless liquids at room temperature with unpleasant odours. The higher acids are wax like solids and are practically odourless due to their low volatility. Carboxylic acids are higher boiling liquids than aldehydes, ketones and even alcohols of comparable molecular masses. This is due to more extensive association of carboxylic acid molecules through intermolecular hydrogen bonding. The hydrogen bonds are not broken completely even in the vapour phase. In fact, most carboxylic acids exist as dimer in the vapour phase or in the aprotic solvents.



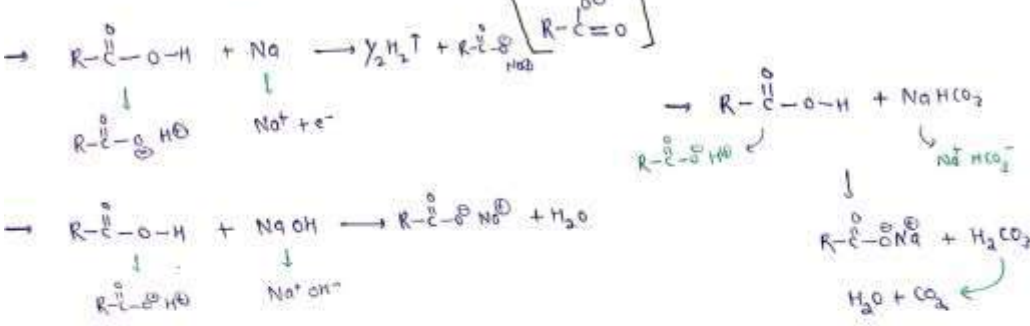
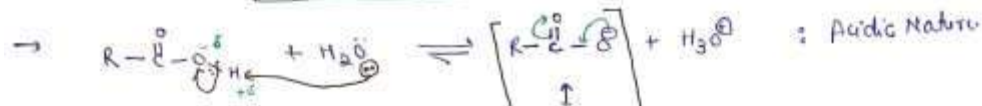
In vapour state or in aprotic solvent

Simple aliphatic carboxylic acids having upto four carbon atoms are miscible in water due to the formation of hydrogen bonds with water. The solubility decreases with increasing number of carbon atoms. Higher carboxylic acids are practically insoluble in water due to the increased hydrophobic interaction of hydrocarbon part. Benzoic acid, the simplest aromatic carboxylic acid is nearly insoluble in cold water. Carboxylic acids are also soluble in less polar organic solvents like benzene, ether, alcohol, chloro form, etc.

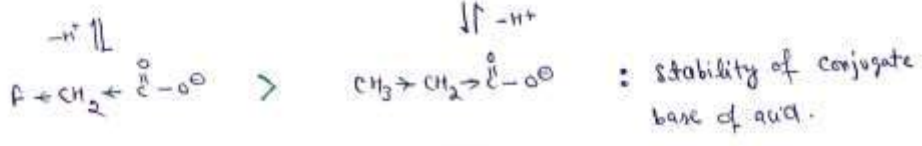
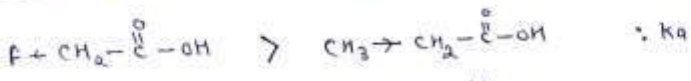
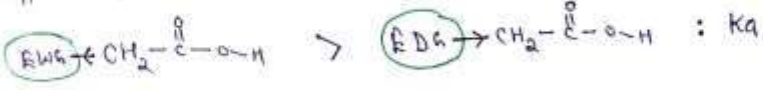




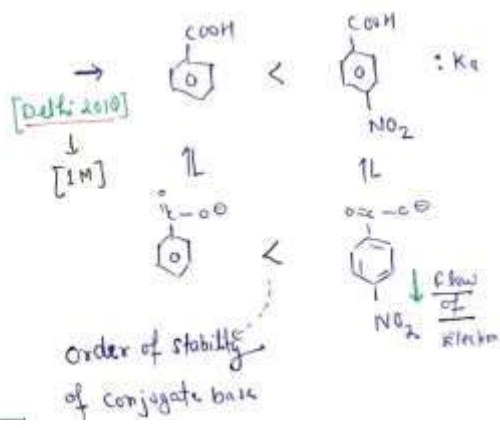
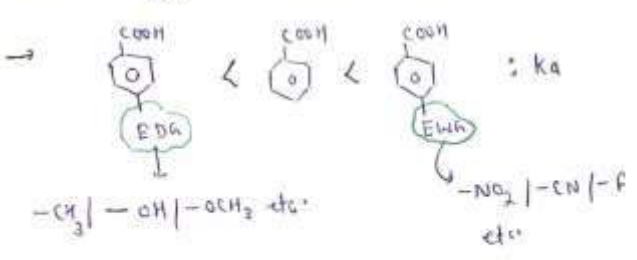
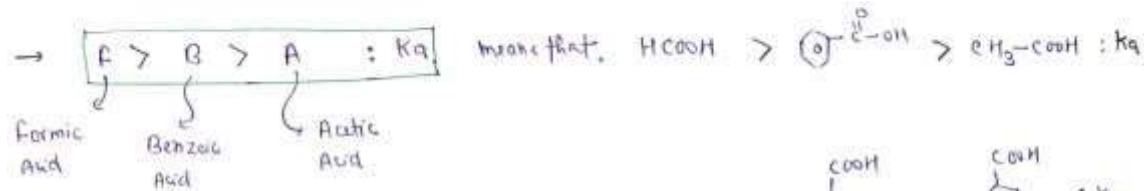
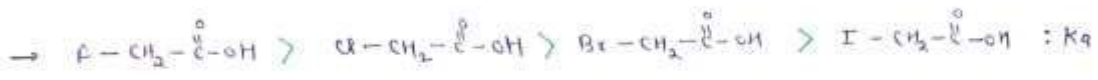
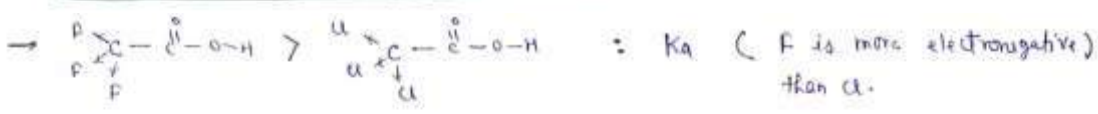
# Acidic Nature of Carboxylic Acid



→ Effect of substituents on acidity of carboxylic acids :-



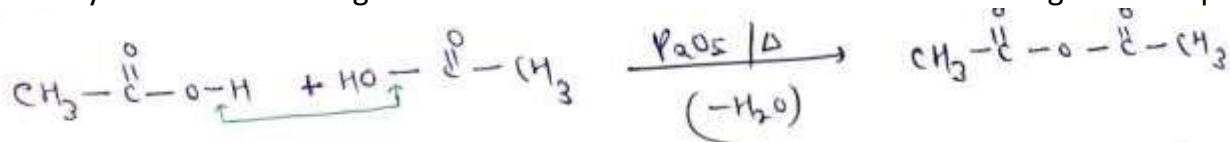
## ⇒ Acidity ( $K_a$ ) & Stability of conjugate base



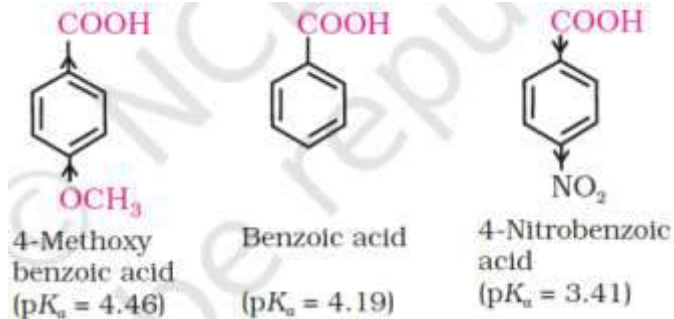
## Reactions Involving Cleavage of O–H Bond

### 1. Formation of anhydride:-

Carboxylic acids on heating with mineral acids such as H<sub>2</sub>SO<sub>4</sub> or with P<sub>2</sub>O<sub>5</sub> give corresponding anhydride.

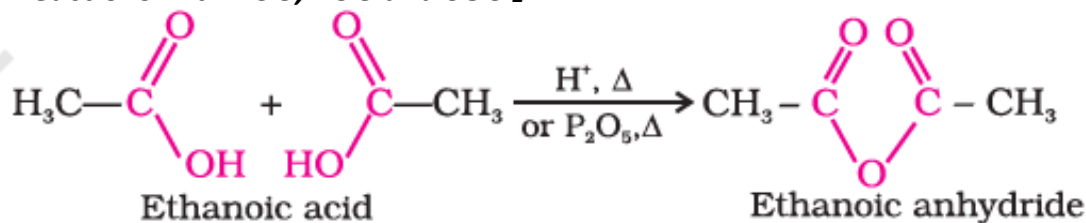


### 2. Esterification:-

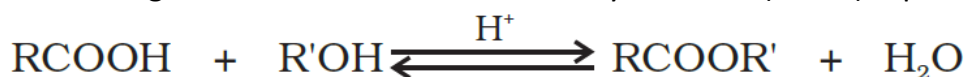


Carboxylic acids are esterified with alcohols or phenols in the presence of a mineral acid such as concentrated H<sub>2</sub>SO<sub>4</sub> or HCl gas as a catalyst.

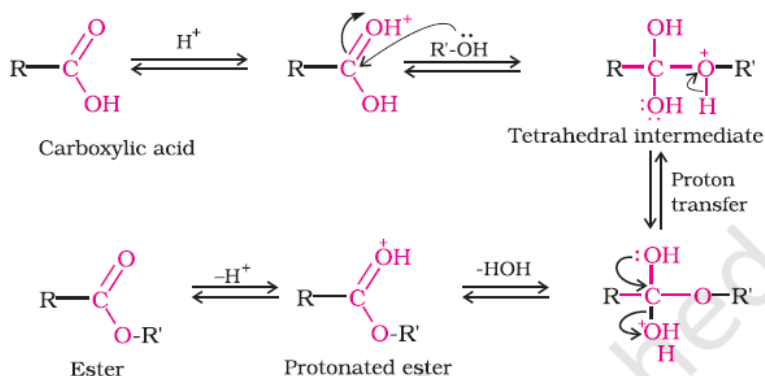
### 3. Reactions with PCl<sub>5</sub>, PCl<sub>3</sub> and SOCl<sub>2</sub>:-



The hydroxyl group of carboxylic acids, behaves like that of alcohols and is easily replaced by chlorine atom on treating with PCl<sub>5</sub>, PCl<sub>3</sub> or SOCl<sub>2</sub>. Thionyl chloride (SOCl<sub>2</sub>) is preferred because the other two.



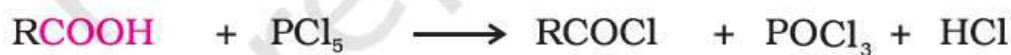
**Mechanism of esterification of carboxylic acids:** The esterification of carboxylic acids with alcohols is a kind of nucleophilic acyl substitution. Protonation of the carbonyl oxygen activates the carbonyl group towards nucleophilic addition of the alcohol. Proton transfer in the tetrahedral intermediate converts the hydroxyl group into <sup>-</sup>OH<sub>2</sub> group, which, being a better leaving group, is eliminated as neutral water molecule. The protonated ester so formed finally loses a proton to give the ester.



products are gaseous and escape the reaction mixture making the purification of the products easier.

#### 4. Reaction with ammonia:-

Carboxylic acids react with ammonia to give ammonium salt which on further heating at high temperature give amides. For example:



Reactions involving  $-\overset{\ominus}{\text{C}}-\text{OH}$  group

#### 1. Reduction

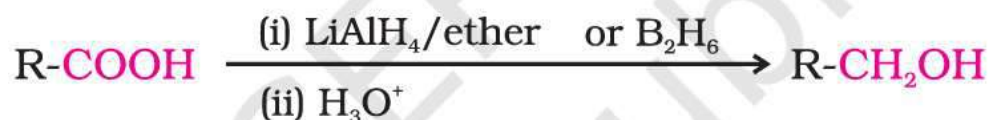
Carboxylic acids are reduced to primary alcohols by lithium aluminium hydride or better with diborane. Diborane does not easily



reduce functional groups such as ester, nitro, halo, etc. Sodium borohydride does not reduce the carboxyl group.

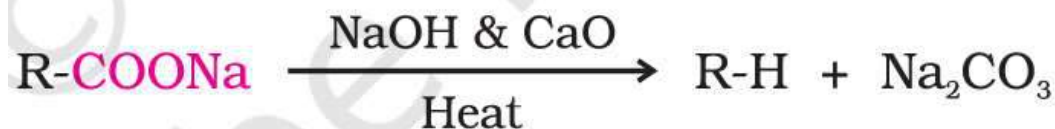
#### 2. Decarboxylation:-

Carboxylic acids lose carbon dioxide to form hydrocarbons when their



sodium salts are heated with sodalime (NaOH and CaO in the ratio of 3 : 1). The reaction is known as decarboxylation.

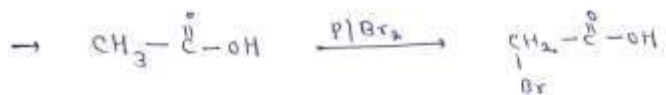
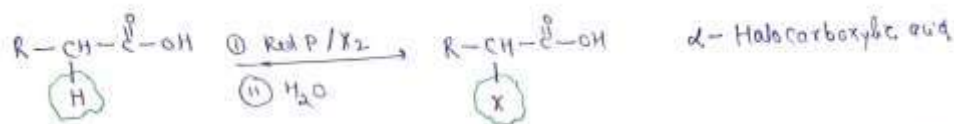
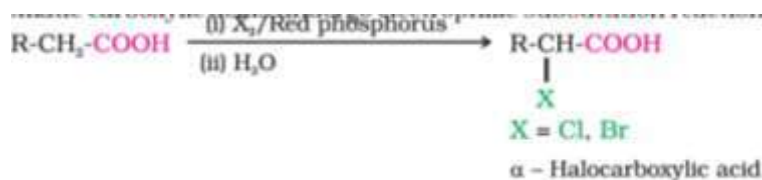
Alkali metal salts of carboxylic acids also undergo decarboxylation on electrolysis of their aqueous solutions and form hydrocarbons having



twice the number of carbon atoms present in the alkyl group of the acid. The reaction is known as **Kolbe electrolysis**

**Reaction on hydrocarbon:-**

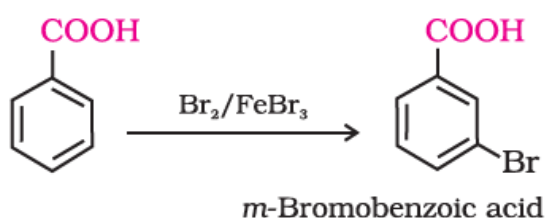
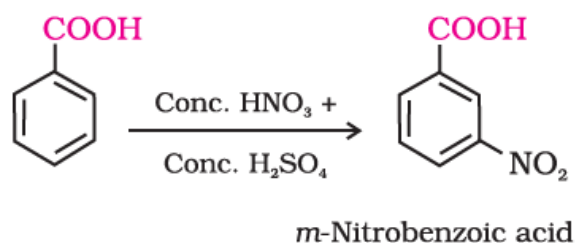
- Halogenation:-** Carboxylic acids having an  $\alpha$ -hydrogen are halogenated at the  $\alpha$ -position on treatment with chlorine or bromine in the presence of small amount of red phosphorus to give  $\alpha$ -halocarboxylic acids. The reaction is known as **Hell-Volhard-Zelinsky reaction**.



[Delhi 2014] → [1M]  
[Delhi 2013] → [1M]  
[CBSE 2016] → [1M]

## 2. Ring substitution

Aromatic carboxylic acids undergo electrophilic substitution reactions in which the carboxyl group acts as a deactivating and meta-directing group. They however, do not undergo **Friedel-Crafts reaction** (because the carboxyl group is deactivating and the catalyst aluminium chloride (Lewis acid) gets bonded to the carboxyl group). Methanoic acid is used in rubber, textile, dyeing, leather and electroplating industries. Ethanoic acid is used as solvent and as vinegar in food industry



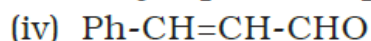
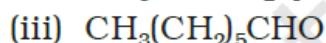
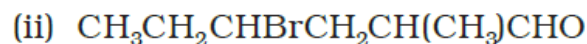
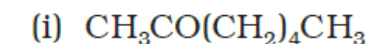
## IMPORTANT QUESTIONS FOR TERM -2

### A. Write the structures of the following organic compound

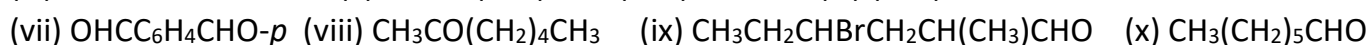
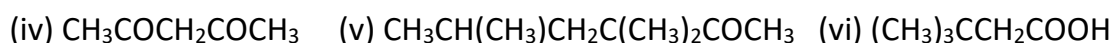
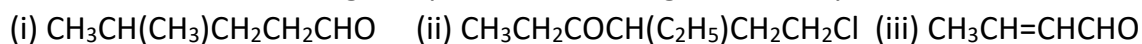
1. Methanal
2. Ethanal
3. 2-Methylpropanal
4. 3-Methylcyclohexanecarbaldehyde
5. 2-Methoxypropanal
6. 3-Bromobenzaldehyde
7. Pentan-2-one
8. 2,4-Dimethylpentan-3-one
9. 2-Methylcyclohexanone
10. 4-Methylpent-3-en-2-one
11. 3-Hydroxybutanal
12. 2-Hydroxycyclopentane carbaldehyde
13. 4-Oxopentanal
14. Di-sec. butyl ketone
15. 4-Fluoroacetophenone

16. 3-Phenylpropanoic acid
17. 3-Methylbut-2-enoic acid
18. 3-Methylbutanal
19. *p*-Nitropropiophenone
20. *p*-Methylbenzaldehyde
21. 4-Methylpent-3-en-2-one
22. 4-Chloropentan-2-one
23. 3-Bromo-4-phenylpentanoic acid
24. Hex-2-en-4-ynoic acid

**A-2 .** Write The IUPAC names of the following ketones and Aldehydes.



**A-3 .** Name the following compounds according to IUPAC system of nomenclature:



**B. ACCOUNT FOR THE FOLLOWING:**

1. Aldehydes and Ketones have lower boiling point than alcohols.
2. Aldehydes are more reactive than Ketones towards Nucleophilic addition reaction
3. Cyclohexanone forms cyanohydrin in good yield but 2,2,6 – tri methylcyclohexanone does not.
4. There are two –  $\text{NH}_2$  group in semi carbazide however only one is involved in the formation of semi carbazones.
5. During the preparation of esters from a carboxylic acid and an alcohol in the presence of an acid catalyst, the water or the ester should be removed as fast as it is formed.
6. Melting Point of an acid with even number of carbon atoms higher than those of its neighbours with odd number of carbon atoms
7. It is necessary to control the pH during the reaction of aldehydes and ketones with ammonia derivatives.
8. Formaldehyde does not take part in Aldol condensation.
9. Benzaldehyde gives a positive test with Tollens reagent but not with Fehling and Benedict's solution.
10. Carboxylic acids do not give the characteristic reactions of carbonyl group.
11. Chloroacetic acid is stronger than acetic acid.
12. The boiling points of aldehydes and ketones are higher than hydrocarbons and ethers of comparable molecular masses.
13. The lower members of aldehydes and ketones such as methanal, ethanal and propanone are miscible with water in all proportions.
14. Would you expect benzaldehyde to be more reactive or less reactive in nucleophilic addition reactions than propanal.
15. Carboxylic acids are higher boiling liquids than aldehydes, ketones and even alcohols of comparable molecular masses.
16. Aliphatic carboxylic acids having upto four carbon atoms are miscible in water.

17. Carboxylic acids are more acidic than phenols.
18. Although phenoxide ion has more number of resonating structures than carboxylate ion, carboxylic acid is a stronger acid than phenol.
19. Electron withdrawing groups increase the acidity of carboxylic acids.
20. Electron donating groups decrease the acidity of carboxylic acids.
21. Arrange the following compounds in increasing order of acid strength. (i)  $\text{CH}_3\text{CH}_2\text{CH}(\text{Br})\text{COOH}$ ,  $\text{CH}_3\text{CH}(\text{Br})\text{CH}_2\text{COOH}$ ,  $(\text{CH}_3)_2\text{CHCOOH}$ ,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$  (ii) Benzoic acid, 4-Nitrobenzoic acid, 3,4-Dinitrobenzoic acid, 4-Methoxybenzoic acid (acid strength)
22. Which acid of each pair shown here would you expect to be stronger? (i)  $\text{CH}_3\text{CO}_2\text{H}$  or  $\text{CH}_2\text{FCO}_2\text{H}$  (ii)  $\text{CH}_2\text{FCO}_2\text{H}$  or  $\text{CH}_2\text{ClCO}_2\text{H}$  (iii)  $\text{CH}_2\text{FCH}_2\text{CH}_2\text{CO}_2\text{H}$  or  $\text{CH}_3\text{CHFCH}_2\text{CO}_2\text{H}$ .

### C. MECHANISM BASED QUESTIONS

1. Give mechanism for Nucleophilic addition reaction in carbonyl compounds.
2. Write the mechanism of reaction between acetaldehyde and HCN.
3. Arrange the following compounds in increasing order of their reactivity in nucleophilic addition reactions. with reasons
  - (i) Ethanal, Propanal, Propanone, Butanone.
  - (ii) Benzaldehyde, *p*-Tolualdehyde, *p*-Nitrobenzaldehyde, Acetophenone.
  - (iii) Acetaldehyde, Acetone, Di-*tert*-butyl ketone, Methyl *tert*-butyl ketone

### D. Give a CHEMICAL TEST to distinguish between following pair of organic compounds

1. Propanal and Propanone
2. Acetophenone and Benzophenone
3. Phenol and Benzoic acid
4. Benzoic acid and Ethyl benzoate
5. Pentan-2-one and Pentan-3-one
6. Benzaldehyde and Acetophenone
7. Ethanal and Propanal
8. Benzaldehyde & Propanal
9. Acetone and Acetaldehyde
10.  $\text{CH}_3\text{CHO}$  &  $\text{CH}_3\text{COCH}_3$
11.  $\text{C}_6\text{H}_5\text{CHO}$  &  $\text{CH}_3\text{CHO}$
12. Acetaldehyde and Benzaldehyde
13. Ethanoic acid and Ethnoyl chloride
14. Methanoic acid and Ethanoic acid
15. Formic acid and Acetic acid

### E. Write short notes on following :

1. Aldol Condensation
2. Cross Aldol Condensation
3. Cannizzaro Reaction
4. Clemmensen Reaction
5. Wolf Kishner Reaction
6. Rosenmund Reaction
7. Etard Reaction
8. Stephen Reaction
9. Gatterman-Koch reaction:
10. Ozonolysis

11. Esterification
12. Decarboxylation
13. Hell Volhard Zelinsky
14. Acetylation

#### F. WORD PROBLEMS REACTION BASED

- G. An organic compound A with molecular formula  $C_8H_{16}O_2$  was hydrolysed with sulphuric acid to give a carboxylic acid B and alcohol C. Oxidation of C with chromic acid produced B. C on dehydration gives but-1-ene. Write reactions involved.
- H. An organic compound A which has a characteristic odour on treatment with NaOH forms two compounds B and C. Compound B has a molecular formula  $C_7H_8O$  which on oxidation gives back compound A. Compound C is sodium salt of acid. C when heated with sodalime yields an aromatic hydrocarbon D. Deduce structures A-D.
- I. A compound 'X' ( $C_2H_4O$ ) on oxidation gives 'Y' ( $C_2H_4O_2$ ). 'X' undergoes haloform reaction. On treatment with HCN 'X' forms a product 'Z' which on hydrolysis gives 2-hydroxy propanoic acid. (i) Write down structures of 'X' and 'Y'. (ii) Name the product when 'X' reacts with dil NaOH. (iii) Write down the equations for the reactions involved.
- J. An organic compound (A) with molecular formula  $C_8H_8O$  forms an orange-red precipitate with 2,4-DNP reagent and gives yellow precipitate on heating with iodine in the presence of sodium hydroxide. It neither reduces Tollens' or Fehlings' reagent, nor does it decolourise bromine water or Baeyer's reagent. On drastic oxidation with chromic acid, it gives a carboxylic acid (B) having molecular formula  $C_7H_6O_2$ . Identify the compounds A and B and explain the reactions involved.
- K. An organic compound with the molecular formula  $C_9H_{10}O$  forms 2,4-DNP derivative, reduces Tollens' reagent and undergoes Cannizzaro reaction. On vigorous oxidation, it gives 1,2-benzenedicarboxylic acid. Identify the compound.

#### L. Write the reactions and the conditions involved in the conversion of:

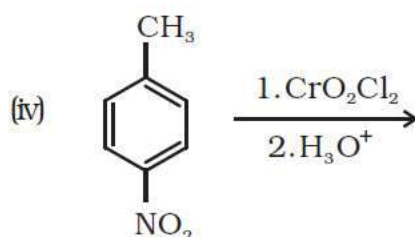
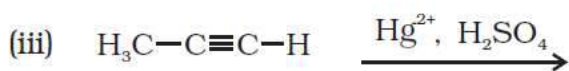
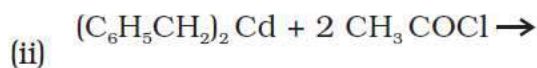
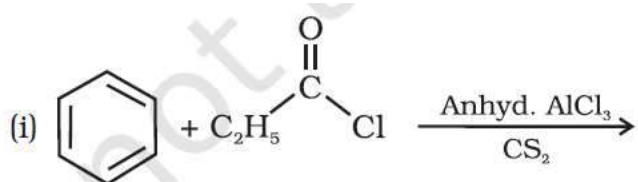
1. Ethanal to 3-Hydroxybutanal
2. Ethanal to But-2-enal
3. Benzaldehyde to Toluene
4. Propanal to Propane
5. Acetone to Propane
6. Benzoyl chloride to Benzaldehyde
7. Acetyl chloride to Acetaldehyde
8. Toluene to Benzaldehyde
9. Ethanol to Ethanal
10. Benzyl chloride to benzyl alcohol
11. Benzyl alcohol to benzoic acid
12. Acetophenone to 2-Phenyl -butan-2-ol
13. Butan-2-one to butan-2-ol
14. Ethanal to Butane-1,3-diol
15. Ethanal to But-2-enoic acid
16. Benzoic acid to Benzaldehyde

17. Ethanol to 3-Hydroxybutanal
18. Benzene to m-Nitroacetophenone
19. Benzaldehyde to Benzophenone

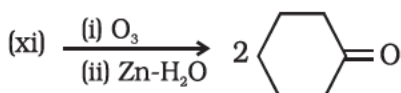
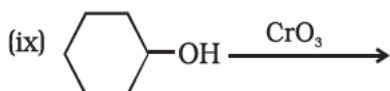
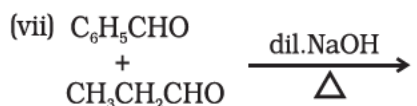
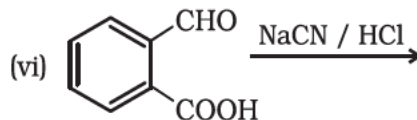
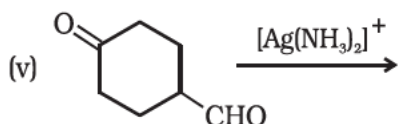
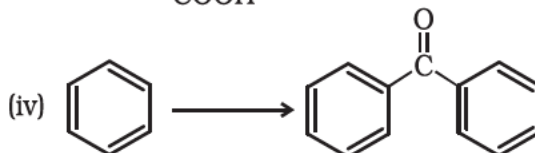
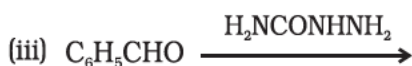
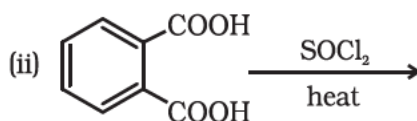
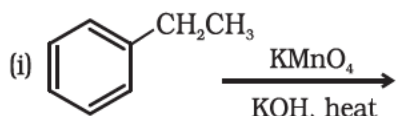
**M. Complete the Following reactions:**

1. Predict the products formed when cyclohexanecarbaldehyde reacts with following reagents. (i) PhMgBr and then  $H_3O^+$  (ii) Tollens' reagent (iii) Semicarbazide and weak acid (iv) Excess ethanol and acid (v) Zinc amalgam and dilute hydrochloric acid

2. Write the structures of products of the following reactions

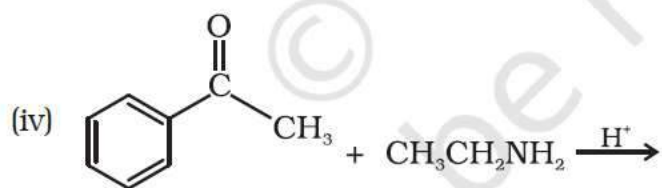
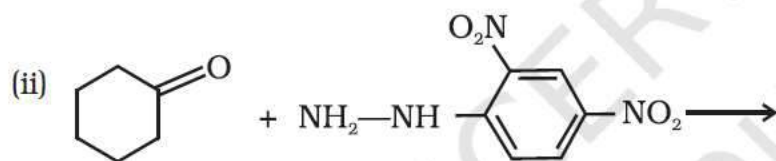
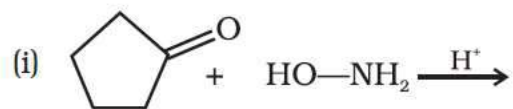


3. Complete each synthesis by giving missing starting material, reagent or products





4. Predict the products of the following reactions:

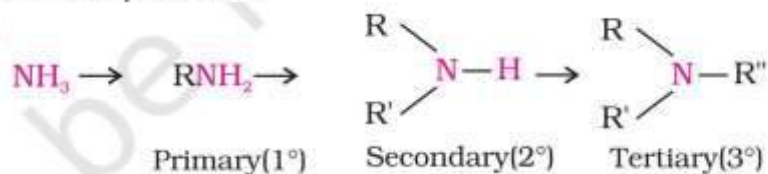


# AMINES

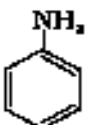
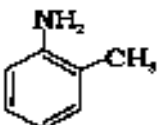
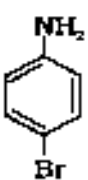
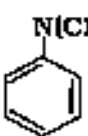
## I .IUPAC Nomenclature Based

Formula	IUPAC Name	Suffix	Prefix
R - NH <sub>2</sub>	Alkanamine	amine	amino

## Classification



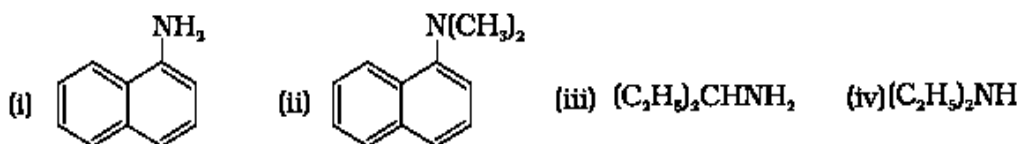
## Common and IUPAC Names of Some Amines

Amine	Common name	IUPAC name
$\text{CH}_3-\text{CH}_2-\text{NH}_2$	Ethylamine	Ethanamine
$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{NH}_2$	<i>n</i> -Propylamine	Propan-1-amine
$\begin{array}{c} \text{CH}_3-\text{CH}-\text{CH}_3 \\   \\ \text{NH}_2 \end{array}$	Isopropylamine	Propan-2-amine
$\begin{array}{c} \text{CH}_3-\text{N}-\text{CH}_2-\text{CH}_3 \\   \\ \text{H} \end{array}$	Ethylmethanamine	<i>N</i> -Methylethanamine
$\begin{array}{c} \text{CH}_3-\text{N}-\text{CH}_3 \\   \\ \text{CH}_3 \end{array}$	Trimethanamine	<i>N,N</i> -Dimethylmethanamine
$\begin{array}{c} \text{C}_2\text{H}_5-\text{N}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3 \\   \\ \text{C}_2\text{H}_5 \end{array}$	<i>N,N</i> -Diethylbutylamine	<i>N,N</i> -Diethylbutan-1-amine
$\text{NH}_2-\text{CH}_2-\text{CH}=\text{CH}_2$	Allylamine	Prop-2-en-1-amine
$\text{NH}_2-(\text{CH}_2)_6-\text{NH}_2$	Hexamethylenediamine	Hexane-1,6-diamine
	Aniline	Aniline or Benzenamine
	<i>o</i> -Toluidine	2-Aminotoluene
	<i>p</i> -Bromoaniline	4-Bromobenzenamine or 4-Bromoaniline
	<i>N,N</i> -Dimethylaniline	<i>N,N</i> -Dimethylbenzenamine

Answer the following

- Write IUPAC names of the following compounds and classify them into primary, secondary and tertiary amines. (i)  $(\text{CH}_3)_2\text{CHNH}_2$  (ii)  $\text{CH}_3(\text{CH}_2)_2\text{NH}_2$  (iii)  $\text{CH}_3\text{NHCH}(\text{CH}_3)_2$  (iv)  $(\text{CH}_3)_3\text{CNH}_2$  (v)  $\text{C}_6\text{H}_5\text{NHCH}_3$  (vi)  $(\text{CH}_3\text{CH}_2)_2\text{NCH}_3$  (vii)  $m\text{-BrC}_6\text{H}_4\text{NH}_2$

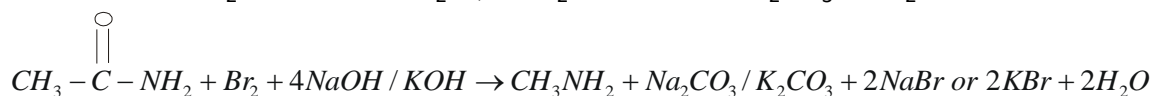
- Classify the following amines as primary, secondary or tertiary:



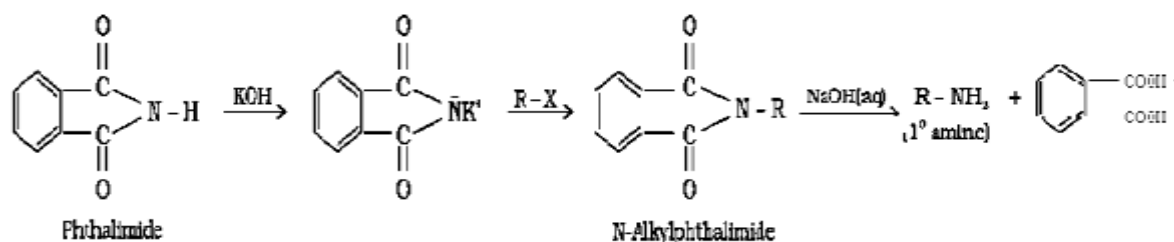
- Write structures of different isomeric amines corresponding to the molecular formula,  $\text{C}_4\text{H}_{11}\text{N}$ .

## II . NAME REACTIONS Based

- Hoffmann bromamide degradation reaction:** When primary amides are treated with bromine in the presence of an alkali, a primary amine containing one carbon less than the amide is formed.

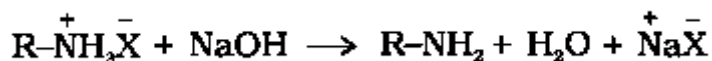
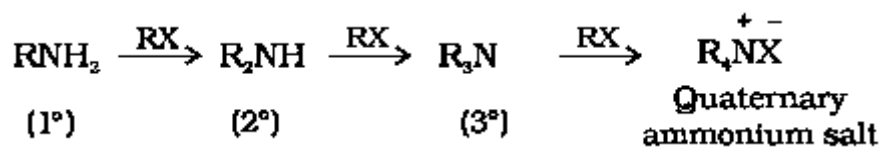


- Gabriel phthalimide synthesis:** Phthalimide on treatment with ethanolic potassium hydroxide forms potassium salt of phthalimide which on heating with alkyl halide followed by alkaline hydrolysis produces the corresponding primary amine.



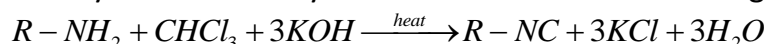
**Note** Aromatic primary amines cannot be prepared by this method because aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide.

- Ammonolysis:** An alkyl or benzyl halide on reaction with an ethanolic solution of ammonia undergoes nucleophilic substitution reaction in which the halogen atom is replaced by an amino ( $-\text{NH}_2$ ) group. This process of cleavage of the  $\text{C-X}$  bond by ammonia molecule is known as **ammonolysis**. The reaction is carried out in a sealed tube at 373 K. The primary amine thus obtained behaves as a nucleophile and can further react with alkyl halide to form secondary and tertiary amines, and finally quaternary ammonium salt.



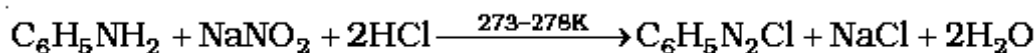
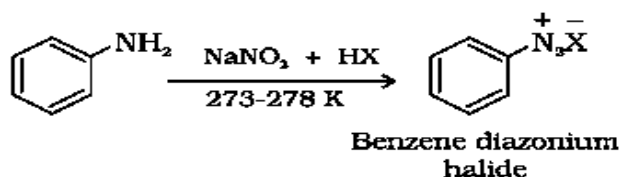
**Note:** Ammonolysis has the disadvantage of yielding a mixture of primary, secondary and tertiary amines and also a quaternary ammonium salt. However, primary amine is obtained as a major product by taking large excess of ammonia.

4. **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.

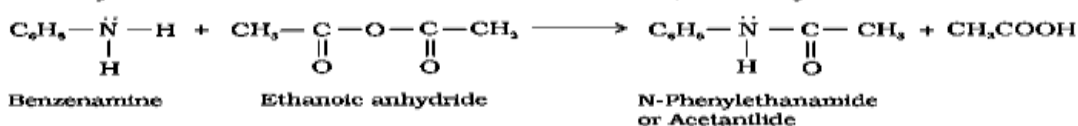
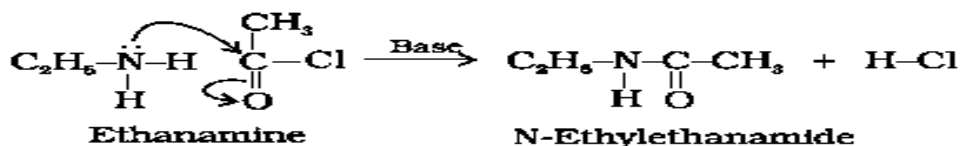


**Note:** Secondary and tertiary amines do not show this reaction. It is used as a test for primary amines

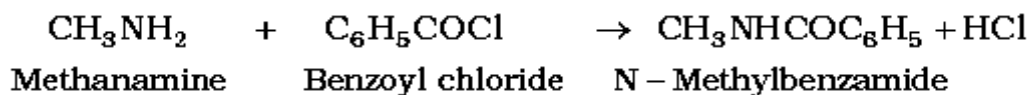
5. **Diazotization :** The reaction of aniline with nitrous acid at 273-278K. Nitrous acid is produced in the reaction mixture by the reaction of sodium nitrite with hydrochloric acid. The conversion of primary aromatic amines into diazonium salts is known as diazotisation.



6. **Acylation:** (Replacement of hydrogen atom of  $-\text{NH}_2$  or  $>\text{N}-\text{H}$  group by the acyl group.) Aliphatic and aromatic primary and secondary amines react with acid chlorides, anhydrides and esters by nucleophilic substitution reaction. This reaction is known as acylation. The products obtained by acylation reaction are known as amides.



7. **Benzoylation:** Amines reacts with benzoyl chloride ( $\text{C}_6\text{H}_5\text{COCl}$ ) to form N Alkylbenzamide



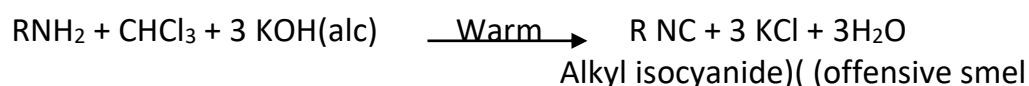
Answer the following

1. Convert: Aniline to phenylisocyanide
2. Why cannot aromatic primary amines be prepared by Gabriel phthalimide synthesis?
3. Complete the following reaction: (i)  $\text{C}_6\text{H}_5\text{NH}_2 + \text{CHCl}_3 + \text{alc.KOH} \rightarrow$
4. Write short notes on the following: (i) Carbylamine reaction (ii) Diazotisation (iii) Hofmann's bromamide reaction (iv) Coupling reaction (v) Ammonolysis (vi) Acetylation (vii) Gabriel phthalimide synthesis.
5. Write structures and IUPAC names of (i) the amide which gives propanamine by Hoffmann bromamide reaction. (ii) the amine produced by the Hoffmann degradation of benzamide.

### III . Chemical Test

#### 1. Isocyanide test (Carbylamine reaction)

- **Primary Aliphatic (e.g.Ethanamine) & Aromatic amines(e.g.Aniline) give this test.**
- **Reagent:** Chloroform( $\text{CHCl}_3$ ) + Alcoholic KOH
- **Test:** Aliphatic and aromatic primary amines on heating with chloroform and ethanolic potassium hydroxide form isocyanides or carbylamines which are foul smelling substances. (Unpleasant odour)
- **Reaction:**



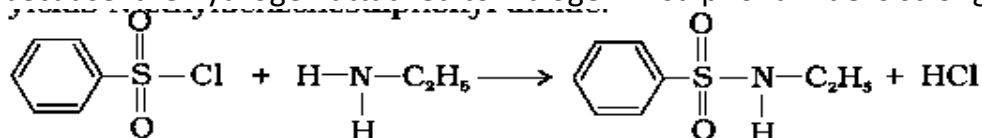
- **Important note:** Secondary and tertiary amines do not give this test.

#### 2. Heinsberg test

- **To distinguish between** Primary ( $1^\circ$ ), Secondary ( $2^\circ$ ), & Tertiary ( $3^\circ$ ) Amines.

- **Reagent:** Benzenesulphonyl chloride  $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$  Heinsberg reagent

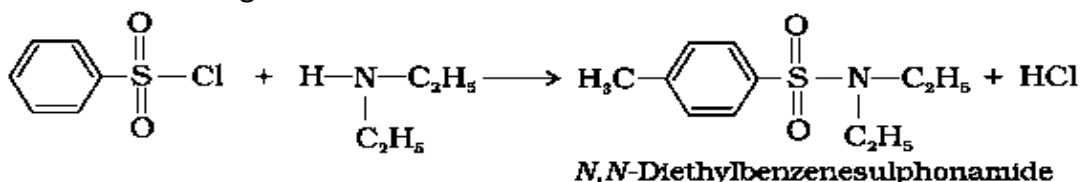
**Test:(i) Primary amine** reacts with benzenesulphonyl chloride (Heinsberg reagent) to give N-Ethylbenzenesulphonyl amide which is soluble in alkali because the hydrogen attached to nitrogen in sulphonamide is strongly acidic.



**N-Ethylbenzenesulphonamide**  
(soluble in alkali)

**(ii) Secondary amine** reacts with benzenesulphonyl chloride (Heinsberg reagent) to give N,N-diethylbenzenesulphonamide which is insoluble in alkali

Since N, N-diethylbenzene sulphonamide does not contain any hydrogen atom attached to nitrogen atom.

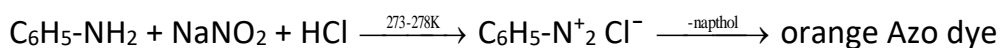


(iii) Tertiary amines do not react with benzenesulphonyl chloride.

**Important note:** Now day's benzenesulphonyl chloride is replaced by *p*-toluenesulphonyl chloride.

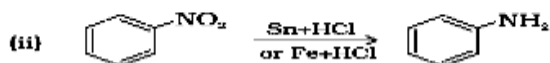
### 3. Azo dye test

- **Aniline & its derivative give this test.**
- **Reagent:** (NaNO<sub>2</sub> + HCl) [Nitrous acid] followed by β-naphthol
- **Test:** Aniline on reaction with NaNO<sub>2</sub> + HCl at 273-278 K gives BDC which forms a brilliant orange dye with β-naphthol in sodium hydroxide.
- **Reaction:**



## IV . IMPORTANT REACTIONS

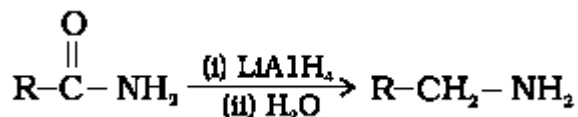
### 1. Reduction of nitro compounds



### 2. Reduction of nitriles

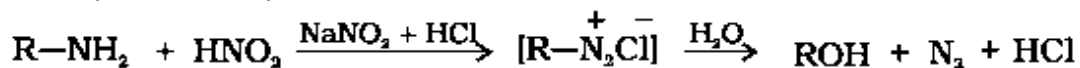


### 3. Reduction of amides

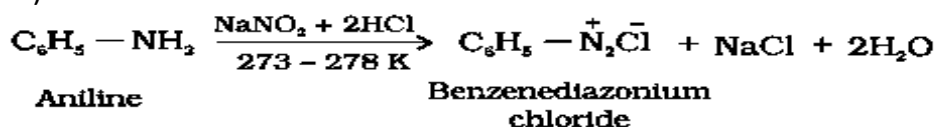


### 4. Reaction with nitrous acid

- Primary aliphatic amines react with nitrous acid to form aliphatic diazonium salts which being unstable, liberate nitrogen gas quantitatively and alcohols

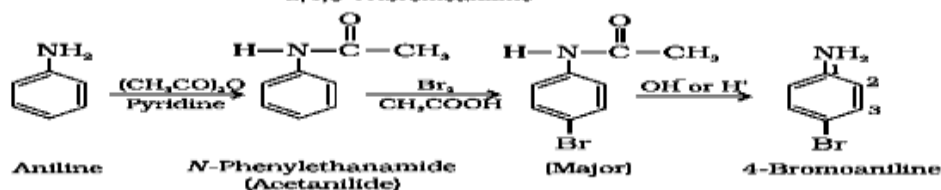
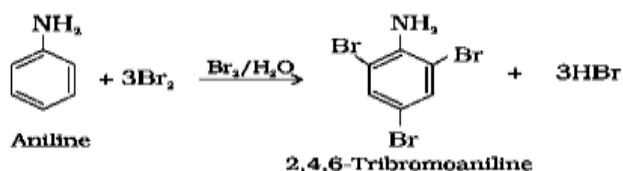


- Aromatic amines react with nitrous acid at low temperatures (273-278 K) to form diazonium salts

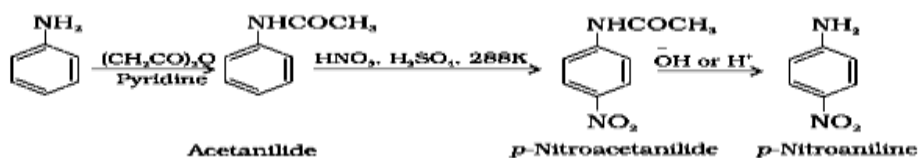
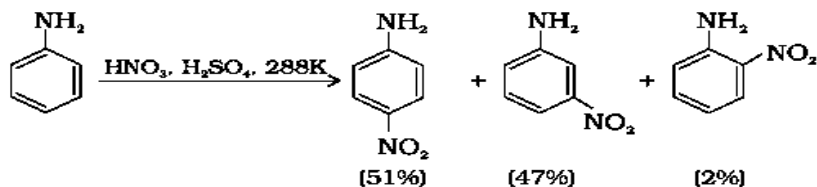


### 5. Electrophilic substitution (-NH<sub>2</sub> group is *ortho* and *para* directing)

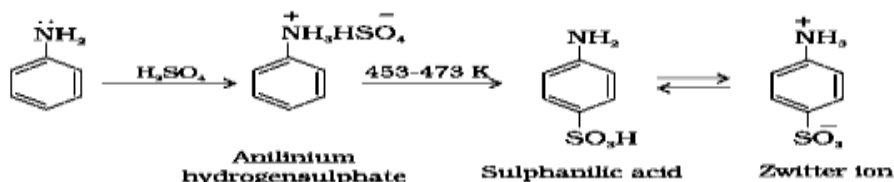
- **Bromination**



• Nitration



• Sulphonation



Aniline does not undergo Friedel-Crafts reaction (alkylation and acetylation) due to salt formation with aluminium chloride, the Lewis acid, which is used as a catalyst

**Reasoning based Questions**

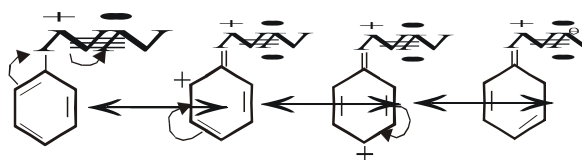
- i) Amines are less acidic than alcohols of comparable molecular masses.
- ii) Primary amines have higher boiling point than tertiary amines?
- iii) Aliphatic amines are stronger bases than aromatic amines?
- iv) Aromatic primary amines cannot be prepared by Gabriel phthalimide synthesis?
- v)  $pK_b$  of aniline is more than that of methylamine.
- vi) Ethylamine is soluble in water whereas aniline is not.
- vii) Methylamine in water reacts with ferric chloride to precipitate hydrated ferric oxide.
- viii) Although amino group is *o*- and *p*- directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of *m*-nitroaniline.
- ix) Aniline does not undergo Friedel-Crafts reaction.
- x) Diazonium salts of aromatic amines are more stable than those of aliphatic amines.
- xi) Gabriel phthalimide synthesis is preferred for synthesising primary amines.

- xii) How do you account for the miscibility of ethoxyethane with water.
- xiii) Direct nitration of aniline is not carried out. Explain why?
- xiv) The presence of a base is needed in the ammonolysis of alkyl halides.
- xv) The observed  $K_b$  order  $\text{Et}_2\text{NH} > \text{Et}_3\text{N} > \text{EtNH}_2$  in aqueous solution. where Et is ethyl
- xvi) Arrange the following in increasing order of basic strength)
- $\text{C}_2\text{H}_5\text{NH}_2$ ,  $\text{C}_6\text{H}_5\text{NHCH}_3$ ,  $(\text{C}_2\text{H}_5)_2\text{NH}$  and  $\text{C}_6\text{H}_5\text{NH}_2$
  - Aniline, *p*-nitroaniline and *p*-toluidine
  - $\text{C}_6\text{H}_5\text{NH}_2$ ,  $\text{C}_2\text{H}_5\text{NH}_2$ ,  $(\text{C}_2\text{H}_5)_2\text{NH}$ ,  $\text{NH}_3$
  - $\text{C}_2\text{H}_5\text{NH}_2$ ,  $(\text{C}_2\text{H}_5)_2\text{NH}$ ,  $(\text{C}_2\text{H}_5)_3\text{N}$ ,  $\text{NH}_3$
  - $\text{C}_2\text{H}_5\text{NH}_2$ ,  $\text{C}_6\text{H}_5\text{NHCH}_3$ ,  $(\text{C}_2\text{H}_5)_2\text{NH}$ ,  $\text{C}_6\text{H}_5\text{NH}_2$
  - $\text{C}_6\text{H}_5\text{NH}_2$ ,  $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$ ,  $(\text{C}_2\text{H}_5)_2\text{NH}$ ,  $\text{CH}_3\text{NH}_2$
  - $\text{C}_6\text{H}_5\text{NH}_2$ ,  $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$ ,  $(\text{C}_2\text{H}_5)_2\text{NH}$  and  $\text{CH}_3\text{NH}_2$
  - $\text{C}_6\text{H}_5\text{NH}_2$ ,  $\text{C}_6\text{H}_5\text{NHCH}_3$ ,  $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$ .
  - $(\text{C}_2\text{H}_5)_2\text{NH}$ ,  $(\text{C}_2\text{H}_5)_3\text{N}$ ,  $\text{C}_2\text{H}_5\text{NH}_2$ ,  $\text{NH}_3$
  - $(\text{CH}_3)_2\text{NH}$ ,  $\text{CH}_3\text{NH}_2$ ,  $(\text{CH}_3)_3\text{N}$ ,  $\text{NH}_3$



## ANSWER OF REASONING QUESTIONS

- i) Amines are less acidic than alcohols because oxygen is more electronegative and small in size than nitrogen, therefore O-H bond breaks early than N – H bond.
- ii) Primary amines have higher boiling point than tertiary amines. In primary amines  $RNH_2$ , the molecules have intermolecular hydrogen bonding but the same cannot be present in the case of tertiary amines ( $R_3N$ ).  $\therefore$  the boiling points of primary amines are higher than the tertiary amines
- iii) Aliphatic amines are stronger bases than aromatic amines. because in aliphatic amines electron releasing group is present, and in aniline, the lone pair of electron of nitrogen atom is involved in resonance with benzene ring hence is not easily available for donation. (Draw the resonating structures of aniline)
- iv) 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.
- v)  $pK_b$  of aniline is more than that of methylamine. Since there is +ve charge on N in some resonating structure therefore it is less basic. Whereas in methyl amine, methyl group donate  $e^-$  towards N. electron density increases that's why it is more basic.
- vi) Ethylamine is soluble in water due to the formation of hydrogen bonds with water whereas aniline due to large hydrocarbon part, the extent H – Bonding decreases.
- vii) Methylamine in water reacts with ferric chloride to precipitate hydrated ferric oxide. because Methylamine being more basic than water, accepts a proton from water liberate  $OH^-$  ions, these  $OH^-$  ions combine with  $Fe^{3+}$  to form a brown ppt of hydrated ferric oxide.
- viii) 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  $H_2SO_4$ . In presence of these acids aniline gets protonated to form the anilinium ion which is *meta* directing.
- ix) Aniline does not undergo Friedel-Crafts reaction. as aniline being a lewis base reacts with lewis acid  $AlCl_3$  to form a salt.
- x) Diazonium salts of aromatic amines are more stable than those of aliphatic amines. Because Aryl diazonium ion is stabilized by dispersal of +ve charge no such dispersal occurs in alkyl diazonium ion. Moreover, alkyl diazonium ion immediately loses  $N_2$  molecule to form alkyl carbocation while aryl diazonium ion does not lose  $N_2$  so easily because aryl carbocation is not stable.



- xi) Gabriel phthalimide synthesis gives pure primary amines without any contamination of secondary and tertiary amines therefore it is preferred for synthesising primary amines.
- xii) Ethoxyethane is miscible, 7.5 per 100 mL water, This is due to the fact that oxygen of ether can form hydrogen bonds with water
- xiii) Direct nitration of aniline yields tarry oxidation products in addition to the nitro derivatives. Moreover, in the strongly acidic medium, aniline is protonated to form the anilinium ion which is *meta* directing. That is why besides the *ortho* and *para* derivatives, significant amount of *meta* derivative is also formed.
- xiv) The presence of a base is needed in the ammonolysis to remove HX and make the reaction forward.

xv) It is the combination of electron releasing nature of alkyl group, H-bonding and steric factors determine the stability of ammonium cations formed in solution therefore  $Et_2NH > Et_3N > EtNH_2$  is order of  $K_b$

## VI . Word problems based on reactions

- i) An aromatic compound A on treatment with aqueous ammonia and heating forms compound B which on heating with  $Br_2$  and KOH forms compound C of molecular formula  $C_6H_7N$ . Write the structures and IUPAC names of compounds A,B,C. **Answer-12 Since C is formed by Hoffmann Bromamide reaction, it is a primary amine So Structure is  $C_6H_5NH_2$ , B is  $C_6H_5CONH_2$  A is carboxylic acid  $C_6H_5COOH$ .**
- ii) A compound A has the molecular formula  $C_7H_7NO$ . On treatment with  $Br_2$  and NaOH it gives B. B gives a foul smelling substance C on treatment with  $CHCl_3$  and KOH. B on treatment with  $NaNO_2$  and HCl at  $0^\circ C$  and mixing with alkaline phenol gives a red dye D. Identify A to D. **Answer-13: A is benzamide B is Aniline, C is phenyl isocyanide D is p- Hydroxy azobenzene**
- iii) A compound A has the molecular formula  $C_7H_7NO$ . On heating with  $P_2O_5$  gives B  $C_7H_5N$ . B on hydrolysis gives an acid C  $C_7H_6O_2$ . B on reduction with  $Na/C_2H_5OH$  gives D  $C_7H_9N$  a basic compound. D on treatment with  $NaNO_2$  and HCl evolves  $N_2$  forming E  $C_7H_8O$ . This on oxidation gives C. C is also formed on heating A with HCl. Identify A to E. **Answer-14: A-Benzamide, B- Phenyl cyanide C - benzoic acid D- Benzylamine E -Benzylalcohol**
- iv) A compound X having molecular formula  $C_3H_7NO$  reacts with  $Br_2$  in presence of KOH to give another compound Y. The Compound Y reacts with  $HNO_2$  to form ethanol and  $N_2$  gas. Identify the compounds X and Y and write the reactions involved. **Answer 24: X= $CH_3CH_2CONH_2$  Y=  $CH_3CH_2NH_2$**
- v) A compound A with molecular formula  $C_2H_3Cl$  on treatment with AgCN gives two isomeric compounds of unequal amounts with the molecular formula  $C_3H_3N$ . The minor of these two products on complete reduction with  $H_2$  in the presence nickel gives a compound B with molecular formula  $C_3H_9N$ . Deduce the structures of A,B,& C and write the reactions involved. **Answer25:A= $CH_3CH_2Cl$ , On reaction with AgCN it gives  $CH_3CH_2CN$  (Minor) &  $CH_3CH_2NC$  (Major) B=  $CH_3CH_2CH_2NH_2$**

## IMPORTANT QUESTIONS FOR TERM-2

### A. DRAW THE STRUCTURE OF :

4. Methanamine
5. Ethanamine
6. N-methylethanamine
7. N,N-dimethylethanamine
8. N-ethyl N-methyl ethanamine
9. Aniline
10. N-methylaniline
11. Benzylamine
12. N-methyl Propane -2-amine

### B. WRITE IUPAC NAMES OF THE FOLLOWING COMPOUNDS AND CLASSIFY THEM INTO PRIMARY, SECONDARY AND TERTIARY AMINES.

1.  $CH_3CH_2NH_2$
2.  $CH_3CH_2NHCH_3$
3.  $CH_3CH_2N(CH_3)_2$
4.  $(CH_3)_2CHNH_2$
5.  $CH_3NHCH(CH_3)_2$
6.  $(CH_3)_3CNH_2$
7.  $C_6H_5NHCH_3$
8.  $C_6H_5NHCH_3$
9.  $(CH_3CH_2)_2NCH_3$

**C. Arrange the following in increasing order of:**

1.  $C_2H_5NH_2$ ,  $C_2H_5OH$ ,  $(CH_3)_3N$  (**boiling point**)
2.  $C_2H_5OH$ ,  $(CH_3)_2NH$ ,  $C_2H_5NH_2$  (**boiling point**)
3.  $C_6H_5NH_2$ ,  $(C_2H_5)_2NH$ ,  $C_2H_5NH_2$ . (**solubility in water**)
4.  $CH_3NH_2$ ,  $(CH_3)_2NH$ ,  $(CH_3)_3N$  (**basic strength in aqueous phase**)
5.  $(C_2H_5)_3N$ ,  $C_2H_5NH_2$ ,  $(C_2H_5)_2NH$  (**basic strength in aqueous phase**)
6.  $C_2H_5NH_2$ ,  $C_6H_5NHCH_3$ ,  $(C_2H_5)_2NH$  and  $C_6H_5NH_2$  (**pK<sub>b</sub> values**)
7. Aniline, *p*-nitroaniline and *p*-toluidine (**basic strength**)
8.  $C_6H_5NH_2$ ,  $C_2H_5NH_2$ ,  $(C_2H_5)_2NH$ ,  $NH_3$  (**basic strength in aqueous phase**)
9.  $C_2H_5NH_2$ ,  $(C_2H_5)_2NH$ ,  $(C_2H_5)_3N$ ,  $NH_3$  (**basic strength**)
10.  $C_2H_5NH_2$ ,  $C_6H_5NHCH_3$ ,  $(C_2H_5)_2NH$ ,  $C_6H_5NH_2$  (**basic strength**)
11.  $C_6H_5NH_2$ ,  $C_6H_5N(CH_3)_2$ ,  $(C_2H_5)_2NH$ ,  $CH_3NH_2$  (**basic strength**)

**D. Account for the following:**

1. Ammonia are basic in nature .
2. Amines are basic in nature.
3. Aliphatic amines are stronger bases than ammonia.
4. The order of basicity of amines in the gaseous phase follows the order: Tertiary amine > Secondary amine > Primary amine >  $NH_3$ .
5. The order of basicity of amines is not regular in the aqueous state.
6. Aliphatic amines are stronger bases than aromatic amines.
7. pK<sub>b</sub> of aniline is more than that of methylamine
8. Aromatic amines are weaker bases than ammonia.
9. The observed K<sub>b</sub> order  $Et_2NH > Et_3N > EtNH_2 > NH_3$  OR  $(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$  in aqueous solution .where Et is ethyl.
10. The observed K<sub>b</sub> order  $Me_2NH > MeNH_2 > Me_3N > NH_3$  OR  $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$  in aqueous solution .where Me is Methyl
11. Primary amines have higher boiling point than tertiary
12. Ethylamine is soluble in water whereas aniline is not.
13. Gabriel phthalimide synthesis is preferred for synthesising primary amines.
14. Aromatic primary amines cannot be prepared by Gabriel phthalimide synthesis.
15. Although amino group is *o*- and *p*- directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of *m*-nitroaniline.
16. Direct nitration of aniline is not carried out.
17. Aniline does not undergo Friedel-Crafts reaction.
18. Amines are less acidic than alcohols of comparable molecular masses .
19. Methylamine in water reacts with ferric chloride to precipitate hydrated ferric oxide
20. Aniline is soluble in aqueous HCl .
21.  $MeNH_2$  is stronger base than  $MeOH$ .
22.  $CH_3CONH_2$  is a weaker base than  $CH_3CH_2NH_2$
23.  $NH_2$  group of aniline acetylated is before carrying out nitration.
24. Acetylation of  $-NH_2$  group of aniline reduce its activating effect
25. Electrophilic substitution in aromatic amines takes place more readily than benzene.

**E. Give a CHEMICAL TEST to distinguish between following pair of organic compounds**

1. Methylamine and dimethylamine
2. Ethylamine and aniline
3. Aniline and benzylamine
4. Aniline and N-methylaniline
5. N-methyl Propane -2-amine and N-ethyl N-methyl ethanamine
6. Secondary and tertiary amines

7. 1<sup>o</sup>, 2<sup>o</sup>, & 3<sup>o</sup> Amines
8. C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub> & C<sub>6</sub>H<sub>5</sub>NHCH<sub>3</sub>

**F. Describe a method for the identification of primary, secondary and tertiary amines. Also write chemical equations of the reactions involved**

**G. WRITE FOLLOWING NAME REACTIONS :**

1. Hofmann's bromamide reaction
2. Ammonolysis
3. Gabriel phthalimide synthesis.
4. Carbylamine reaction
5. Diazotisation
6. Coupling reaction
7. Acetylation
8. Benzoylation

**H. Write structures and IUPAC names of (i) the amide which gives propanamine by Hoffmann bromamide reaction. (ii) the amine produced by the Hoffmann degradation of benzamide.**

**I. Write chemical equations for the following reactions: (i) Reaction of ethanolic NH<sub>3</sub> with C<sub>2</sub>H<sub>5</sub>Cl. (ii) Ammonolysis of benzyl chloride and reaction of amine so formed with two moles of CH<sub>3</sub>Cl.**

**J. An aromatic compound A on treatment with aqueous ammonia and heating forms compound B which on heating with Br<sub>2</sub> and KOH forms compound C of molecular formula C<sub>6</sub>H<sub>7</sub>N. Write the structures and IUPAC names of compounds A, B, C**

**K. Write the reactions of (i) aromatic and (ii) aliphatic primary amines with nitrous acid.**

**L. Write chemical equations for the following conversions:**

1. CH<sub>3</sub>-CH<sub>2</sub>-Cl into CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>-NH<sub>2</sub>
2. C<sub>6</sub>H<sub>5</sub>-CH<sub>2</sub>-Cl into C<sub>6</sub>H<sub>5</sub>-CH<sub>2</sub>-CH<sub>2</sub>-NH<sub>2</sub>
3. Benzene into aniline
4. Benzene into N, N-dimethylaniline
5. Cl-(CH<sub>2</sub>)<sub>4</sub>-Cl into hexan-1,6-diamine
6. Ethanoic acid into methanamine
7. Hexanenitrile into 1-aminopentane
8. Methanol to ethanoic acid
9. Ethanamine into methanamine
10. Ethanoic acid into propanoic acid
11. Methanamine into ethanamine
12. Nitromethane into dimethylamine
13. Propanoic acid into ethanoic acid
14. Nitrobenzene to benzoic acid
15. Benzene to *m*-bromophenol
16. Benzoic acid to aniline
17. Aniline to 2,4,6-tribromofluorobenzene
18. Benzyl chloride to 2-phenylethanamine
19. Chlorobenzene to *p*-chloroaniline
20. Aniline to *p*-bromoaniline
21. Benzamide to toluene
22. Aniline to benzyl alcohol.

M. COMPLETE THE FOLLOWING REACTIONS

1.  $C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow[273K]{NaNO_2+HCl} B$
2.  $CH_3CH_2I \xrightarrow{NaCN} A \xrightarrow[Partial\ hydrolysis]{OH^-} B \xrightarrow{NaOH+Br_2} C$
3.  $CH_3CH_2Br \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow[0^\circ C]{HNO_2} C$
4.  $CH_3COOH \xrightarrow[\Delta]{NH_3} A \xrightarrow{NaOBr} B \xrightarrow{NaNO_2/HCl} C$
5.  $C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow[273K]{HNO_2} B$
6.  $C_6H_5NH_2 + CHCl_3 + alc.KOH \rightarrow$
7.  $C_6H_5NH_2 + Br_2 (aq) \rightarrow$
8.  $C_6H_5NH_2 + H_2SO_4 (conc.) \rightarrow$
9.  $C_6H_5NH_2 + (CH_3CO)_2O \rightarrow$
10.  $CH_3CN \xrightarrow[\Delta]{H_2O/H^+} A \xrightarrow[\Delta]{NH_3} B \xrightarrow{NaOH+Br_2} C$
11.  $CH_3COOH \xrightarrow[\Delta]{NH_3} A \xrightarrow{NaOH+Br_2} B + CHCl_3 + alc.KOH \rightarrow C$