

# DAV CENTENARY PUBLIC SCHOOL, PASCHIM ENCLAVE, NEW DELHI-87

## CHEMISTRY



**Class - XII**

**Question Bank Term- II 2021-22**

# **CHEMISTRY**

## **CLASS XII**

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

<b>S.No</b>	<b>UNIT</b>	<b>No. of Periods</b>	<b>MARKS</b>
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	
	<b>TOTAL</b>	<b>49</b>	<b>35</b>

### **Unit III: Electrochemistry 7 Periods**

Redox reactions, EMF of a cell, standard electrode potential, Nernst equation and its application to chemical cells, Relation between Gibbs energy change and EMF of a cell, conductance in electrolytic solutions, specific and molar conductivity, variations of conductivity with concentration, Kohlrausch's Law, electrolysis.

### **Unit IV: Chemical Kinetics 5 Periods**

Rate of a reaction (Average and instantaneous), factors affecting rate of reaction: concentration, temperature, catalyst; order and molecularity of a reaction, rate law and specific rate constant, integrated rate equations and half-life (only for zero and first order reactions).

### **Unit V: Surface Chemistry 5 Periods**

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.

### **Unit VIII: d and f Block Elements 7 Periods**

General introduction, electronic configuration, occurrence and characteristics of transition metals, general trends in properties of the first-row transition metals – metallic character, ionization enthalpy, oxidation states, ionic radii, color, catalytic property, magnetic properties, interstitial compounds, alloy formation.

Lanthanoids - Electronic configuration, oxidation states and lanthanides contraction and its consequences.

### **Unit IX: Coordination Compounds 8 Periods**

Coordination compounds - Introduction, ligands, coordination number, color, magnetic properties and shapes, IUPAC nomenclature of mononuclear coordination compounds. Bonding, Werner's theory, VBT, and CFT.

### **Unit XII: Aldehydes, Ketones and Carboxylic Acids 10 Periods**

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

Carboxylic Acids: Nomenclature, acidic nature, methods of preparation, physical and chemical properties & uses.

### **Unit XIII: Amines 7 Periods**

Amines: Nomenclature, classification, structure, methods of preparation, physical and chemical properties, uses, identification of primary, secondary and tertiary amines

## ELECTRO CHEMISTRY

1. Electrochemistry is the branch of chemistry which deals with the relationship between electrical energy and chemical energy and inter-conversion of one form into another.

2. An electrochemical cell consists of two metallic electrodes dipped in electrolytic solutions. The cells are of two types:

(a) Electrolytic cells (b) Galvanic cells

3. A galvanic cell consists of two half cells. Each half cell contains an electrolytic solution and a metallic electrode. The electrode at which- oxidation takes place is called an anode and the electrode at which reduction takes place is called the cathode. The half-cells are separated from each other by means of a salt bridge.

4. The passage of current from one electrode to the other indicates the existence of potential difference between them. This difference of potential which causes current to flow from the electrode of higher negative potential is called the electromotive force (emf).

5. Functions of salt bridge: completes the circuit & maintains electrical neutrality of the cell

6. The potential of SHE is assigned an arbitrary value of zero.  $E^\circ = 0 \text{ V}$ . It is used as a reference electrode for measuring the standard electrode potentials. .

7. When the elements are arranged in order of their standard electrode potentials, a series known as electrochemical series is obtained.

8. Standard emf of a cell,

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = E^\circ_{\text{Right}} - E^\circ_{\text{Left}}$$

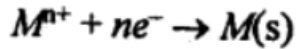
9. Relation between Gibb's free energy &  $E^\circ_{\text{cell}}$

$$\Delta G^\circ = -nFE^\circ_{\text{cell}}$$

If  $E^\circ_{\text{cell}}$  is positive,  $\Delta G^\circ$  would be negative and reaction would be spontaneous. If  $E^\circ_{\text{cell}}$  is negative,  $\Delta G^\circ$  would be positive and the reaction would be non-spontaneous.

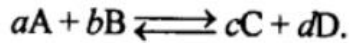
10. A species with higher standard reduction potential has greater tendency to accept electrons to undergo reduction or vice versa.

11. **The potential of an electrode** in contact with its ions in solution varies with the concentration of the ion. Thus, for a redox reaction.



Nernst equation is  $E = E_{M^{n+}/M}^{\circ} + \frac{RT}{nF} \ln [M^{n+}]$

12. For an electro chemical cell for which the overall reaction is :



$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{2.303RT}{nF} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

At 298 K,  $\frac{2.303RT}{nF} = \frac{0.0591}{n}$

Then equation becomes

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

13. The equilibrium constant,  $K_C$  is related to  $E_{\text{cell}}^{\circ}$

$$E_{\text{cell}}^{\circ} = \frac{2.303RT}{nF} \log K_c = \frac{0.0591}{n} \log K_c \text{ at } 298 \text{ K.}$$

$$\Delta G^{\circ} = -nFE_{\text{cell}}^{\circ} = -2.303 RT \log K_c$$

14. Resistance is the measure of obstruction to the flow of current.

$$R \propto \frac{l}{A} \Rightarrow R = \rho \frac{l}{A} \text{ (where } \rho = \text{specific resistance or resistivity. Unit of R is ohm).}$$

15. **Resistivity** is defined as the resistance of a conductor of 1cm length and having an area of cross-section equal to 1cm<sup>2</sup>.  $\rho = \frac{RA}{l}$  (unit of resistivity is ohm-cm)

16. Conductance is reciprocal of resistance,  $G = 1/R$

Unit of conductance is ohm<sup>-1</sup> or mho or Siemen (S).

17. Specific conductance  $\kappa$  (*kappa*) is reciprocal of specific resistance

$$\kappa = G \times G^* \Rightarrow \kappa = \frac{1}{R} \times \frac{l}{A} \text{ or } \kappa = l/\rho$$

18. **Molar conductance** ( $\Lambda_m$ ) is defined as the conductance of the volume of solution which contains one mole of the solute and is placed between two parallel electrodes which are one centimeter apart and having sufficient area to hold the whole of the solution.

Unit of molar conductance is  $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$  or  $\text{S cm}^2 \text{ mol}^{-1}$

$\lambda_m = \kappa / C$  where  $C$  = concentration of solution in moles per litre (or Molarity)

$$\lambda_m \Rightarrow \frac{\kappa \times 1000}{M} \quad (\text{if } \kappa = S\text{cm}^{-1})$$

$$\lambda_m \Rightarrow \frac{\kappa}{M \times 1000} \quad (\text{if } \kappa = S\text{m}^{-1})$$

19. Effect of Dilution on Molar conductance: The value of molar conductance increases with dilution and finally attains a maximum value at infinite dilution. ( $\lambda_m^0$ )

20. Variation of molar conductance with concentration:

(a) Strong electrolytes:

**conductance at infinite dilution ( $\Lambda_m^\infty$ )**

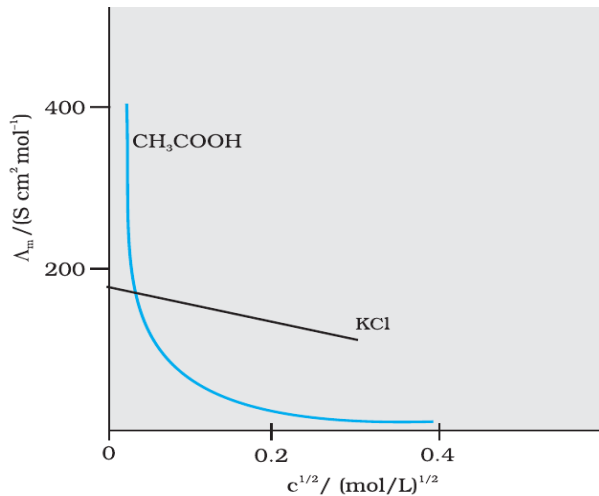
$$\Lambda_m = \Lambda_m^\infty \text{ when } C \rightarrow 0$$

The variation of  $\Lambda_m$  with concentration is given by

$$\Lambda_m = \Lambda_m^\infty - b\sqrt{C} \text{ where } b = \text{constant}$$

(b) Weak electrolytes:

The variation of  $\Lambda_m$  with  $\sqrt{C}$  is very large and so much so that we cannot obtain molar conductance at infinite dilution ( $\Lambda_m^\infty$ ) by extrapolation of the  $\Lambda_m$  Vs.  $\sqrt{C}$  plots.



21. Kohlrausch's Law - "the limiting molar conductivity of an electrolyte can be expressed as the sum of the contributions of the cation and the anion of the electrolyte."

$$\Lambda^0 = \nu_+ \lambda_+^0 + \nu_- \lambda_-^0$$

22. Faraday's laws of electrolysis:

- (a) First law: The amount of a substance deposited or liberated at an electrode is directly Proportional to the quantity of electricity passed through the electrolyte.

$$Q \propto I \times t$$

$$m = ZIt$$

$I$  = current in amperes

$t$  = time in seconds, and

$Z$  = constant called electrochemical equivalent.

where  $m$  = mass of substance deposited or liberated.

$Z$  = constant called electrochemical equivalent

- (b) Second law: When the same quantity of electricity is passed through solutions of different electrolytes, the weight of different substances deposited or liberated at the respective electrodes are proportional to their chemical equivalent weights.

23. The charge on one mole of electrons is approximately equal to 96500 coulombs. This quantity of electricity is called Faraday constant (F).

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### SA Type I Questions (2 Marks)

- The conductivity of metals decreases while that of electrolytes increases with increase in Temperature. Why?
- The conductivity of an aqueous solution of NaCl in a cell is  $92 \Omega^{-1} \text{ cm}^{-1}$  the resistance offered by this cell is  $247.8 \Omega$ . Calculate the cell constant?
- How many electrons flow when a current of 5 A is passed through a solution for 193 sec. Given  $F = 96500 \text{ C}$ .  $N_0 = 6.002 \times 10^{23} \text{ mol}^{-1}$ ?
- There are two possible reactions for cathode in the electrolysis of aqueous  $\text{ZnCl}_2$ :  
 $\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Zn}(\text{s}) \quad E^0 = -0.76 \text{ V}$   
 $2\text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq}) \quad E^0 = -0.83 \text{ V}$   
 Which one will take place? Why?
- Calculate pH of following half-cell.  
 Pt,  $\text{H}_2 / \text{H}_2\text{SO}_4$ , if its electrode potential is 0.03V.

### SA Type II Questions (3 Marks)

- (a) Calculate  $G^\circ$  for the reaction  
 $\text{Zn}(\text{s}) + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu}(\text{s})$   
 Given:  $E^\circ$  for  $\text{Zn}^{2+}/\text{Zn} = -0.76\text{V}$  and  $E^\circ$  for  $\text{Cu}^{2+}/\text{Cu} = +0.34 \text{ V}$   
 $R = 8.314 \text{ JK}^{-1}\text{mol}^{-1}$ ;  $F = 96500 \text{ Cmol}^{-1}$
- Out of the following pairs, predict with reason which pair will allow greater conduction of electricity:

- (i) Silver wire at 30°C or silver wire at 60°C.  
(ii) 0.1 M CH<sub>3</sub>COOH solution or 1 M CH<sub>3</sub>COOH solution.  
(iii) KCl solution at 20°C or KCl solution at 50°C.
3. Calculate emf of the following cell  
Cd /Cd<sup>2+</sup> (0.10 M)//H<sup>+</sup> (0.20 M)/H<sub>2</sub> (0.5 atm) /Pt  
[Given E° for Cd<sup>2+</sup> /Cd = -0.403V]
4. The molar conductivity of 0.025 mol L<sup>-1</sup> methanoic acid is 46.1 S cm<sup>2</sup> mol<sup>-1</sup>. Calculate its degree of dissociation and dissociation constant Given λ°(H<sup>+</sup>)=349.6 S cm<sup>2</sup> mol<sup>-1</sup> and λ°(HCOO<sup>-</sup>) = 54.6 S cm<sup>2</sup> mol<sup>-1</sup>
5. Consider the reaction: Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> + 14H<sup>+</sup> + 6e<sup>-</sup> → 2Cr<sup>3+</sup> + 7H<sub>2</sub>O . What is the quantity of electricity in coulombs needed to reduce 1 mol of Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> ?
6. Predict the products of electrolysis obtained at the electrodes in each case when the electrodes used are platinum.  
(a) An aqueous solution of AgNO<sub>3</sub>.  
(b) A dilute aqueous solution of H<sub>2</sub>SO<sub>4</sub>.
7. Fill in the blanks-  
(i) 1 F is the charge present on \_\_\_\_\_ of electrons.  
(ii) 1 F passed through CuSO<sub>4</sub> sol deposits \_\_\_\_\_ of Cu.
8. Can a galvanic cell act as electrolytic cell? How?  
(A). What is an electrochemical series? How does it predict the feasibility of a certain redox reaction?  
(B). The arrangement of metals and ions in increasing order of their electrode potential values is known as electrochemical series. The reduction half reaction for which the reduction potential is lower than the other will act as anode and one with greater value will act as cathode .Reverse reaction will not occur.
9. What are the factors on which conductivity of an electrolyte depend?
10. How is standard electrode potential of a cell related to :-  
1) Equilibrium constant?  
2) Gibbs free energy change.

### LA Type Questions – 5 Marks

**1. Read the passage given below and answer the following questions:**

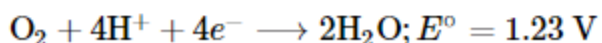
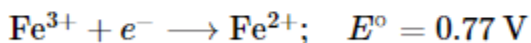
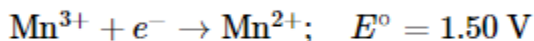
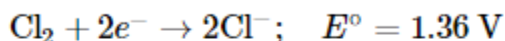
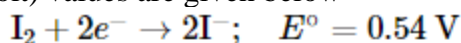
Standard electrode potentials are used for various processes:

- (i) It is used to measure relative strengths of various oxidants and reductants.  
(ii) It is used to calculate standard cell potential.  
(iii) It is used to predict possible reactions.

A set of half-reactions (in acidic medium) along with their standard reduction potential, E°(in



volt) values are given below –



Choose the most appropriate answer:

- (i)  $\text{Cl}^-$  is oxidised by  $\text{O}_2$ . Is this correct?  
(ii)  $\text{Mn}^{3+}$  is not stable in acidic medium, while  $\text{Fe}^{3+}$  is stable. Why?  
(iii) Which is out of the following is the strongest reducing agent in the aqueous solution?  
(a)  $\text{I}^-$     (b)  $\text{Cl}^-$     (c)  $\text{Mn}^{2+}$     (d)  $\text{Fe}^{2+}$   
(iv) What is the  $E^\circ_{\text{cell}}$  for the following reaction –  
$$\text{I}_2 + 2\text{KI} \rightleftharpoons 2\text{KI} + \text{Cl}_2$$
  
(v) What affects potential of an electrode?

Ans. (i) False

(ii) Reduction potential of  $\text{Mn}^{3+}$  is more than  $\text{Fe}^{3+}$ .

(iii)  $\text{Mn}^{2+}$ .

(iv) -0.82 V

(v) Concentration of ions in the solution and temperature.

2. Molar conductivity of solution is the conductance of solution containing one mole of electrolyte, kept between two electrodes having unit length between them and large cross-sectional area, so as to contain the electrolyte. In other words, molar conductivity is the conductance of the electrolytic solution kept between the electrodes of a conductivity cell at unit distance but having area of cross-section large enough to accommodate sufficient volume of solution that contains one mole of the electrolyte. It is denoted by  $\lambda_m$ .

(i) Write the mathematical expression for molar conductivity ..

(ii) What is the unit of molar conductivity  $\lambda_m$  ?

(iii) Solutions of two electrolytes 'A' and 'B' are diluted. The  $\lambda_m$  of 'B' increases 1.5 times while that of A increases 25 times. Which of the two is a strong electrolyte?

(iv) Molar conductivity of ionic solution depends on \_\_\_\_\_.

(v) The cell constant of a conductivity cell \_\_\_\_\_.

Ans: (i) Molar Conductivity =  $k \times 10000 / \text{Molarity}$

(ii)  $\text{Scm}^2\text{mol}^{-1}$

(iii) B

- (iv) Concentration of electrolytes in solution  
 (v) remains constant for a cell.

### ANSWERS : SA 2 MARKS

1. With increase in temperature, the K.E. of metal cation increases and obstructs the free flow of electrons decreasing the conducts of metal while in case of electrolytes, increased temperature increases the mobility of ions this increases the conductance of ions.

2. Specific conductivity = Cell constant/ Resistance

$$\begin{aligned} \text{Cell constant} &= \text{conductivity} \times \text{Resistance} \\ &= 92 \Omega^{-1} \text{ cm}^{-1} \times 247.8 = 22797.6 \Omega^{-1} \text{ cm}^{-1} \end{aligned}$$

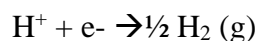
3.  $Q = It = 5 \times 193 = 965 \text{ C}$

$$96500 \text{ C} = 1 \text{ mol of electrons} = 6.022 \times 10^{23} \text{ mol}^{-1}$$

$$\begin{aligned} 965 \text{ C} &= 6.022 \times 10^{23} \times 965/96500 \\ &= 6.022 \times 10^{21} \text{ electrons.} \end{aligned}$$

4.  $\text{Zn}^{2+}$  is reduced to Zn preferentially at cathode because  $\text{Zn}^{2+}$  has higher reduction potential (-0.76V) than  $\text{H}_2\text{O}$  (-0.83V)

5.  $\text{pH} = -\log [\text{H}^+]$



$$E_{\text{cell}} = E_{\text{cell}}^0 - 0.059/n \log 1/[\text{H}^+]$$

$$0.03 = 0 - 0.059 / 1 \log 1/[\text{H}^+]$$

$$\text{pH} = 5.07 \text{ V}$$

6. (a) Silver is deposited at cathode and oxygen is liberated at anode.



(b)  $\text{H}_2$  gas at cathode and  $\text{O}_2$  gas at anode.



7. (i) 1 mole (ii)  $\frac{1}{2}$  mole.

8. Yes, a galvanic cell can be converted into electrolytic cell by applying an external opposite potential greater than its own electrical potential.

9. The conductivity of an electrolyte depends upon

- i) The nature of electrolyte added
- ii) Size of the ions produced and their solvation
- iii) Concentration of the electrolyte
- iv) Temperature.

10. (i) Standard electrode potential and equilibrium constant

$$E_{\text{cell}}^0 = \frac{2.303RT}{nF} \log k_c$$

Where  $E_{\text{cell}}^0$  = standard electrode potential of cell

R = Gas constant

T = temperature in Kelvin

n = no .of electrons.

F = Faraday's constant and

K<sub>c</sub> = Equilibrium constant

(ii) Standard electrode potential and Gibbs free energy change-

$$\Delta G^{\circ} = -n F E^{\circ} \text{ cell}$$

Where  $\Delta G^{\circ}$  = Change in Gibbs' free energy

n = No. of electrons

### ANSWERS: SA 3 MARKS

1.

$$\begin{aligned} \text{(a) } E^{\circ} \text{ cell} &= E^{\circ}_{\text{Cu}^{+2}/\text{Cu}} - E^{\circ}_{\text{Zn}^{+2}/\text{Zn}} \\ &= 0.34 - (-0.76) \\ &= 1.10 \text{ V} \end{aligned}$$

$$\begin{aligned} \Delta G^{\circ} &= -nFE^{\circ} \\ &= -2 \times 1.10 \times 96500 \\ &= -212300 \text{ J/mol or } -212.3 \text{ kJ/mol} \end{aligned}$$

2. (i) Silver wire at 30°C because as temperature decreases, resistance decreases so conduction increases.

(ii) 0.1 M CH<sub>3</sub>COOH, because on dilution degree of ionization increases hence conduction increases.

(iii) KCl solution at 50°C, because at high temperature mobility of ions increases and hence conductance increases.

$$\begin{aligned} 3. \quad E_{\text{cell}} &= E^{\circ}_{\text{cell}} - 0.0591/n \log [\text{Cd}^{2+}] / [\text{H}^{+}]^2 \\ E^{\circ}_{\text{cell}} &= 0 - (-0.403\text{V}) = 0.403\text{V} \\ &= 0.0403 - 0.0591/2 \log (0.10) \times 0.5 / (0.2)^2 = 0.400\text{V} \end{aligned}$$

4.

$$\begin{aligned} \Lambda^{\circ}_{\text{m}}(\text{HCOOH}) &= \lambda^{\circ}(\text{H}^{+}) + \lambda^{\circ}(\text{HCOO}^{-}) \\ &= 349.6 + 54.6 \\ &= 404.2 \text{ S cm}^2 \text{ mol}^{-1} \\ \Lambda^{\text{C}}_{\text{m}} &= 46.1 \text{ S cm}^2 \text{ mol}^{-1} \\ \therefore \alpha &= \frac{\Lambda^{\text{C}}_{\text{m}}}{\Lambda^{\circ}_{\text{m}}} = \frac{46.1}{404.2} = 0.114 \\ \text{HCOOH} &\rightleftharpoons \text{HCOO}^{-} + \text{H}^{+} \\ \text{Initial conc.} & \quad c \quad \quad \quad 0 \quad \quad \quad 0 \\ \text{at equi,} & \quad c(1-\alpha) \quad \quad \quad c\alpha \quad \quad \quad c\alpha \\ \therefore K_a &= \frac{c\alpha \cdot c\alpha}{c(1-\alpha)} = \frac{c\alpha^2}{1-\alpha} \\ &= \frac{0.025 \times (0.114)^2}{1-0.114} = 3.67 \times 10^{-4} \end{aligned}$$

5.

From the reaction, 1 mol of  $\text{Cr}_2\text{O}_7^{2-}$  require  $6F$   
 $= 6 \times 96500 = 579000 \text{ C}$   
 $\therefore 579000 \text{ C}$  of electricity are required for  
reduction of  $\text{Cr}_2\text{O}_7^{2-}$  to  $\text{Cr}^{3+}$

### 5 MARKS QUESTIONS

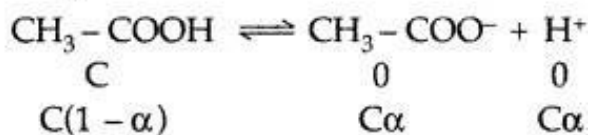
1. i) The conductivity of 0.001 M acetic acid is  $4 \times 10^{-5} \text{ S/cm}$ . Calculate the dissociation constant of acetic acid, if molar conductivity at infinite dilution for acetic acid is  $390 \text{ Scm}^2/\text{mol}$ .

$$\Lambda_m^c = \frac{K \times 1000}{\text{Molarity}}$$

$$= \frac{4 \times 10^{-5} \text{ S cm}^{-1} \times 1000 \text{ cm}^3 \text{L}^{-1}}{0.001 \text{ mol L}^{-1}}$$

$$= 40 \text{ Scm}^2 \text{ mol}^{-1}$$

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^\circ} = \frac{40}{390} = 0.1025$$



$$k_\alpha = \frac{[\text{CH}_3 - \text{COO}^-][\text{H}^+]}{[\text{CH}_3 - \text{COOH}]} = \frac{\text{C}\alpha \cdot \text{C}\alpha}{\text{C}(1 - \alpha)} = \frac{\text{C}\alpha^2}{1 - \alpha}$$

$$k = \frac{10^{-3} \times (1.025 \times 10^{-1})^2}{1 - 0.1025} = \frac{10^{-5} \times 0.105}{0.8975}$$

$$\therefore k = 1.46 \times 10^{-6}$$

ii) State Kohlrausch law of independent migration of ions. Why does the conductivity of a solution decrease with dilution?

Ans: Kohlrausch law of independent migration of ions states that the limiting molar conductivity can be represented as the sum of the individual contribution of the anion and cation of the electrolyte.

$$\Lambda_m^0 \text{ for } A_xB_y = x\lambda^{\circ+} + y\lambda^{\circ-}$$

$$\text{For acetic acid } \Lambda^{\circ}(\text{CH}_3\text{COOH}) = \lambda^{\circ}\text{CH}_3\text{COO}^- +$$

$$\lambda^{\circ}\text{H}^+ \Lambda^{\circ}(\text{CH}_3\text{COOH}) = \Lambda^{\circ}(\text{CH}_3\text{COOK}) + \Lambda^{\circ}(\text{HCl}) - \Lambda^{\circ}(\text{KCl})$$

Calculate the emf of the following cell at 25°C :

$\text{Ag(s)} | \text{Ag}^+ (10^{-3} \text{ M}) || \text{Cu}^{2+} (10^{-1} \text{ M}) | \text{Cu(s)}$  Given  $E_{\text{cell}}^0 = +0.46 \text{ V}$  and  $\log 10^n = n$ .

Ans: As  $\text{Fe} + 2\text{H}^+ \rightarrow \text{Fe}^{2+} + \text{H}_2 (n=2)$

According to Nernst equation

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.0591}{2} \log \frac{[\text{Fe}^{2+}]}{[\text{H}^+]^2}$$

$$\Rightarrow E_{\text{cell}} = 0.44 - \frac{0.0591}{2} \log \frac{10^{-3}}{1^2}$$

$$\therefore E_{\text{cell}} = 0.44 - \frac{0.0591}{2} \times (-3)$$

$$= 0.44 + 0.0887 = 0.529 \text{ V}$$

2. Conductivity of  $2.5 \times 10^{-4} \text{ M}$  methanoic acid is  $5.25 \times 10^{-5} \text{ Scm}^{-1}$ . Calculate its molar conductivity and degree of dissociation.

Ans: Given:  $\lambda_{(\text{H}^+)}^0 = 349.5 \text{ Scm}^2 \text{ mol}^{-1}$

And  $\lambda_{(\text{HCOO}^-)}^0 = 50.5 \text{ Scm}^2 \text{ mol}^{-1}$ . (All India 2015) Answer:

Concentration is  $2.5 \times 10^{-4} \text{ M}$

$$K = 5.25 \times 10^{-5} \text{ Scm}^{-1}$$

$$\Lambda_{\text{cm}} = (K \times 1000) / \text{Concentration}$$

$$= \frac{5.25 \times 10^{-5} \times 1000}{2.5 \times 10^{-4}} \text{ Scm}^2 \text{ mol}^{-1}$$

$$= \frac{5.25 \times 10^2}{2.5} = \frac{525}{2.5} = 210 \text{ Scm}^2 \text{ mol}^{-1}$$

Molar conductivity at infinite dilution,

$$\Lambda_m^0 = \lambda^0 \text{H}^+ + \lambda^0 \text{HCOO}^- = (349.5 + 50.5)$$

$$= 400 \text{ Scm}^2 \text{ mol}^{-1}$$

Degree of dissociation,

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^0} = \frac{210}{400} = \frac{21}{40} = 0.525$$

## 4. CHEMICAL KINETICS

### IMPORTANT POINTS :

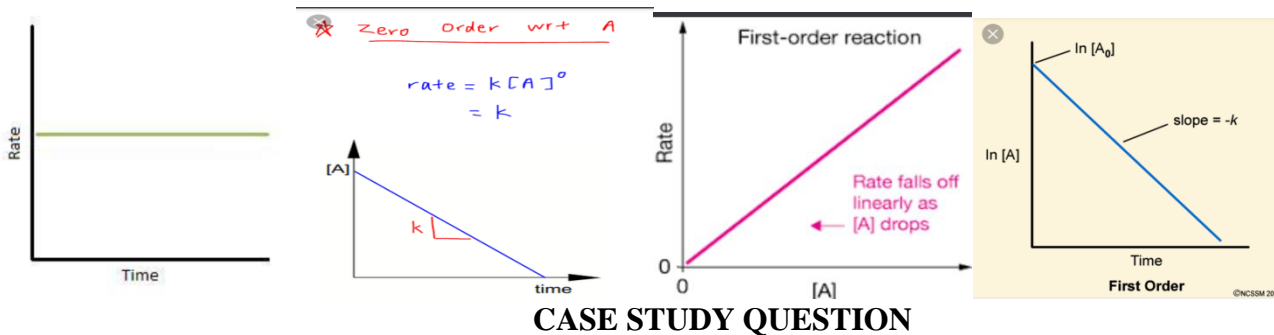
No	CONCEPT	DETAILS (THEORY & FORMULA)
	Rate of Reaction	Change of concentration of reactants & products per unit time. Rate = decrease in concentration of reactant/time taken OR Rate = increase in concentration of product/time interval Unit = mol L <sup>-1</sup> s <sup>-1</sup>
	Expression or reaction rate	Consider a reaction, N <sub>2</sub> +3H <sub>2</sub> -----> 2NH <sub>3</sub> R = -Δ[N <sub>2</sub> ]/Δt = -1/3Δ[H <sub>2</sub> ]/Δt = 1/2Δ[NH <sub>3</sub> ]/Δt Rate of disappearance of N <sub>2</sub> & H <sub>2</sub> = -Δ[N <sub>2</sub> ]/Δt = -Δ[H <sub>2</sub> ]/Δt Rate of appearance of ammonia = Δ[NH <sub>3</sub> ]/Δt Rate of disappearance of N <sub>2</sub> = rate of reaction Rate of disappearance of H <sub>2</sub> = 3 x rate of reaction & Rate of formation of NH <sub>3</sub> = 2 x rate of reaction
	Factors affecting reaction rate	Reaction rate increases with increase in concentration of reactants, temperature & catalyst. A catalyst decreases the activation energy and promotes more reactants to cross energy barrier.
	Order of reaction (n)	Sum of no of power of concentration terms of reactants in rate law. It is an experimental quantity, can be zero or fractional value.
	Molecularity of reaction (m)	The number of molecules which simultaneously collide to form products in elementary reaction. It is a theoretical value & can't be zero or fractional.
	Integrated rate equation	For zero order reaction = k = [A] <sub>0</sub> - [A] / t For first order = k = (2.303/t) log [A] <sub>0</sub> / [A]
	Unit of rate constant	for any order = mol <sup>1-n</sup> L <sup>n-1</sup> s <sup>-1</sup> (where n is the order of reaction)
	Half -life of a reaction	Time in which half of the reaction is completed or half of the reactant is consumed. For zero order t <sub>1/2</sub> = [R] <sub>0</sub> / 2k, for first order t <sub>1/2</sub> = 0.693/k
	Pseudo 1 <sup>st</sup> order reaction	The bimolecular reaction in which one of the reactants is taken in excess so that the reaction follows 1 <sup>st</sup> order kinetics.

S.No.	Order of reaction	Molecularity of reaction
1	It is sum of the powers of the concentration of the reactants in the rate law expression	The number of reacting species taking part in an elementary reaction, which must collide to give products is called molecularity of reaction.
2	Order of reaction is an experimental quantity.	It is theoretical value.
3	It can be zero and even a fraction.	It cannot be zero or fractional.
4	Order is applicable to elementary as well as complex reactions.	Molecularity is applicable only for elementary reactions.

## GRAPHICAL REPRESENTATIONS OF ZERO & FIRST ORDER REACTION

ZERO ORDER REACTION

FIRST ORDER REACTION

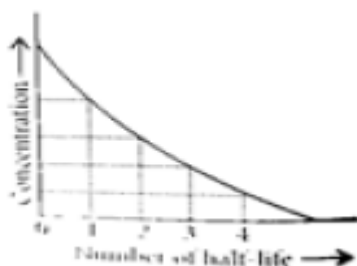


1. The half-life of a reaction is the time required for the concentration of reactant to decrease by half, i.e.,  $[A]_t = [A]/2$

For first order reaction,

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

This means  $t_{1/2}$  is independent of initial concentration. Figure shows that typical variation of concentration of reactant exhibiting first order kinetics. It may be noted that though the major portion of the first order kinetics may be over infinite time, but the reaction will never cease, as the concentration of reactant will be zero only at infinite time.



Answer the following questions:

- (i) A first order reaction has a rate constant  $k=3.01 \times 10^{-3} /s$ . How long it will take to decompose half of the reactants?
- (ii) The rate constant for a first order reaction is  $7.0 \times 10^{-4} s^{-1}$ . If initial concentration of reactant is 0.080 M, what is the half-life of reaction?
- (iii) For the half-life period of a first order reaction, is independent of initial concentration. Is this true or false?
- (iv) The rate of a first order reaction is  $0.04 \text{ mol L}^{-1} \text{ s}^{-1}$  at 10 minutes and  $0.03 \text{ mol L}^{-1} \text{ s}^{-1}$  at 20 minutes after initiation. What is half life of the reaction?
- (v) Draw the plot of  $t_{1/2}$  vs initial concentration  $[A]_0$  for a first order reaction.

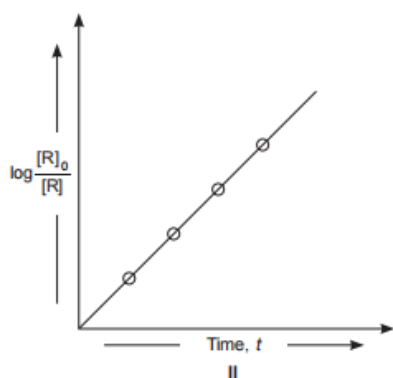
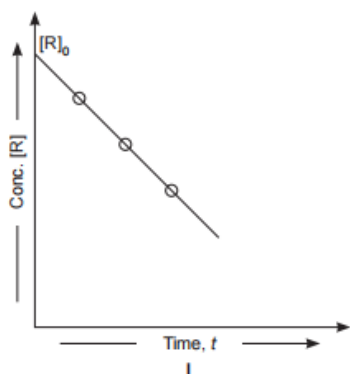
Ans 1.(i) 230.23 s

(ii) 990 s

(iii) true

(iv) 24.06 min

2. Observe the following graphs and answer the questions based on these graphs.



- (a) What is order of reaction shown in graph I?  
 (b) What is slope in graph II?  
 (c) How does  $t_{1/2}$  varies with initial concentration in zero order reaction?  
 (d) If  $t_{1/2}$  of first order reaction is 40 minutes, what will be  $t_{99.9\%}$  for first order reaction?  
 (e) What is  $t_{1/2}$  of zero-order reaction in terms of ' $k$ '?

Answer: 2. a) 0

b)  $k/2.303$  where  $k$  is the rate constant

c)  $t_{1/2}$  is directly proportional to initial concentration.

d)  $t_{99.9\%} = 10t_{1/2} = 10 \times 40 = 400$  minutes

e)  $t_{1/2} = R_0/2k$  for zero order reaction



### Very Short Answer Questions (1 Mark)

1) What is the effect of adding a catalyst on :

(a) Activation energy ( $E_a$ ) and

(b) Gibbs energy ( $\Delta G$ ) of a reaction.

Answer – (a)  $E_a$  decreases (b) Gibbs energy doesn't change.

2) What is the order of reaction whose rate constant has the same unit as the rate of reaction?

Answer – Zero order reaction

3) What is the overall order of reaction which has the rate expression  $r = k [A]^2 [B]^0$ ?

Answer –  $2+0 = 2^{\text{nd}}$  order reaction

4) Unit of  $1^{\text{st}}$  order reaction and pseudo  $1^{\text{st}}$  order reaction is same. This statement is true or not.

Answer – True

5) If a  $1^{\text{st}}$  order reaction takes 90 minutes for 75% completion. What will be its half-life?

Answer - 45 minutes.

6) A reaction is  $2^{\text{nd}}$  order in A. How is the rate affected if the concentration of A is doubled?

Answer – rate of reaction becomes quadruples.

7) How is the rate constant affected when temperature is raised by  $10^{\circ}\text{C}$ ?

Answer – Generally the rate constant becomes doubled.

8) Define the term instantaneous rate of reaction.

Answer – The change in concentration of either reactants or products when time interval is taken as zero.

9) How the half-life of a reaction varies with change in initial concentration of a reactant?

Answer –  $t_{1/2} \propto [R_0]^{1-n}$ , where n is the order of reaction.

10) What is the unit of rate constant of a  $3/2$  order reaction?

Answer –  $\text{mol}^{-1/2} \text{L}^{1/2} \text{s}^{-1}$

### SHORT ANSWER TYPE QUESTIONS (2/3 MARK)

1) In a reaction  $2A \rightarrow B$ , the concentration of A decreases from 0.5 M to 0.4 M in 10 minutes. Calculate the rate during this time interval.

Answer – rate =  $-1/2 \Delta[A]/\Delta t$ , =  $- [0.40-0.50]/10$ , =  $0.01 \text{ mol L}^{-1} \text{ s}^{-1}$

2) The rate constant of a first order reaction is  $60 \text{ s}^{-1}$ . How much time it will take to reduce the concentration of the reactant to  $1/10^{\text{th}}$  of its initial value?

Answer –  $t = 2.303/k \log [R]_0/[R]$ , =  $2.303/60 \log 10$ , =  $3.8 \times 10^{-2}$  seconds.

3) A  $1^{\text{st}}$  order reaction has the rate constant  $k = 5.5 \times 10^{-12} \text{ s}^{-1}$ . Find its half-life.

Answer –  $t_{1/2} = 0.693/k$ , =  $0.693/5.5 \times 10^{-12}$ , =  $1.3 \times 10^{11}$  sec.

4) Show that a  $1^{\text{st}}$  order reaction takes 10 times more time to complete 99.9% reaction than its half-life.

Answer –  $t_{1/2} = 0.693/k$

Find  $t_{99.9} = 2.303/k \log 100/0.1$ , =  $2.303/k \cdot 3 \log 10$ , =  $6.909/k$

Compare  $t_{1/2}$  &  $t_{99.9}$  we get  $t_{99.9} = t_{1/2} \times 10$

5) The decomposition of  $\text{NH}_3$  on Pt surface is a zero order reaction. What are the rate of formations of  $\text{N}_2$  &  $\text{H}_2$  if  $k = 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$ .

Answer – rate of formation of  $\text{N}_2 = 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$  &

rate of formation of  $\text{H}_2 = 7.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$

6) A 1<sup>st</sup> order reaction is 40% complete in 50 minutes. Calculate the value of rate constant. At what time will the reaction be 80% completed?

Answer – find k by taking values a = 100 & a-x = 60 i.e. = 0.01028 min<sup>-1</sup> and then using this value of k, find the time when the reaction will complete 80%, i.e. = 156.52 min.

7) The following results have been obtained during the kinetic studies of the reaction 2A+B → C+D. Write the rate law expression.

Expt.	[A] mol L <sup>-1</sup>	[B] molL <sup>-1</sup>	Initial rate of formation of D ,molL <sup>-1</sup> min <sup>-1</sup>
1	0.1	0.1	6.0 x 10 <sup>-3</sup>
2	0.3	0.2	7.2 x 10 <sup>-2</sup>
3	0.3	0.4	2.88 x 10 <sup>-1</sup>
4	0.4	0.1	2.4 x 10 <sup>-2</sup>

Ans: Initial rate = k[A]<sup>x</sup> [B]<sup>y</sup>

$$k(0.1)^x(0.1)^y = 6.0 \times 10^{-3} \quad \text{-----(1)}$$

$$k(0.3)^x(0.2)^y = 7.2 \times 10^{-2} \quad \text{-----(2)}$$

$$k(0.3)^x(0.4)^y = 2.88 \times 10^{-1} \quad \text{-----(3)}$$

$$k(0.4)^x(0.1)^y = 2.4 \times 10^{-2} \quad \text{-----(4)}$$

$$\text{eq:3/eq:2 } 2^y = 4$$

$$y = 2$$

$$\text{eq:4/eq:1 } 4^x = 4$$

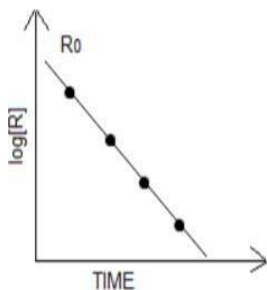
$$x = 1$$

Therefore; rate = k[A][B]<sup>2</sup>

8. Observe the graph in diagram and answer the following questions.

(i) If slope is equal to -2.0x10<sup>-6</sup>sec<sup>-1</sup>, what will be the value of rate constant?

(ii) How does the half-life of zero order reaction related to its rate constant?



Ans: i) Slope = -k where k = -2.0x10<sup>-6</sup>sec<sup>-1</sup>

1+1

ii) t<sub>1/2</sub> = R<sub>0</sub>/2k

9. Define order of reaction ? Write the condition under which a bi molecular reaction follows first order kinetics.

Ans. Sum of powers of the concentration of the reactants in the rate law expression. When one of the reactant is present in large excess.

10. A first order reaction is 40% complete in 80 minutes. Calculate the value of rate Constant (k). In what time will the reaction be 90% completed?

3

[Given: log 2=0.3010,log 3=0.4771,log4=0.6021,log 5 =0.6771,log 6=0.7782]

$$\begin{aligned}
 k &= \frac{2.303}{t} \log \frac{[A]_0}{[A]} \\
 &= \frac{2.303}{80} \log \frac{100}{60} \\
 &= \frac{2.303}{80} \times (1 - 0.7782) \\
 &= 0.0064 \text{ min}^{-1} \\
 t &= \frac{2.303}{k} \log \frac{[A]_0}{[A]} \\
 &= \frac{2.303}{0.0064} \log \frac{100}{10} \\
 &= 360 \text{ min}
 \end{aligned}$$

### 5 MARKS QUESTION

1. (a) 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.

(b) Reaction is first order in A and second order in B.

Write the differential rate equation. How is the rate affected on increasing the concentration of B three times? How is the rate affected when the concentrations of both A and B are doubled?

Ans. (a) Given  $t_{1/2} = 5730$  years,  $[\text{R}]_0 = 100$ ,  $[\text{R}] = 80$

$$K = 0.693/t_{1/2} = 0.693/5730 = 1.21 \times 10^{-4} \text{ year}^{-1}$$

$$t = (2.303/K) \log[\text{R}]_0/[\text{R}] = (2.303/1.21 \times 10^{-4}) \log 100/80 = (1.9033 \times 10^4)(\log 100 - \log 80)$$

$$= 1.9033 \times 10^4 (2 - 1.9031) = 1.9033 \times 10^4 (0.0969) = 1845 \text{ year}$$

(b) (i) Rate =  $K[\text{A}]^1 [\text{B}]^2$

(ii) Rate =  $K[\text{A}]^1 [3\text{B}]^2 = 9K[\text{A}]^1 [\text{B}]^2$  hence, it becomes 9 times.

(iii) Rate =  $K[2\text{A}]^1 [2\text{B}]^2 = 8K[\text{A}]^1 [\text{B}]^2$  hence, it becomes 8 times.

2. 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?**

**Ans.** Let the order of the reaction with respect to A be  $x$  and with respect to B be  $y$ .

Therefore,  $r_0 = k[\text{A}]^x [\text{B}]^y$

$5.07 \times 10^{-5} = k[0.20]^x [0.30]^y$  .....(i)

$5.07 \times 10^{-5} = k[0.20]^x [0.10]^y$  .....(ii)

$1.43 \times 10^{-4} = k[0.40]^x [0.05]^y$  .....(iii)

Dividing equation (i) by (ii), we obtain

$$\frac{5.07 \times 10^{-5}}{5.07 \times 10^{-5}} = \frac{k[0.20]^x [0.30]^y}{k[0.20]^x [0.10]^y}$$

$$1 = \frac{[0.30]^y}{[0.10]^y}$$

$$\left(\frac{0.30}{0.10}\right)^0 = \left(\frac{0.30}{0.10}\right)^y$$

$y = 0$

Continue in next column

Dividing equation (iii) by (ii), we obtain

$$\frac{1.43 \times 10^{-4}}{5.07 \times 10^{-5}} = \frac{k[0.40]^x [0.05]^y}{k[0.20]^x [0.30]^y}$$

$$\frac{1.43 \times 10^{-4}}{5.07 \times 10^{-5}} = \frac{[0.40]^x}{[0.20]^x} \left[ \begin{matrix} \text{Since } y = 0, \\ [0.05]^y = [0.30]^y = 1 \end{matrix} \right]$$

$$2.821 = 2^x$$

$$\log 2.821 = x \log 2 \quad (\text{Taking log on both sides})$$

$$x = \frac{\log 2.821}{\log 2}$$

$$= 1.496$$

$$= 1.5 \text{ (approximately)}$$

Hence, the order of the reaction with respect to A is 1.5 and with respect to B is zero.

3) (a) For a reaction  $A+B \longrightarrow P$ , the rate is given by  $\text{Rate} = k[A][B]^2$  2+3

(i) How is the rate of reaction affected if the concentration of B is doubled?

(ii) What is the overall order of reaction if A is present in large excess?

(b) A first order reaction takes 30 minutes for 50% completion. Calculate the time required for 90% completion of this reaction. ( $\log 2 = 0.3010$ )

Ans. a) (i) Rate will increase 4 times of the actual rate of reaction 2+3

ii) 2<sup>nd</sup> order

$$= 0.693/k$$

$$30 \text{ min} = 0.693/k$$

$$k = 0.0231 \text{ min}^{-1}$$

$$k = \frac{2.303}{t} \log \frac{[A_0]}{[A]}$$

$$t = \frac{2.303}{0.0231} \log \frac{100}{10}$$

$$t = \frac{2.303}{0.0231} \text{ min}$$

$$t = 99.7 \text{ min}$$

3. For the hydrolysis of methyl acetate in aqueous solution, the following results were obtained

t/s	0	30	60
$[\text{CH}_3\text{COOCH}_3]$ $\text{mol L}^{-1}$	0.60	0.30	0.15

(i) Show that it follows pseudo first order reaction, as the concentration of water remains constant.

(ii) Calculate the average rate of reaction between the time intervals 30 to 60 seconds. (Given  $\log 2 = 0.3010$ ,  $\log 4 = 0.6021$ )

Ans

$$(i) \quad K = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$$

where  $[A]_0$  = Initial concentration of reactant

$[A]$  = Final concentration of reactant.

At  $t_1 = 30 \text{ sec}$ ,

$$K = \frac{2.303}{30} \log \frac{0.60}{0.30}$$

$$K = 0.07677 \log 2$$

$$K = 0.0231 \text{ s}^{-1}$$

for  $t = 60 \text{ sec}$

$$K = \frac{2.303}{60} \log \frac{0.60}{0.15}$$

$$K = 0.07677 \log 2$$

$$K = 0.0231 \text{ s}^{-1}$$

As 'k' is same for both the readings hence it is pseudo first order reaction.

$$K = \frac{-\Delta[\text{CH}_3\text{COOCH}_3]}{\Delta t}$$

ii)

$$K = -\left(\frac{0.15 - 0.30}{60 - 30}\right)$$

$$= \frac{0.15}{30} = 0.005 \text{ mol L}^{-1}\text{s}^{-1}$$

4. a) The following data were obtained during the first order thermal decomposition of  $\text{SO}_2\text{Cl}_2$  at a constant volume:



Experiment	Time ( $\text{s}^{-1}$ )	Total pressure (atm)
1	0	0.4
2	100	0.7

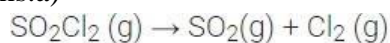
Calculate the rate constant. (Given:  $\log 4 = 0.6021$ ,  $\log 2 = 0.3010$ ) [3]

b) For a reaction:  $2\text{NH}_3(\text{g}) \rightarrow \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$  Rate = k 3+2

(i) Write the order and molecularity of this reaction.

(ii) Write the units of

K Ans. a)



At  $t = 0$ ,  $P_0 = 0.4$

At  $t = t$ ,  $P_0 - P = 0.4 - P$

The total pressure of the thermal decomposition of  $\text{SO}_2\text{Cl}_2$  at time  $t$ ,

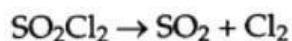
$$P_t = (P_0 - P) + P + P$$

$$P_t = P_0 + P$$

$$\text{Hence, } P = P_t - P_0$$

$$P_0 - P = P_0 - (P_t - P_0) = 2P_0 - P_t$$

We know,



At  $t = 0$  s      0.4 atm    0 atm    0 atm

At  $t = 100$  s     $(0.4 - x)$  atm     $x$  atm     $x$  atm

$$P_t = 0.4 - x + x + x = 0.4 + x$$

$$0.7 = 0.4 + x$$

$$x = 0.3$$

for first order reaction.

$$K = \frac{2.303}{t} \log \frac{P_0}{2P_0 - P_t}$$

$$= \frac{2.303}{100} \log \frac{0.4}{2 \times 0.4 - 0.7} = \frac{2.303}{100} \log \frac{0.4}{0.1}$$

$$K = \frac{2.303 \times 0.602}{100}$$

$$K = 1.386 \times 10^{-2} \text{ s}^{-1}$$

b.(i) zero order, bimolecular/ unimolecular (ii)  $\text{mol L}^{-1}\text{s}^{-1}$

5. a) 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 100s if the initial concentration of A is  $1.0 \text{ mol L}^{-1}$ .

b) 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. 3+2

Ans (a)

The units of  $k$  show that the reaction is of first order.

$$\text{Hence, } k = \frac{2.303}{t} \log \frac{[R_0]}{[R]}$$

$$\text{or, } 2.0 \times 10^{-2} = \frac{2.303}{100} \log \frac{1.0}{[R]}$$

$$\text{or, } \log [R] = -0.8684$$

$$\therefore [R] = \text{Antilog}(-0.8684) = 0.1354 \text{ mol L}^{-1}$$

b)

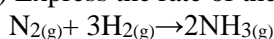
$$\text{Decay constant } (k) = \frac{0.693}{t_{1/2}} = \frac{0.693}{5730} \text{ year}^{-1}$$

$$t = \frac{2.303}{k} \log \frac{[A_0]}{[A]}$$

$$= \frac{2.303}{(0.693/5730 \text{ years}^{-1})} \log \frac{100}{80}$$

$$= \frac{2.303 \times 5730}{0.693} \times 0.0969 = 1845 \text{ years.}$$

6. (i) Express the rate of the following reaction in terms of the formation of ammonia:



If the rate constant of a reaction is  $k = 3 \times 10^{-4} \text{ s}^{-1}$ , then identify the order of the reaction.

(ii) For a reaction  $R \rightarrow P$ , half-life ( $t_{1/2}$ ) is observed to be independent of the initial concentration of reactants. What is the order of reaction?

(iii) Define the following:

- (a) Elementary step in a reaction
- (b) Rate of a reaction

Ans(i)

1+1+1+1+2

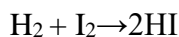
$$\frac{-d[\text{N}_2]}{dt} = \frac{-1}{3} \frac{d[\text{H}_2]}{dt} = +\frac{1}{2} \frac{d[\text{NH}_3]}{dt}$$

(ii)  $\text{s}^{-1}$  is the unit for rate constant of first order reaction.

(iii) The  $t_{1/2}$  of a first order reaction is independent of initial concentration of reactants.

(a) Elementary step in is action: Those reactions which take place in one step are called elementary reactions.

Example: Reaction between  $\text{H}_2$ , and  $\text{I}_2$  to form  $2\text{HI}$



(b) Rate of a reaction : The change in the concentration of anyone of the reactants or products per unit time is called rate of reaction.

7. (a) A reaction is of second order with respect to a reactant. How will the rate of reaction be affected if the concentration of this reactant is Doubled, (ii) reduced to half?

b) The rate constant for a reaction of zero order in A is  $0.0030 \text{ molL}^{-1}\text{s}^{-1}$ . How long will it take for the initial concentration of A to fall from 0.10 M to 0.075 M?

Ans

(a) Since Rate =  $K[A]^2$

For second order reaction Let  $[A] = a$  then Rate =  $Ka^2$

(i) If  $[A] = 2a$  then Rate =  $K(2a)^2 = 4Ka^2$

∴ Rate of reaction becomes 4 times

ii) If  $[A] = a/2$  then Rate =  $K(a/2)^2 = K(a/4)$

Then rate of reaction becomes  $1/4$  times.

b) Time,  $t = \frac{1}{K}[(A)_0 - (A)]$

$$\text{or, } t = \frac{1}{0.003} (0.10 - 0.075)$$

$$\therefore \text{Time, } t = \frac{1}{0.003} \times \frac{0.025}{1} = \frac{25}{3} = 8.3 \text{ seconds}$$

7. a) Distinguish between 'rate expression' and 'rate constant' of a reaction. 2+3

b) Rate constant  $k$  for a first order reaction has been found to be  $2.54 \times 10^{-3} \text{ sec}^{-1}$ .

Calculate its  $3/4^{\text{th}}$  life, ( $\log 4 = 0.6020$ )

Ans: a. Rate Expression: The expression which expresses the rate of reaction in terms of molar concentrations of the reactants with each term raised to their power, which may or may not be same as the stoichiometric coefficient of that reactant in the balanced chemical equation.

Rate constant: The rate of reaction when the molar concentration of each reactant is taken as unity.

b) For first order reaction:

$$\begin{aligned} t_{3/4} &= \frac{2.303}{k} \log 4 \\ &= \frac{2.303}{2.54 \times 10^{-3} \text{ sec}^{-1}} \times 0.6020 = 545.8 \text{ sec.} \\ &= 9.09 \text{ min.} \end{aligned}$$

8. a) Write two differences between 'order of reaction' and 'molecularity of reaction' 3+2

a) If the half-life period of a first order reaction in A is 2 minutes, how long will it take [A] to reach 25% of its initial concentration?

Ans ( a)

Order of reaction	Molecularity of reaction
(i) It is the sum of powers raised on concentration terms in the rate expression.	It is the number of atoms, ions or molecules that must collide with one another simultaneously so as to result in to a chemical reaction.
(ii) It can be fractional as well as zero.	It is always a whole number.

(b)

$$t = \frac{2.303}{k} \log \frac{[A_0]}{[A]}$$

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

$$2 \text{ min} = \frac{2.303}{k} \log 2$$

$$t_{75\%} = \frac{2.303}{k} \log \frac{100}{25}$$

$$t_{75} = \frac{2.303}{k} \log 4$$

Divide (i) by (ii)

$$\frac{t_{75\%}}{2 \text{ min}} = \frac{\log 4}{\log 2} = \frac{2 \log 2}{\log 2}$$
$$t_{75} = 4 \text{ min}$$

9. (a) For a reaction  $A + B \longrightarrow P$  the rate is given by  $\text{Rate} = k [A]^2 [B]$  2+3

a. How is the rate of reaction affected if the concentration of A is doubled ?

b. What is the overall order of reaction if B is present in large excess ?

(b) A first order reaction takes 23.1 minutes for 50% completion. Calculate the time required for 75% completion of this reaction. (Given :  $\log 2=0.301, \log 3=0.4771, \log 4=0.6021$ ).

Ans: (a) (i) If concentration of A is doubled, the rate of reaction becomes four times.

(ii) If B is present in large excess, overall order of reaction will be equal to 2.

$$(b) \quad t_{1/2} = \frac{0.693}{k} \Rightarrow k = \frac{0.693}{23.1} \text{ min}^{-1} = 0.03 \text{ min}^{-1}$$

$$\text{Now, } t_{3/4} = \frac{2.303}{k} \log \frac{[R]_0}{[R]_0/4}$$

$$\Rightarrow t_{3/4} = \frac{2.303}{0.03} \log 4 = \frac{2.303 \times 0.6021}{0.03}$$

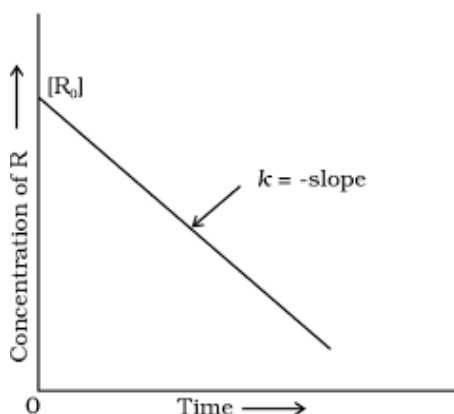
$$\Rightarrow t_{3/4} = \frac{1.386}{0.03} = 46.2 \text{ min}$$

10. (a) Plot a graph showing variation in the concentration of reactants against time for a zero-order reaction. 1+1+3

(b) What do you mean by zero-order reaction?

(c) The initial concentration of the first-order reaction,  $N_2O_5(g) \rightarrow 2NO_2(g) + 1/2O_2(g)$  was  $1.24 \times 10^{-2} \text{ mol L}^{-1}$  at 300K. The concentration of  $N_2O_5$  after '1' hour was  $0.20 \times 10^{-2} \text{ mol L}^{-1}$ . Calculate the rate constant of the reaction at 300K.

Ans: a)





b) It is a reaction for which the rate of the reaction is proportional to zero power of the concentration of reactants, i. e , and order is zero. Or ,this is a reaction for which the rate of the reaction is independent of the concentration of the reactants.

c) For a first order reaction,  $k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$

Given,  $[R]_0 = 1.24 \times 10^{-2} \text{ mol L}^{-1}$ ,

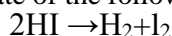
$[R] = 0.20 \times 10^{-2} \text{ mol L}^{-1}$ ,  $t = 1 \text{ hr}$

$$\therefore k = \frac{2.303}{1 \text{ hr}} \log \frac{1.24 \times 10^{-2} \text{ mol L}^{-1}}{0.20 \times 10^{-2} \text{ mol L}^{-1}}$$

$$= 1.8249 \text{ hr}^{-1} = 0.0304 \text{ min}^{-1}$$

11. Rate of a reaction is the change in on concentration of anyone of the Reactants or anyone of the products in unit time.

i) Express the rate of the following reaction in terms of reactants and Products:



ii) If rate expression for the above reaction is,  $\text{rate} = k[\text{H I}]^2$ , What is the Order of the reaction?

iii) Define order of a reaction.

iv) When the molecularity and the order of the above reaction are the same ? Give reason.

$$r = \frac{dx}{dt} = \frac{-1}{2} \frac{d[\text{H I}]}{dt}$$

In terms of products

$$r = \frac{dx}{dt} = \frac{d[\text{H}_2]}{dt} = \frac{d[\text{I}_2]}{dt}$$

$$\text{ie } r = \frac{dx}{dt} = \frac{-1}{2} \frac{d[\text{H I}]}{dt} = \frac{d[\text{H}_2]}{dt} = \frac{d[\text{I}_2]}{dt}$$

ii)  $r = K [\text{H I}]^2$

$\therefore \text{Order} = 2$

(iii) Order is the sum of the powers of the concentration terms in the rate law rate

$$= K[\text{A}]^x [\text{B}]^y$$

$$\therefore \text{Order} = x+y$$

iv) Yes.  $2\text{HI} \longrightarrow \text{H}_2 + \text{I}_2$   $\text{rate} = K[\text{HI}]^2 \therefore \text{Order} = 2$

Molecularity is the number of reacting species taking part in an elementary reaction which must collide simultaneously in order to bring about a chemical reaction.

$\therefore$  Here molecularity = 2

$[\text{N}_2\text{O}_5](\text{M})$	Time(min)
0.400	0.00
0.289	20.0
0.209	40.0
0.151	60.0
0.109	80.0

12. Nitrogen pentoxide decomposes according to equation:

3+1+1



This first order reaction was allowed to proceed at 40° Can be the data below were collected:

- (a) Calculate the rate constant. Include units with your answer.  
 (b) What will be the concentration of  $\text{N}_2\text{O}_5$  after 100 minutes?  
 (c) Calculate the initial rate of reaction

Ans (a)  $k = 2.303/t \log[A_0]/[A]$

Substituting the values, we get

$$K = \frac{2.303}{20} \log \frac{0.400}{0.289}$$

or  $K = \frac{2.303}{20} \log 1.3840$

or  $K = 0.11515 \log 1.3840$

$\therefore K = 0.0163 \text{ min}^{-1}$

(b)  $K = \frac{2.303}{t} \log \frac{[A_0]}{[A]}$

$\therefore 0.0163 = \frac{2.303}{100} \log \frac{0.400}{[A]}$

or  $\log \frac{0.400}{[A]} = \frac{0.0163 \times 100}{2.303}$

or  $\log \frac{0.400}{[A]} = 7.0777$

$\therefore [A] = 0.078 \text{ M}$

(c) Initial Rate,  $R = K [\text{N}_2\text{O}_5]$   
 $= 0.0163 \text{ min}^{-1} (0.400 \text{ M})$   
 $= 0.00652 \text{ M min}^{-1}$

13. (a) 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, what is the order of the reaction with respect to A and B.

b) For a reaction  $\text{R} \rightarrow \text{P}$ , half-life ( $t_{1/2}$ ) is observed to be independent of the initial concentration of reactants. What is the order of reaction?

c. Identify the order of a reaction if the units of its rate constant are  $\text{L}^{-1} \text{mols}^{-1}$

a)

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

$$\text{Rate} = [\text{A}]^\alpha [\text{B}]^\beta$$

$$r_1 = 5.07 \times 10^{-5} = (0.20)^\alpha (0.30)^\beta \quad \dots(i)$$

$$r_2 = 5.07 \times 10^{-5} = (0.20)^\alpha (0.10)^\beta \quad \dots(ii)$$

$$r_3 = 1.43 \times 10^{-4} = (0.40)^\alpha (0.05)^\beta \quad \dots(iii)$$

$$\frac{r_1}{r_2} = \frac{5.07 \times 10^{-5}}{5.07 \times 10^{-5}} = \frac{(0.2)^\alpha (0.30)^\beta}{(0.2)^\alpha (0.10)^\beta} = 1 = (3)^\beta$$

$\therefore \beta = 0$

$$\frac{r_3}{r_2} = \frac{1.43 \times 10^{-4}}{5.06 \times 10^{-5}} = \frac{(0.40)^\alpha (0.05)^\beta}{(0.20)^\alpha (0.10)^\beta}$$

$$= 2.826 = 2^\alpha \left(\frac{1}{2}\right)^\beta$$

$$2.826 = 2^\alpha \quad (\text{as } \beta = 0)$$

Taking log on both the sides, we get

$$\log 2.826 = \alpha \log 2$$

$$\Rightarrow 0.4511 = \alpha \times 0.3010$$

$$\alpha = \frac{0.4511}{0.3010} = 1.498 \approx 1.5$$

$\therefore$  Order with respect to A = 1.5

and order with respect to B = 0

b) The  $t_{1/2}$  of a first order reaction is independent of initial concentration of reactants.

c) Zero order reaction.

14. a) The thermal decomposition of  $\text{HCO}_2\text{H}$  is a first-order reaction with a rate constant of  $2.4 \times 10^{-3} \text{ s}^{-1}$  at a certain temperature. Calculate how long will it take for three-fourths of the initial quantity of  $\text{HCO}_2\text{H}$  to decompose, ( $\log 0.25 = -0.6021$ ) 3+2

(b) The decomposition of phosphine,  $\text{PH}_3$ , proceeds according to the following equation :

It is found that the reaction follows the following rate equations:  $4\text{PH}_3(\text{g}) \rightarrow \text{P}_4(\text{g}) + 6\text{H}_2(\text{g})$

It is found that the reaction follows the following rate equations: Rate

$$= k[\text{PH}_3]$$

The half-life of  $\text{PH}_3$  is 37.9 s at  $120^\circ\text{C}$

(i) How much time is required for  $3/4$  of  $\text{PH}_3$  to decompose?

(ii) What fraction of the original sample of  $\text{PH}_3$  remains behind after 1 minute?

Ans

3+2

$$t = \frac{2.303}{k} \log \frac{a}{a-x}$$

$$k = 2.4 \times 10^{-3}$$

$$x = \frac{3}{4} = 0.75$$

$$t = \frac{2.303}{2.4 \times 10^{-3}} \log \frac{1}{1-0.75}$$

$$= \frac{2.303}{2.4 \times 10^{-3}} \log 0.25$$

$$= \frac{2.303}{2.4 \times 10^{-3}} \times 0.6020 = 577.6 \text{ sec.}$$

(b) (i) Hence  $t_{1/2} = 37.9 \text{ s}$

Let initial concentration = a

$$x = \frac{3}{4} a$$

$$t = \frac{2.303}{k} \log \frac{a}{a-x}$$

$$t = \frac{2.303}{0.693} \log \frac{a}{\frac{1}{4}a}$$

$$t_{1/2} = \frac{2.303 \times 37.9}{0.693} \log 4$$

$$t = \frac{2.303 \times 37.9 \times 0.6010}{0.693}$$

$$t = 75.82 \text{ s.}$$

(ii)  $\log \frac{[C_0]}{[C_1]} = \frac{K \times 60}{2.303}$

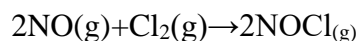
$$K = \frac{2.303 \log 2}{37.9}$$

$$\log \frac{[C_0]}{[C_1]} = \frac{60}{37.9} \log 2$$

$$\frac{[C_0]}{[C_1]} = 2.99$$

$$\frac{[C_0]}{[C_1]} = 0.334 = \text{Fraction of PH}_3 \text{ after 1 minute}$$

15. (i) For the reaction



the following data were collected. All the measurements were taken at 263K:

- Write the expression for rate law.
- Calculate the value of rate constant and specify its units.
- What is the initial rate of disappearance of  $\text{Cl}_2$  in exp.4?

Experiment No.	Initial [NO](M)	Initial [Cl <sub>2</sub> ](M)	Initial rate of disappearance of Cl <sub>2</sub> (M/min)
1	0.15	0.15	0.60
2	0.15	0.30	1.20
3	0.30	0.15	2.40
4	0.25	0.25	?

- (iii) If half life period of first order reaction is x and 3/4 life period of same reaction is 'y' how are V and 'y' related to each other?

Ans: (i) 1+2+3

(a) Rate law =  $k[\text{NO}]^2 [\text{Cl}_2]$

(b) (ii)  $0.60 \text{ M min}^{-1} = K [0.15]^2 [0.15] \text{M}^3$

$\therefore k = 177.7 \text{ M}^{-2} \text{ min}^{-1}$

(iii) Initial rate of disappearance of  $\text{Cl}_2$  in exp. 4 Formula :

Rate =  $K[\text{NO}]^2 [\text{Cl}_2]$

$\therefore$  Initial rate =  $177.7 \text{ M}^{-2} \text{ min}^{-1} \times (0.25)^2 \times (0.25) \text{ M}^3 = 2.8 \text{ M min}^{-1}$

(ii)

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

$$\Rightarrow t_{1/2} = \frac{0.693}{k} = x \quad \dots(i)$$

$$t_{3/4} = \frac{2.303}{k} \log \frac{[\text{R}]_0}{[\text{R}]_0/4}$$

$$= \frac{2.303}{k} \log 4 = \frac{2.303}{k} \times 0.6021$$

$$\Rightarrow t_{3/4} = \frac{1.386}{k} = y \quad \dots(ii)$$

From (i) and (ii), we get

$$y = 2x$$

$$[\because t_{3/4} = 2t_{1/2}]$$

## SURFACE CHEMISTRY

The branch of chemistry deals with the surface phenomenon is called surface chemistry.

i) Adsorption – The accumulation of species at the surface rather than in bulk of an adsorbent is called adsorption.

ii) Desorption – Removal of adsorbed particles from the surface of an adsorbent is called desorption. It is essential so that the new reactant molecules can adsorb & reaction is going on.

(iii) Adsorption – Adsorption & absorption both take place simultaneously.

(iv) Types of adsorptions –

**Physical adsorption** – weak vander Waal force involved, reversible, decreases with increase of temperature, enthalpy of adsorption is low.

**Chemical adsorption** – strong chemical bond involved, irreversible, first increases with increase of temperature and then decreases, enthalpy of adsorption is high.

(v) Adsorption isotherm – The variation in the amount of gas adsorbed by the adsorbent with pressure at constant temperature can be expressed by a graph, called adsorption isotherm.

(vi) Factors affecting adsorption:

(a) Increase with increase in surface area.

(b) Low temp is favorable for physical adsorption & high temp for chemical adsorption

(c) Increases with increase of pressure.

(d) Easily liquefiable gases are readily adsorbed.

(vii) Colloid – a heterogeneous system in which a substance is dispersed (1-1000nm size) in another substance called dispersion medium.

(viii) Dialysis – process to remove the unwanted substances from a colloidal system using a membrane.

(ix) Electro dialysis – when dialysis takes place in electrical field to remove ionic impurities.

(x) Brownian movement-Zig-zag motion of colloidal particles is called Brownian movement.

(xi) Tyndall effect – scattering of beam of light by the colloidal particles is called Tyndall effect so that the path of the light becomes visible.

(xii) Electrophoresis – the movement of colloidal particles towards one of the electrodes when an electric field is applied. (Reason - because the colloidal particles have same charge.)

(xiii) Peptization – converting a freshly prepared precipitate into a colloidal solution using a suitable medium, in the presence of trace of an electrolyte called peptizing agent, is called peptization.

(xiv) Coagulation – process of settling down or precipitation of colloidal particles using various methods (heating, shaken or an electrolyte is added) is called coagulation. The electrolyte used for the coagulation a colloid is called coagulating agent.

(xv) Hardy Schulz rule – the coagulating or flocculating power of an ion is directly proportional to the charge on the ion. More charge = more coagulating power.

$\text{Na}^+ < \text{Mg}^{2+} < \text{Al}^{3+}$  - for coagulating negatively charged colloids.

$\text{Cl}^- < \text{SO}_4^{2-} < \text{PO}_4^{3-}$  for coagulating positively charged colloids.

(xvi) A potential develops between fixed layer and diffused layer around colloidal particles in a colloidal system is called ZETA potential.

### 1. VERY SHORT ANSWERS TYPE QUESTIONS (1 mark each)

(i) What are the appropriate conditions favorable for physical adsorption?

Ans - Low T, high P & greater surface area.

ii) What happens when a freshly prepared precipitate of  $\text{Fe}(\text{OH})_3$  is treated with  $\text{FeCl}_3$  solution in water?

Ans- Peptization takes place (Colloidal solution of hydrated  $\text{Fe}_2\text{O}_3$  is formed)

iii) In chemisorptions, enthalpy of adsorption is high. Give reason.

Ans- Due to stronger chemical bond formation between adsorbent & adsorbate.

iv) What is the charge on  $\text{AgI}$  colloidal sol formed when  $\text{AgNO}_3$  is added to excess of  $\text{KI}$ ?

Ans- Negative charged  $\text{Ag I/I}^-$

v) What are the main reasons for the stability of colloidal sol?

Ans- Similar Charge on colloidal particles and Brownian movement.

vi) Write the dispersed phase and dispersion medium of milk.

Ans – Both are liquids. (Milk is an oil in water type emulsion)

vii) Write one similarity between Physisorption & Chemisorptions.

Ans - Both are exothermic processes and surface phenomenon.

viii) What is protective colloid?

Ans – Lyophilic colloids which protect the lyophobic colloids from coagulation are called protective colloids.

ix) What is coagulation?

Ans – Precipitation of colloidal particles is called coagulation. It is the reverse process of peptization.

x) Colloids can exhibit Tyndall effect. Why?

Ans – Colloidal particles are **big enough to scatter beam of light**.

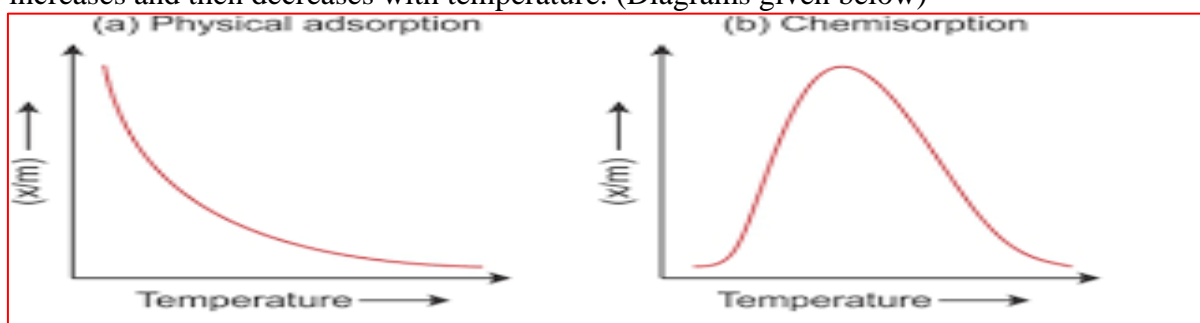
## 2. SHORT ANSWERS TYPE QUESTIONS (2 marks each)

(a) Compare lyophilic and lyophobic sols. (Any two points)

Ans – Lyophilic sols are formed easily and more stable whereas lyophobic sols formed with mechanical or chemical efforts and are less stable.

(b) Explain the effect of temperature on physical and chemical adsorption.

Ans – Physical adsorption decreases with increase of temperature whereas chemical adsorption first increases and then decreases with temperature. (Diagrams given below)



(c) Why is adsorption always exothermic?

Ans - Adsorption is always exothermic because the force of attraction (physical or chemical) increases when particles of a dispersed phase are adsorbed on the surface of dispersion medium and we know that whenever force of attraction increases (Bond formation) the certain amount of energy is released ( $-\Delta H$ ).

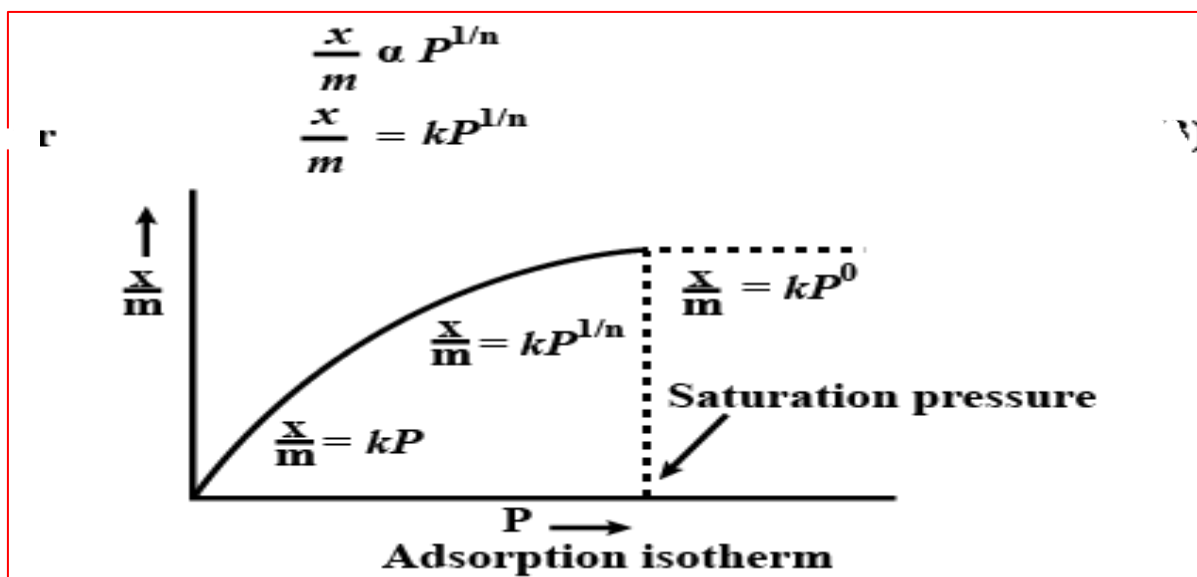
(d) How are Multimolecular and associated colloids different?

Ans – Multimolecular colloids means the aggregation of molecules in colloidal dimension whereas associated colloids mean the aggregation of ions when concentration of dispersed phase is equal to or greater than CMC. Exa. Gold sol is the example of Multimolecular colloids and micelle is

the example of associated colloids.

(e) What is meant by adsorption isotherm? Write equations for the adsorption of gases on solid surface and adsorption from solutions.

Ans – Adsorption isotherm is the graphical representation to show effect of pressure or concentration of a solution on rate of adsorption at constant temperature.



**$x/m = k \cdot p^{1/n}$  (for gases) &  $x/m = k \cdot C^{1/n}$  (for solution)**

**3. SHORT ANSWERS TYPE QUESTIONS (3 marks each)**

1. List any three point of difference between Physical & Chemical adsorption.

Ans- (Learn any three)

Physical adsorption	Chemical adsorption
1. The forces operating in this case are weak Vander wall's forces.	1. The Forces operating are chemical bonds (ionic or covalent bond).
2. The heat of adsorption is low about 20-40 KJ mol <sup>-1</sup>	2. The heat of absorption are high about 40-400 KJ mol <sup>-1</sup>
3. The process is reversible, desorption can be occur by increasing tem. Or decreasing pressure.	3. The process is irreversible. Efforts to free the adsorbed gas give different Compounds.
4. It does not require any activation energy.	4. It requires activation chergy.
5. It takes place at the low temperature and decreases with increase in the temperature.	5. This type of adsorption first increases with increase in temperature
6. It is not specific in nature all gases adsorbes on all solids to same extent.	6. It is highly specific in nature occurs only by the possibility of formation of chemical bond.
7. It increases with the increase insurface area of the adsorbent.	7. It also increases with the increases with the increase in surface area of adsorbent.
8. It forms multimolecular layer.	8. It forms unimolecular layer.

2. Give reason –

- a) Finally divided substance is more effective as an adsorbent.
- b) Physical adsorption is reversible whereas chemical adsorption is irreversible.
- c) Lyophilic sols protect lyophobic sols from coagulation.

Ans - (a) Finally divided substance has greater of surface area.



(b) Physical adsorption is caused by weak Vander Waals forces whereas chemical adsorption is caused by formation of bonds.

(c) Lyophilic sols form a protective layer around the lyophobic sol particles.

3. What happens when-?

(a) A beam of light is passed through a colloidal sol.

(b) An electrolyte NaCl is added to hydrated ferric oxide sol.

(c) Electric current is passed through a colloidal sol.

Ans – (a) Path of light becomes visible due to Tyndall effect.

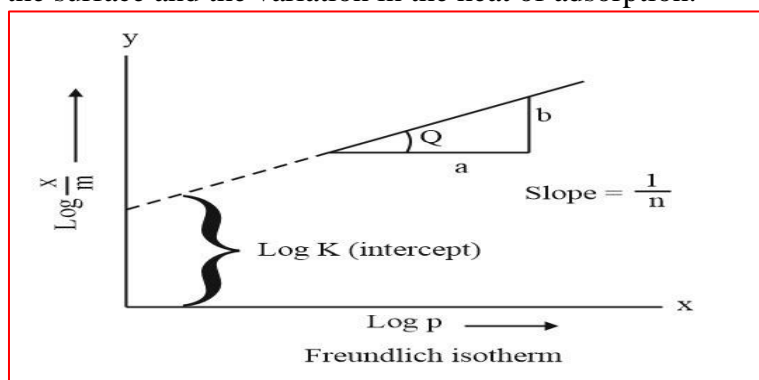
(b) Coagulation of hydrated ferric oxide sol takes place.

(c) All the colloidal particles having same charge so they move towards oppositely charged electrode.

#### **4. CASE STUDY BASED QUESTION (5 MARKS EACH)**

1. Read the passage carefully and observe the graph and answer questions (a) to (e).

The Freundlich equation or Freundlich adsorption isotherm, an adsorption isotherm, is an empirical relationship between the quantity of a gas adsorbed into a solid surface and the gas pressure. The same relationship is also applicable for the concentration of a solute adsorbed onto the surface of a solid and the concentration of the solute in the liquid phase. In 1909, Herbert Freundlich gave an expression representing the isothermal variation of adsorption of a quantity of gas adsorbed by unit mass of solid adsorbent with gas pressure. This equation is known as Freundlich adsorption isotherm or Freundlich adsorption equation. As this relationship is entirely empirical, in the case where adsorption behavior can be properly fit by isotherms with a theoretical basis, it is usually appropriate to use such isotherms instead (see for example the Langmuir and BET adsorption theories). The Freundlich equation is also derived (non-empirically) by attributing the change in the equilibrium constant of the binding process to the heterogeneity of the surface and the variation in the heat of adsorption.



a) What value is shown by  $x/m$  in the graph?

b) What is the slope of this graph? What is the range of slope?

c) What does the intercept of line represent?

d) Write the logarithmic representation of this graph.

e) What modification is made during adsorption from a solution by a solid adsorbent?

Ans – (a) rate of adsorption

(b)  $1/n$  and its value are ranging between 0-1

(c)  $\log k$  where  $k$  is a constant and its value depends upon nature of adsorbate & adsorbent.

d)  $\log x/m = \log k + 1/n \log p$

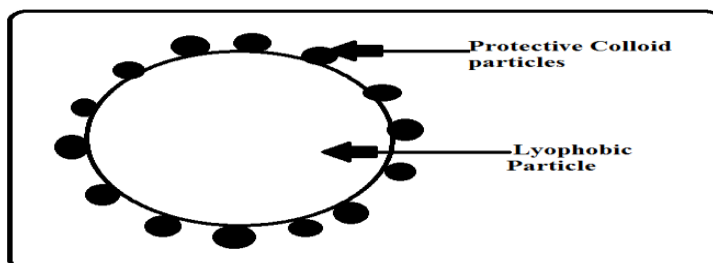
e) Concentration is taken into consideration in place of pressure.

2. Read the passage given below and answer the questions that follow-

We should know that a protective colloid is a lyophilic colloid that when present in small quantities keeps lyophobic colloids from precipitating under the coagulating action of

electrolytes. We should know that lyophilic sols are more stable than lyophobic sols. It is due to the fact that lyophilic colloids are extensively solvated that means colloidal particles are covered by a sheath of the liquid in which they are dispersed.

It is interesting to know that 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. Some examples of protective colloids that we should remember are mentioned below along with their gold number. Knowledge of the gold number is important. We should know that Gold Number is the number of milligrams of a protective colloid which prevents the coagulation of 10 ml of a standard hydro gold sol, on coagulation changes from red to blue, which is prevented by a protective colloid. Coagulation of gold sol is indicated by colour change from red to blue/purple when particle size just increases. We should know that more is the gold number; less is the protective power of the lyophilic colloid since it means that the amount required is more. The amount is taken in terms of weight in milligrams. Starch (gold no. =25), Gum Arabic (gold no. =0.15), Egg albumin (gold no. =0.08) Gelatin (gold no.=0.005)

- If water is a dispersion medium then the sols are called ----- & -----.
- Which one from the given in the passage is the best protective colloid?
- How is the protective power of a lyophilic colloid related with the Gold Number?
- Lyophobic sols are more stable and therefore no protection is required at all. This statement is TRUE or FALSE.
- How does an electrolyte coagulate the lyophobic sols?

Ans – (a) Hydrophilic & Hydrophobic

(b) Gelatin

(c) Less Gold Number, more protective power.

(d) FALSE

(e) Oppositely charged ion of the electrolyte neutralizes the charge of sol particles and coagulate.

### The d & f Block Elements

The d -Block elements:

a) The elements lying in the middle of periodic table belonging to groups 3 to 12 are known as d – block elements.

b) Their general electronic configuration is  $(n - 1)d^{1-10}ns^{1-2}$  where  $(n - 1)$  stands for penultimate (last but one) shell.

• Transition element:

a) 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.

b) Zinc, cadmium, mercury are not regarded as transition metals due to completely filled  $d$  – orbital.

• The f-Block elements:

The elements constituting the *f*-block are those in which the 4*f* and 5*f* orbitals are progressively filled in the latter two long periods.

- Lanthanoids:

The 14 elements immediately following lanthanum, i.e., Cerium (58) to Lutetium (71) are called lanthanoids. They belong to first inner transition series. Lanthanum (57) has similar properties. Therefore, it is studied along with lanthanoids.

- Actinoids:

The 14 elements immediately following actinium (89), with atomic numbers 90 (Thorium) to 103 (Lawrencium) are called actinoids. They belong to second inner transition series. Actinium (89) has similar properties. Therefore, it is studied along with actinoids.

- Four transition series:

a) 3d – transition series. The transition elements with atomic number 21(Sc) to 30(Zn) and having incomplete 3d orbital's is called the first transition series.

b) 4d – transition series. It consists of elements with atomic number 39(Y) to 48 (Cd) and having incomplete 4d orbital's. It is called second transition series.

c) 5d – transition series. It consists of elements with atomic number 57(La), 72(Hf) to 80(Hg) having incomplete 5d orbital's. It is called third transition series.

d) 6d – transition series. It consists of elements with atomic number 89(Ac), 104(Rf) to 112 (Uub) having incomplete 6d orbital's. It is called fourth transition series.

- **General Characteristics of transition elements:**

a) Metallic character:

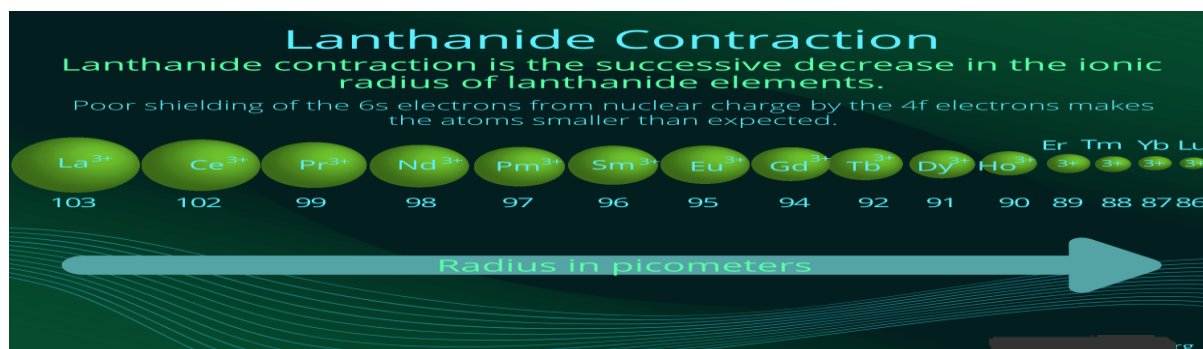
All transition elements are metallic in nature, i.e. they have strong metallic bonds. This is because of presence of unpaired electrons. This gives rise to properties like high density, high enthalpies of atomization, and high melting and boiling points.

b) Atomic radii: The atomic radii decrease from Sc to Cr because the effective nuclear charge increases. The atomic size of Fe, Co, Ni is almost same because the attraction due to increase in nuclear charge is cancelled by the repulsion because of increase in shielding effect. Cu and Zn have bigger size because the shielding effect increases and electron- electron repulsions increases.

c) Lanthanoid Contraction:

The steady decrease in the atomic and ionic radii of the transition metals as the atomic number increases is called lanthanoid contraction. This is because of filling of 4*f* orbital's before the 5*d* orbitals which show poor shielding effect. This contraction in size is quite regular. This is called lanthanoid contraction.

It is because of lanthanoid contraction that the atomic radii of the second row of transition elements are almost similar to those of the third row of transition elements.



d) Ionisation enthalpy: There is slight and irregular variation in ionization energies of transition metals due to irregular variation of atomic size. The I.E. of 5d transition series is higher than 3d and 4d transition series because of Lanthanoid Contraction.

e) Oxidation state:

Transition metals show variable oxidation states due to tendency of (n-1)d as well as ns electrons to take part in bond formation.

f) Magnetic properties:

Most of transition metals are paramagnetic in nature due to presence of unpaired electrons. It increases from Sc to Cr and then decreases because number of unpaired electrons increases from Sc to Cr and then decreases.

g) Catalytic properties:

Most of transition metals are used as catalyst because of (i) presence of incomplete or empty d – orbital's, (ii) large surface area, (iii) variable oxidation state, (iv) ability to form complexes, e.g., Fe, Ni, V<sub>2</sub>O<sub>3</sub>, Pt, Mo, Co and used as catalyst.

h) Formation of coloured compounds:

They form coloured ions due to presence of incompletely filled d – orbital's and presence of unpaired electrons, which undergo d – d transition by absorbing colour from visible region and radiating complementary colour.

i) Formation of complexes:

Transition metals form complexes due to (i) presence of vacant d – orbital's of suitable energy (ii) smaller size (iii) higher charge on cations.

j) Interstitial compounds:

Transition metals have voids or interstitials in which C, H, N, B etc. can fit into resulting in formation of interstitial compounds. They are non – stoichiometric, i.e., their composition is not fixed, e.g., steel. They are harder and less malleable and ductile.

k) Alloys formation: They form alloys due to similar ionic size; metals atoms can replace each other crystal lattice.

### **CASE-BASED/PASSAGE-BASED INTEGRATED QUESTIONS**

Read the given passage and answer the questions that follow:

(I) The d-block of the periodic table contains the elements of the groups 3 to 12 and are known as transition elements. In general, the electronic configuration of these elements is  $(n - 1) d^{1 - 10} ns^{1 - 2}$ .

The d-orbital's of the penultimate energy level in their atoms receive electrons giving rise to the three rows of the transition metals i.e., 3d, 4d and 5d series. However, Zn, Cd and Hg are not regarded as transition elements. Transition elements exhibit certain characteristic properties like variable oxidation states, complex formation, formation of colored ions, alloys, catalytic activity etc. Transition metals are hard (except Zn, Cd and Hg) and have a high melting poi

(a) Why are Zn, Cd and Hg non-transition elements?

Ans. It is because neither they nor their ions have incompletely filled d-orbital's.

(b) Which transition metal of 3d series does not show variable oxidation state?

Ans. Scandium (Sc) and Zinc (Zn).

(c) Why do transition metals and their compounds show catalytic activity?

Ans. It is because they show variable oxidation state, can form intermediate complexes and have large surface area for adsorption of gases.

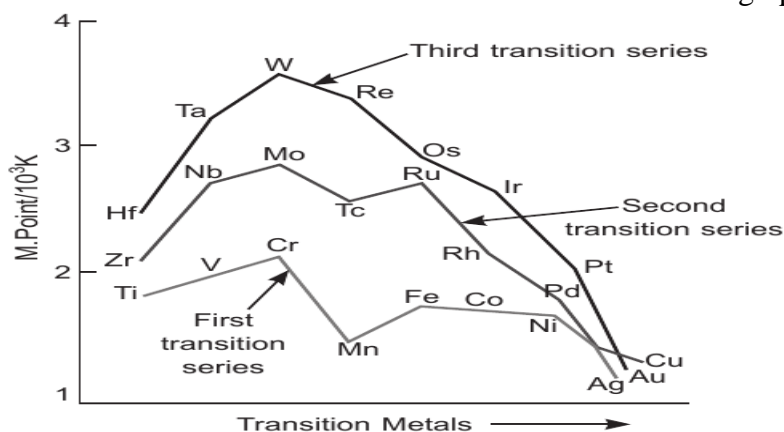
(d) Why are melting points of transition metals high?

Ans. It is due to strong inter atomic forces of attraction due to presence of unpaired electron

(e) Why is  $\text{Cu}^{2+}$  ion coloured while  $\text{Zn}^{2+}$  ion is colorless?

Ans. It is because  $\text{Cu}^{2+}$  has one unpaired electron and undergoes d-d transition by absorbing light from visible region and radiate blue colour, whereas  $\text{Zn}^{2+}$  is colourless due to absence of unpaired

(II) Observe the graph of transition metal and their melting points and answer the questions based on weak metallic bond which is due to absence of the graph and related concepts.



(a) Why does W (tungsten) have highest melting point?

Ans. It is due to presence of unpaired electrons and there is more frequent metal-metal bonding in 5d series than 3d and 4d series.

(b) Which element in 3d series has lowest enthalpy of atomization and why?

Ans. Zinc has lowest enthalpy of atomization due to weak metallic bond which is due to absence of unpaired electrons.

(c) Why is mercury liquid?

Ans. It is due to larger size, absence of unpaired electron and weak inter atomic attraction and weaker metallic bond.

(d) Why are transition metals less electro positive?

Ans. It is due to smaller atomic size and higher ionization enthalpies.

(e) How does density vary from left to right in 3d series and why?

Ans. Density goes on increasing from Sc to Cu because atomic mass increases more than atomic volume.

(III) Observe the table given below belonging to 3d series, their first, second, third ionization enthalpy and  $E^\circ \text{M}^{2+}/\text{M}$  and  $E^\circ \text{M}^{3+}/\text{M}^{2+}$  and answer the questions that follow based on table and related concepts.

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
I <sup>st</sup> ionisation enthalpy	631	656	650	652	717	762	758	736	745	905 kJ ml <sup>-1</sup>
II <sup>nd</sup> ionisation enthalpy	1245	1320	1376	1635	1513	1564	1648	1757	1962	1736
III <sup>rd</sup> ionisation enthalpy	2451	2721	2874	2995	3258	2964	3238	3401	3561	3839
E <sup>o</sup> <sub>M<sup>2+</sup>/M</sub> in volts	–	–1.63V	–1.18V	–0.91V	–1.18V	–0.44V	–0.28V	–0.25V	+0.34V	–0.76V
E <sup>o</sup> <sub>M<sup>3+</sup>/M<sup>2+</sup></sub> in volts	–	–0.37V	–0.26V	–0.41V	+1.57V	+0.77V	+1.97V	–	–	–

(a) Why does zinc have highest first ionization enthalpy?

Ans. It is because Zn has completely filled '4s' orbital which is stable.

(b) Why is 3<sup>rd</sup> ionization enthalpy of Mn high?

Ans. It is because after losing 2 electrons, it becomes 3d<sup>5</sup> which is more stable.

(c) Why is Cr<sup>3+</sup> more stable than Cr<sup>2+</sup>?

Ans. It is because Cr<sup>3+</sup>(t<sub>2g</sub><sup>3</sup>) half-filled orbitals are more stable than Cr<sup>2+</sup>(3d<sup>4</sup>).

(d) Why is E<sup>o</sup> Mn<sup>2+</sup>/Mn = –1.18V?

Ans. It is due to low enthalpy of atomization, sublimation enthalpy, ionization enthalpy.

(e) Why is E<sup>o</sup> Cu<sup>2+</sup>/Cu = +0.34V?

Ans. It is due to high ionization enthalpy and low hydration enthalpy.

(f) Why is Fe<sup>3+</sup> more stable than Fe<sup>2+</sup>?

Ans. Fe<sup>3+</sup> (3d<sup>5</sup>) is half filled which is more stable than Fe<sup>2+</sup> (3d<sup>6</sup>).

(g) Why is Mn<sup>3+</sup> good oxidizing agent and E<sup>o</sup> Mn<sup>3+</sup>/Mn<sup>2+</sup> = 1.57V?

Ans It is because it can gain one electron easily to form Mn<sup>2+</sup>(3d<sup>5</sup>) which is more stable that is why E<sup>o</sup> Mn<sup>3+</sup>/Mn<sup>2+</sup> = 1.57V

### ONE MARK QUESTION

1. Zinc, cadmium and mercury are not considered as transition metals. Why?

Ans. Zinc, cadmium and mercury have fully filled d<sup>10</sup> configuration. Therefore, they are not considered as transition metal.

2. Write the general configuration of d- block elements.

Ans. General electronic configuration of d- block elements is (n-1)d<sup>1-10</sup> ns<sup>1-2</sup>.

3. Transition metals generally form coloured ions. Why?

Ans. Due to presence of unpaired electron, crystal field splitting & d-d transition.

4. Which of the following will be coloured?

Sc<sup>3+</sup>, V<sup>2+</sup>, Mn<sup>2+</sup>, Cu<sup>+</sup>, Ni<sup>2+</sup>.

Ans Coloured ions will be those which have unpaired electrons in their d orbitals.

<b>Sc<sup>3+</sup></b>	Colourless
<b>V<sup>2+</sup></b>	Coloured
<b>Mn<sup>2+</sup></b>	Coloured
<b>Cu<sup>+</sup></b>	Colourless
<b>Ni<sup>2+</sup></b>	Coloured

5. Give reasons for the catalytic properties shown by transition metals.

Ans Ability to show multiple oxidation state / ability to form complex / having large surface area.

6. Why transition metals form large number of interstitial compounds?

Ans. Because small non- metallic atoms (like H, B, C, N etc.) are able to fit in the interstitial sites of transition metal lattice to form interstitial compounds.

7. Why do transition elements shows variable oxidation states?

Ans –Due to participation of (n-1) d and ns electron in bond formation as the energy difference between these orbital's are less.

8. Name a transition element which does not exhibit variable oxidation states.

Ans- Scandium. (Zn will be wrong answer as Zn is not considered as transition metal)

9. Which of the 3d series of the transition metals exhibits the largest number of oxidation states and why?

Ans – In 3d series Mn shows the highest oxidation state of +7 as it has maximum no. of unpaired electrons i.e.,  $3d^5$ .

10. Why is the highest oxidation state of a transition metals exhibited in its oxide or fluoride only?

Ans – Oxygen and fluorine have small size and high electro negativity. Hence, they can oxidize the metals to the highest oxidation state.

### **TWO (2) MARKS QUESTIONS**

1.  $\text{Cu}^+$  is not stable in aqueous solution. Why?

Ans- Many Cu(I) compounds are unstable in aqueous solution and undergo disproportionate.



The stability of  $\text{Cu}^{2+}$  rather than  $\text{Cu}^+$  is due to more –ve hydration enthalpy of  $\text{Cu}^{2+}$  than  $\text{Cu}^+$  which is much more and compensate for the II ionization enthalpy.

2. Which is the stronger reducing agent  $\text{Cr}^{2+}$  or  $\text{Fe}^{2+}$  and why?

Ans  $\text{Cr}^{2+}$  is the stronger reducing agent because in case of  $\text{Cr}^{2+}$  to  $\text{Cr}^{3+}$  change in configuration is from  $d^4$  to  $d^3$  and in  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  the change is from  $d^6$  to  $d^5$ . In medium like water  $d^3$  is more stable as compared to  $d^5$  due to half- filled  $t_{2g}$  configuration.

3.  $\text{Co}^{2+}$  is stable in aqueous solution but in the presence of complexing agent, it is easily oxidized. Why?

Ans -In the presence of complexing agent, oxidation state of Co changes from +2 to +3 due to CFSE which is more and compensate the  $\Delta_i H_3$ .

4.  $E^0$  for  $\text{Mn}^{3+}/\text{Mn}^{2+}$  is more positive than for  $\text{Fe}^{3+}/\text{Fe}^{2+}$ . Why?

Ans.  $\text{Mn}^{3+}$  has the configuration  $3d^4$  while that of  $\text{Mn}^{2+}$  is  $3d^5$ . So  $\text{Mn}^{3+}$  easily undergo reduction to  $\text{Mn}^{2+}$  having stable  $3d^5$  configuration resulting in higher value of standard reduction potential.

$\text{Fe}^{3+}$  is more stable than  $\text{Fe}^{2+}$  because of having  $3d^5$  configuration and reduction to  $\text{Fe}^{2+}$  will not be easy resulting in the decreased value of  $E^0$ .

5. The highest oxidation state is exhibited in oxo-anions of a transition metal and not in metal fluorides. Suggest a reason.

Ans. The ability of oxygen to stabilize these high oxidation states exceeds that of fluorine due to ability of oxygen to form multiple bonds to metals. Thus the highest Mn fluoride is  $\text{MnF}_4$  whereas the highest oxide is  $\text{Mn}_2\text{O}_7$ .

6.  $\text{Ce}^{4+}$  is a good oxidizing agent and  $\text{Eu}^{2+}$  is a good reducing agent. Why?

Ans. The most stable oxidation state in lanthanoids is +3 and all lanthanoids try to attain it. Thus,  $\text{Ce}^{4+}$  will easily accept an electron i.e. get reduced thus behaving like a good oxidizing agent. The opposite applies to  $\text{Eu}^{2+}$  which loses an electron to attain +3 oxidation state behaving as a good reducing agent.

7. Explain 'Misch metal' and write its use.

Ans. It is an alloy of 95% Lanthanoid and 5% iron and traces of S, C, Ca and Al. Used in lighter flint, bullet tips etc.

8. What is the General electronic configuration and common oxidation state of Lanthanoids?

Ans. General electronic configuration =  $4f^{1-14} 5d^{0-1} 6s^2$  and common oxidation state is +3.

### THREE (3) MARKS QUESTIONS

1. Explain Lanthanoid contraction, its cause & consequence?

Ans. Lanthanoid contraction – The cumulative effect of the regular decrease in size or radii of Lanthanoid with increase in atomic number is called Lanthanoid contraction.

**Causes** – The shape of  $f$  orbital's is diffused. They have poorer shielding effect due to which the effective nuclear charge increases with increase in atomic number. This causes a decrease in atomic radii

**Consequences** – Due to Lanthanoid contraction-

i) Radii of the members of the third transition series is similar to those of second transition series.

ii) It becomes difficult to separate the Lanthanoids.

iii) The basic strength of  $\text{Ln}(\text{OH})_3$  decrease in the series

2. Answer the following questions -

1. Why does copper not replace hydrogen from acids?

Ans. The unique behavior of Cu, having appositve  $E^0 = +0.34\text{V}$  accounts for its inability to liberate hydrogen from acids.

2. Why  $E^0$  values for Mn, Ni and Zn are more negative than expected?

Ans. The stability of the half-filled  $d$  sub-shell in  $\text{Mn}^{2+}$  and the completely filled  $d^{10}$  configuration in  $\text{Zn}^{2+}$  are related to their  $E^0$  values, whereas for Ni is related to the highest negative H.

3. Why first ionization enthalpy of Cr is lower than that of Zn?

Ans. The value of first ionization enthalpy of Cr is lower because of the absence of any change in the  $d$  configuration and the value for Zn is higher because it represents an



ionization from the 4s level.

### **FIVE (5) MARKS QUESTIONS**

1. Give reasons-

- (i) Transition metals have high melting points.
- (ii) Second and third transition series have similar radii.
- (iii) Second ionization is difficult from Cu and Cr whereas it is easy for Zn.
- (iv) Most of the transition elements are paramagnetic.
- (v) The  $d^1$  configuration is very unstable in ions. Why?

Ans (i) In transition metals besides ns electrons, (n-1) d electrons can also participate in bonding making stronger metallic bonds. This increases their melting points.

(ii) Due to Lanthanoid contraction, there is a decrease in size of 5d series. This makes their sizes same as sizes of elements of 4d series.

(iii) In Cr the electronic configuration is  $3d^5 4s^1$  and for Cu, it is  $3d^{10} 4s^1$ . In these after first ionization, which removes the electron from 4s, second ionization requires disturbance in half filled or fully filled configuration which requires high enthalpy whereas the configuration of Zn is  $3d^{10} 4s^2$ . Here after second ionization, the configuration of Zn is completely filled. Therefore, second ionization is easier for Zn but difficult for Cr and Cu.

(iv) Para magnetism in transition elements arises due to presence of one or more unpaired electrons in atomic orbital's.

(v) The ions with  $d^1$  configuration have the tendency to lose the only electron present in d-sub shell to acquire stable  $d^0$  configuration.

2. Mention the type of compounds formed when small atoms like H,C and N get trapped inside the crystal lattice of transition metals. Also give physical and chemical characteristics of these compounds.

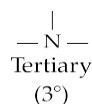
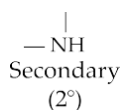
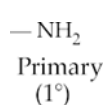
Ans. Interstitial compounds are formed when small atoms like H, C or Na re trapped inside the crystal lattices of metals. They are usually non stoichiometric and are neither typically ionic non covalent. The principal physical and chemical characteristics of these compounds are as follows:

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

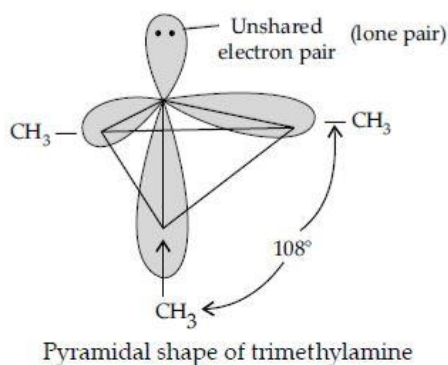
## Amines

Nomenclature, classification, structure, methods of preparation, physical and chemical properties, uses, identification of primary, secondary and tertiary amines.

Revision Notes:- Classification of amines:

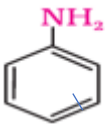


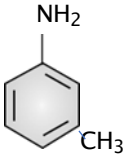
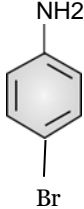
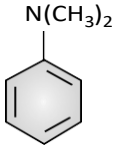
Structure of amine:



Nitrogen orbital's in amines are  $sp^3$  hybridized and the geometry is pyramidal. Due to the presence of unshared pair of electrons, the angle C—N—E is less than  $109.5^\circ$ .

➤ Nomenclature of some Alkyl amines and Aryl amines:

Amine	Common name	IUPAC name
$\text{CH}_3\text{—CH}_2\text{—NH}_2$	Ethylamine	Ethan amine
$\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—NH}_2$	<i>n</i> -Propyl amine	Propan-1-amine
$\begin{array}{c} \text{CH}_3\text{—CH—CH}_3 \\   \\ \text{NH}_2 \end{array}$	Iso propyl amine	Propan-2-amine
$\begin{array}{c} \text{CH}_3\text{—N—CH}_2\text{—CH}_3 \\   \\ \text{H} \end{array}$	Ethyl methylamine	N-Methyl ethanamine
$\begin{array}{c} \text{CH}_3\text{—N—CH}_3 \\   \\ \text{CH}_3 \end{array}$	Tri methylamine	N,N-Di methyl methanamine
$\begin{array}{c} \text{C}_2\text{H}_5\text{—N—CH}_2^1\text{—CH}_2^2\text{—CH}_2^3\text{—CH}_3^4 \\   \\ \text{C}_2\text{H}_5 \end{array}$	N,N-Diethyl butylamine	N,N-Diethylbutan-1-amine
$\text{NH}_2\text{—CH}_2^1\text{—CH}^2\text{=CH}_2^3$	Allylamine	Prop-2-en-1-amine
$\text{NH}_2\text{—(CH}_2\text{)}_6\text{—NH}_2$	Hexa methylene diamine	Hexane-1,6-diamine
	Aniline	Aniline or Benzenamine

	<i>o</i> -Toluidine	2-Aminotoluene
	<i>p</i> -Bromoaniline	4-Bromo benzylamine or 4-Bromoaniline
	N,N-Dimethylaniline	N,N-Dimethyl Benzenamine

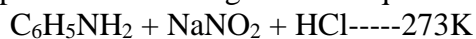
➤ Identification of primary, secondary and tertiary amines:

S.N o.	Test	Primary amine	Secondary amine	Tertiary amine
(i)	Reaction with nitrous acid.	Gives alcohol with effer vescence of N <sub>2</sub> gas.	Gives oily nitroso amine which gives Liebermann's nitroso amine test.	Forms nitrite in cold soluble in water and on heating gives nitroso amine
(ii)	<b>Hinsberg Test:</b> Reaction with benzene sulphonyl chloride (Hinsberg' sreagent).	Gives N-alkyl benzene-sulphonamide which is soluble in alkali.	Gives N, N-dialkyl benzene sulphonamide which is insoluble in alkali.	No reaction.
(iii)	<b>Carbyl aminetest:</b> Reaction with chloroform and alcoholic KOH.	Forms carbylamine or iso cyanide (RNC) with characteristic unpleasant odour.	No reaction.	No reaction.
(iv)	<b>Hoffmann's mustard oil reaction:</b> Reaction with CS <sub>2</sub> and HgCl <sub>2</sub> .	Forms N-substituted iso thio cyanate with characteristic unpleasant smell of mustard oil.	No reaction.	No reaction.

Short Answer Question- 2 Marks

Q.1 (i) Write IUPAC name of the following compound : (CH<sub>3</sub>)<sub>2</sub>N — CH<sub>2</sub>CH<sub>3</sub>

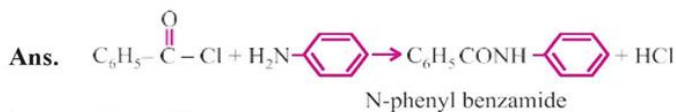
(ii) Complete the following reaction equation:



Ans. (i) N, N-Dimethyl ethanamine

(ii)  $\text{ArN}_2^+\text{Cl}^- + \text{N}_2 + \text{H}_2\text{O}$  (where Ar is C<sub>6</sub>H<sub>5</sub>)

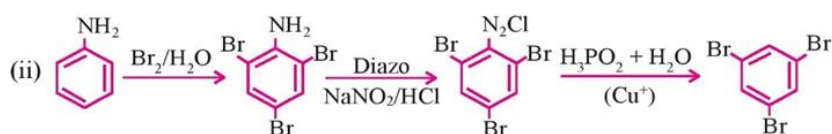
Q. 2. Write chemical reaction of  $C_6H_5NH_2 + C_6H_5COCl$  and name product obtained.



Q. 3. How will you convert :

(i) 3-methylaniline  $\rightarrow$  3-nitrotoluene

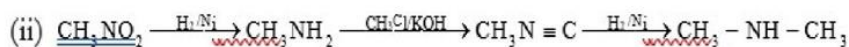
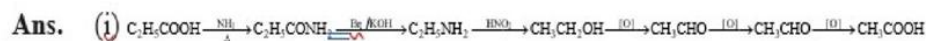
(ii) Aniline  $\rightarrow$  1, 3, 5-tribromobenzene



Q. 4. How will you convert :

(i) Propanoic acid  $\rightarrow$  Ethanoic acid

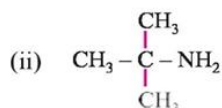
(ii) Nitromethane  $\rightarrow$  Dimethylamine



Q. 5. Draw the structures of the following compounds :

(i) N-isopropylaniline

(ii) t-butylamine

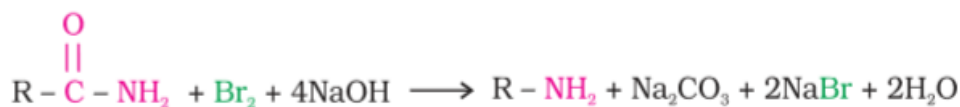


Q.6. Write the chemical equations involved in the following reactions:

(i) Hoffmann-bromamide degradation reaction,

(ii) Carbyl amine reaction.

Ans.(i)



(where R=alkyl group, Ar=aryl group)

Ans(ii)



Q.7 Give reasons:

- (i) Electrophilic substitution in aromatic amines takes place more readily than benzene.
- (ii)  $\text{CH}_3\text{CONH}_2$  is a weaker base than  $\text{CH}_3\text{CH}_2\text{NH}_2$

Ans (i)  $-\text{NH}_2$  group of aromatic amines strongly activates the aromatic ring through Delocalization of the lone pair of electron soft he N-atom over the aromatic ring. Due to The strong activating effect to the  $-\text{NH}_2$  group, aromatic amines undergo electrophilic substitution reactions readily than benzene.

(ii) Due to resonance, the lone pair of electrons on the nitrogen atom in  $\text{CH}_3\text{CONH}_2$  is delocalized over the keto group.



as a result, electron density on the N-atom in  $\text{CH}_3\text{CONH}_2$  decreases. On the other hand, in  $\text{CH}_3\text{CH}_2\text{NH}_2$ , due to +I effect of the ethyl group, out after protecting the  $-\text{NH}_2$  group by the electron density on the N-atom increases consequently,  $\text{CH}_3\text{CONH}_2$  is a weaker base than  $\text{CH}_3\text{CH}_2\text{NH}_2$

Q. 8. Why does acetylation of  $-\text{NH}_2$  group of aniline reduce its activating effect?

Ans. Direct nitration of aniline is not possible on account of  $-\text{NH}_2$  group present. The acetyl group being electron withdrawing attracts the lone pair of electrons of the N - atom towards carbonyl group. As a result, the activation effect of  $-\text{NH}_2$  group is reduced, that is, that lone pair of electrons on nitrogen is less available for donation to benzene ring by resonance

Q.9 Give reasons:

- (i) Aniline is a weaker base than cyclohexylamine
- (ii) It is difficult to prepare pure amines by ammonolysis of alkyl halides.

Ans. (i) Cyclohexylamine is a weaker base than aniline because aniline is a resonance hybrid of various resonance structures. As a result, in aniline the electron donating capacity of nitrogen for protonation is considerably decreased.

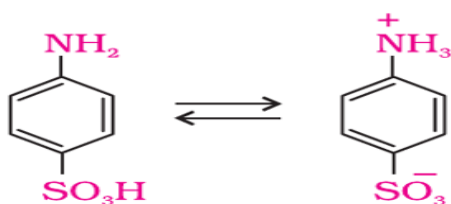
(ii) Ammonolysis of alkyl halides does not give single amine but gives a mixture of primary, secondary and tertiary amines.

Q.10 Explain

- (i) Aromatic primary amines cannot be prepared by Gabrielphthalimide synthesis

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

- (ii) Draw structure of Sulphanilic acid & its Zwitter ion.



Sulphanilic acid

Zwitter ion

Q.11

Account for :

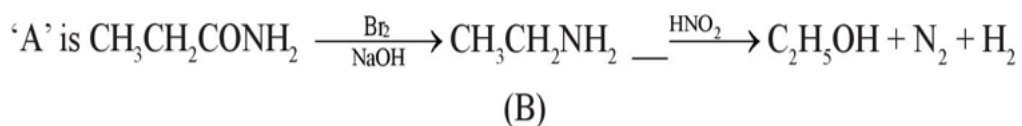
- (i) Amino group in aniline is *o*- and *p*- directing in aromatic electrophilic substitution reactions. Aniline on nitration gives a substantial amount of *m*-nitroaniline.
- (ii) Aniline does not go Friedel Crafts reaction.

- Ans. (i) It is because aniline is protonated to form anilinium cation, in which  $\text{NH}_3^{\oplus}$  group is meta-directing.
- (ii) It is because aniline is basic, can form adduct with  $\text{AlCl}_3$ , electrophile cannot be generated.

Q.12

A compound 'A' having molecular formula  $\text{C}_3\text{H}_7\text{ON}$  reacts with  $\text{Br}_2$  in presence of  $\text{NaOH}$  to give compound 'B'. This compound 'B' reacts with  $\text{HNO}_2$  to form alcohol and  $\text{N}_2$  gas. Identify compound 'A' and 'B' and write the reaction involved.

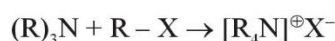
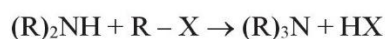
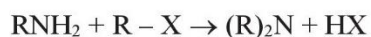
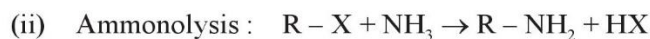
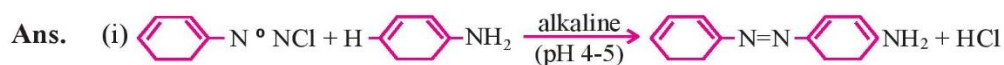
Ans.



**Q. 13. Write short notes on :**

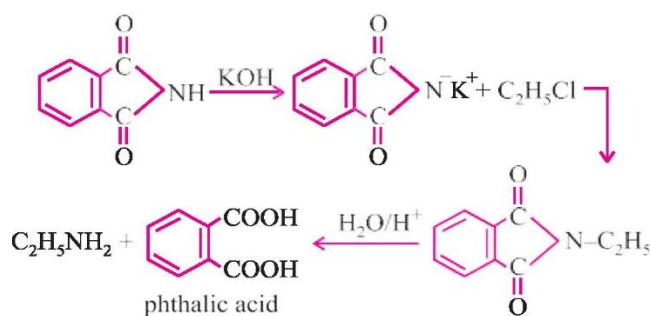
(i) **Coupling reaction**

(ii) **Ammonolysis**



**Q. 14. Prepare pure sample of 1° amine from 1° alkyl halide.**

**Ans. By Gabriel Phthalimide Reaction**



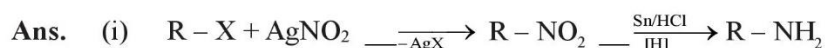
### ANSWER-II TYPE QUESTIONS (3 Marks)

**Q. 1. What happens when :**

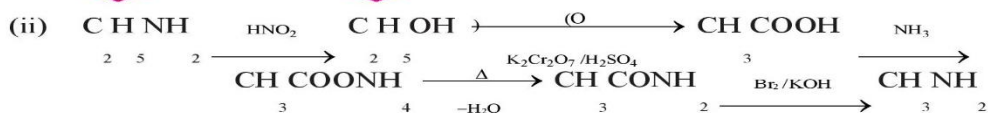
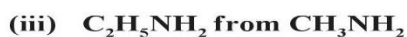
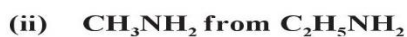
(i) **An alkyl halide reacts with  $AgNO_2$  and product is reduced.**

(ii) **An alkyl halide is treated with  $AgCN$  and product is hydrolysed.**

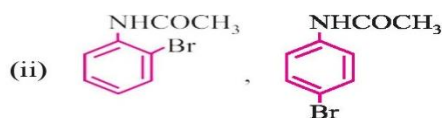
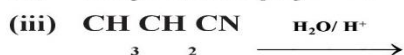
(iii) **Methyl magnesium is treated with cyanogens chloride.**



**Q. 2. How would you prepare :**



**Q. 3. Write the structure of the products in each case :**

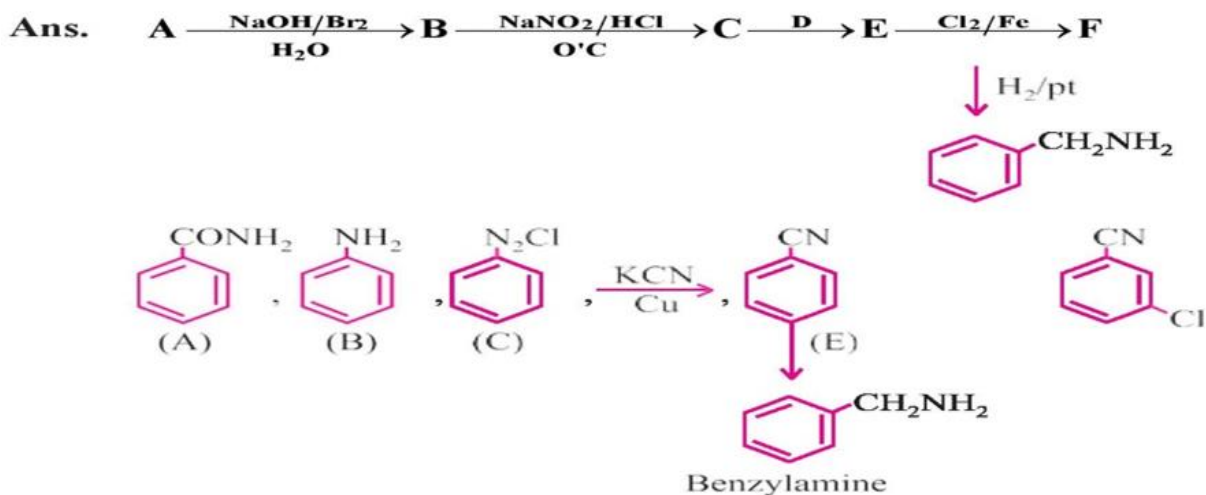


**Q. 4. Write the structures of A, B and C in following**





**Q. 5. Write the structure of reagents/organic compounds 'A' to 'F' :**



Case Study Question 1:

3 Marks

Read the passage given below and answer the following questions:

A mixture of two aromatic compounds (A) and (B) was separated by dissolving in chloroform followed by extraction with aqueous KOH solution. The organic layer containing compound (A), when heated with alcoholic solution of KOH produce  $\text{C}_7\text{H}_5\text{N}$  (C) associated with unpleasant odour.

The following questions are multiple choice question. Choose the most appropriate answer:

(i) What is A?

- (a)  $\text{C}_6\text{H}_5\text{NH}_2$  (b)  $\text{C}_6\text{H}_5\text{CH}_3$   
 (c)  $\text{C}_6\text{H}_5\text{CHO}$  (d) None of these

(ii) The reaction of (A) with alcoholic solution of KOH to produce (C) of unpleasant odour is called

- (a) Sandmeyer reaction (b) Carbylamine reaction  
 (c) Ullmann reaction (d) Reimer-Tiemann reaction.

(iii) In the chemical reaction,  $\text{CH}_3\text{CH}_2\text{NH}_2 + \text{CHCl}_3 + 3\text{KOH} \rightarrow (\text{A}) + (\text{B}) + 3\text{H}_2\text{O}$ , the compounds (A) and (B) are respectively

- (a)  $\text{C}_2\text{H}_5\text{NC}$  and  $\text{KCl}$  (b)  $\text{C}_2\text{H}_5\text{CN}$  and  $\text{KCl}$   
 (c)  $\text{CH}_3\text{CH}_2\text{CONH}_2$  and  $\text{KCl}$  (d)  $\text{C}_2\text{H}_5\text{NC}$  and  $\text{K}_2\text{CO}_3$

Answers:

- (i) a (ii) b (iii) a

## LONG ANSWER TYPE QUESTIONS (5 Marks)

Q. 1. Arrange the following :

(i) In decreasing order of  $pK_b$  values :

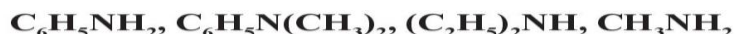


(ii) In increasing order of basic strength :

(a) Aniline, p-nitroaniline and p-toluidine

(b)  $C_6H_5NH_2$ ,  $C_6H_5NHCH_3$ ,  $C_6H_5CH_2NH_2$

(iii) In decreasing order of basic strength :



(iv) Decreasing order of basic strength in gas phase :



(v) Increasing order of boiling point :

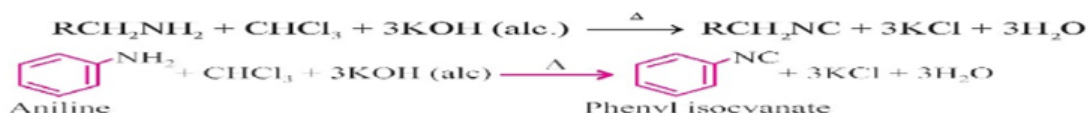


- Ans. (i)  $C_6H_5NH_2 > C_6H_5NHCH_3 > C_2H_5NH_2 > (C_2H_5)_2NH$   
(ii) (a) p-nitroaniline < aniline < p-toluidine  
(b)  $C_6H_5NH_2 < C_6H_5NHCH_3 < C_6H_5CH_2NH_2$   
(iii)  $(C_2H_5)_2NH > CH_3NH_2 > C_6H_5N(CH_3)_2 > C_6H_5NH_2$   
(iv)  $(C_2H_5)_3N > (C_2H_5)_2NH > C_2H_5NH_2 > NH_3$   
(v)  $(CH_3)_2NH < C_2H_5NH_2 < C_2H_5OH$

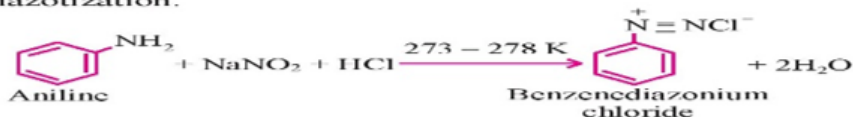
Q. 2 Write short note on the following :

- Carbylamine reaction
- Diazotization
- Hoffmann's bromide reaction
- Coupling reaction
- Ammonolysis

Ans. (i) **Carbylamine reaction** : When primary amine (aromatic or aliphatic) warmed with chloroform and alc. KOH, isocyanides are formed which can be identified by their offensive smell. This test is used to identify the presence of primary amine or chloroform.



(b) **Diazotization** : When primary aromatic amine is treated with  $NaNO_2$  and  $HCl$  at 273-278 K, diazonium salt is obtained. This reaction is known as diazotization.



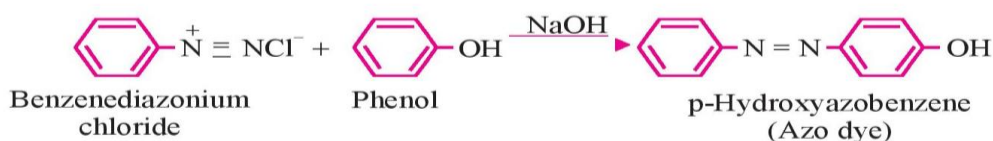
Benzenediazonium chloride is a very important synthetic compound, which can be changed into haloarenes, phenol, cyanobenzene, benzene etc.

- (c) **Hoffmann's bromide reaction** : When any primary amide (aliphatic or aromatic) is treated with bromine and alkali, it gives the amine with one less carbon atom.

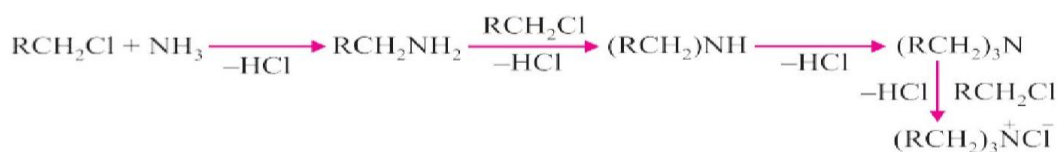


This reaction is used to reduce one carbon atom from a compound.

- (d) **Coupling reaction** : When benzenediazonium chloride is treated with phenols or aromatic amines, azo dyes are produced in which diazo ( $-\text{N}=\text{N}-$ ) group is retained. Coupling reactions generally take place at p-position of phenol or aromatic amines.

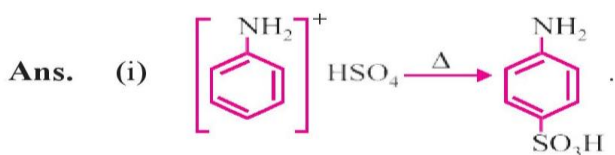


- (e) **Ammonolysis** : Reaction of alkyl halides with ammonia is known as ammonolysis. Ammonolysis generally gives the mixture of 1°, 2°, 3° amines and quaternary ammonium salt.

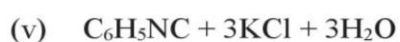


**Q. 3. Complete the following reactions :**

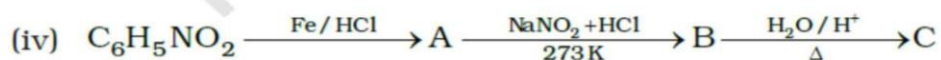
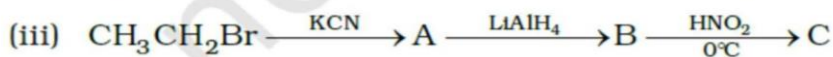
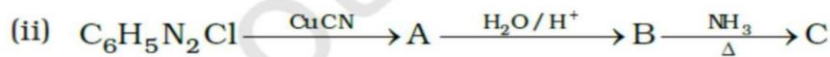
- $\text{C}_6\text{H}_5\text{NH}_2 + \text{H}_2\text{SO}_4(\text{conc.}) \rightarrow$
- $\text{C}_6\text{H}_5\text{N}_2\text{Cl} + \text{C}_2\text{H}_5\text{OH} \rightarrow$
- $\text{C}_6\text{H}_5\text{NH}_2 + (\text{CH}_3\text{CO})_2\text{O} \rightarrow$
- $\text{C}_6\text{H}_5\text{N}_2\text{Cl} + \text{H}_3\text{PO}_2 + \text{H}_2\text{O} \rightarrow$
- $\text{C}_6\text{H}_5\text{NH}_2 + \text{CHCl}_3 + 3\text{KOH}(\text{alc.}) \rightarrow$



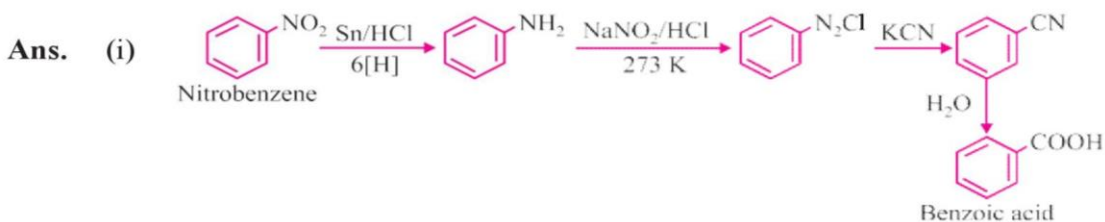
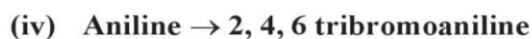
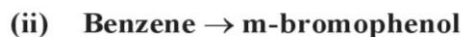
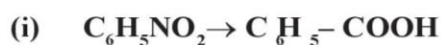
- $\text{C}_6\text{H}_6 + \text{N}_2 + \text{HCl} + \text{CH}_3\text{CHO}$
- $\text{C}_6\text{H}_5\text{NHCOCH}_3 + \text{CH}_3\text{COOH}$

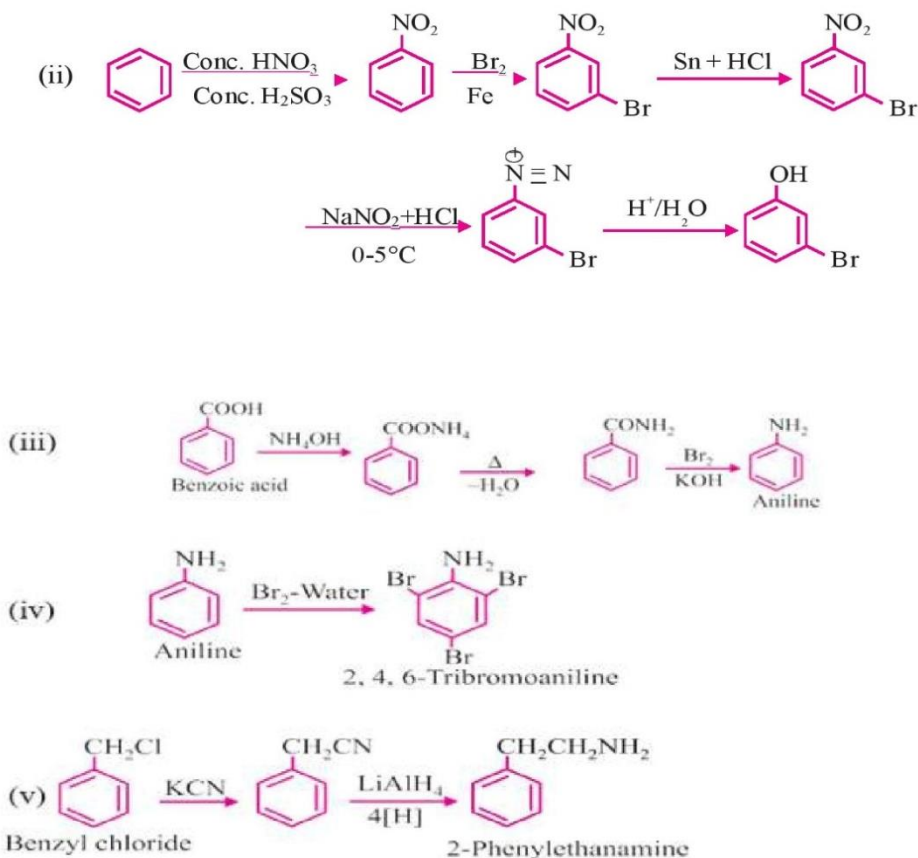


**Q. 4. Write A, B and C in the given reactions :**



**Q. 5. Accomplish the following conversions :**





Q. 6. Given reasons : (i) Acetylation of aniline reduces its activation effect.

(ii)  $\text{CH}_3\text{NH}_2$  is more basic than  $\text{C}_6\text{H}_5\text{NH}_2$

(iii) Although  $-\text{NH}_2$  group is o/p directing, yet aniline on nitration gives a significant amount of m-nitroaniline

Ans. (i) Due to the resonance, the electron pair of nitrogen atom gets delocalised towards carbonyl group/resonating structures.

(ii) Because of +I effect in methylamine electron density at nitrogen increases whereas in aniline resonance takes place and electron density on nitrogen decreases / resonating structures.

(iii) Due to protonation of aniline / formation of anilinium ion

Q.6 (B) Arrange the following in increasing order of their basic strength: (Aq. phase)

(i)  $\text{C}_2\text{H}_5\text{NH}_2$ ,  $\text{C}_6\text{H}_5\text{NH}_2$ ,  $\text{NH}_3$ ,  $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$  and  $(\text{C}_2\text{H}_5)_2\text{NH}$

(ii)  $\text{C}_2\text{H}_5\text{NH}_2$ ,  $(\text{C}_2\text{H}_5)_2\text{NH}$ ,  $(\text{C}_2\text{H}_5)_3\text{N}$ ,  $\text{C}_6\text{H}_5\text{NH}_2$

Ans (i)  $\text{C}_6\text{H}_5\text{NH}_2 < \text{NH}_3 < \text{C}_6\text{H}_5\text{CH}_2\text{NH}_2 < \text{C}_2\text{H}_5\text{NH}_2 < (\text{C}_2\text{H}_5)_2\text{NH}$

(ii)  $\text{C}_6\text{H}_5\text{NH}_2 < \text{C}_2\text{H}_5\text{NH}_2 < (\text{C}_2\text{H}_5)_3\text{N} < (\text{C}_2\text{H}_5)_2\text{NH}$

## ALDEHYDES, KETONES & CARBOXYLIC ACIDS

### SHORT ANSWERS TYPES QUESTION (2 MARKS)

Q1. Give one chemical test to distinguish between (a) Pentan-2-one and Pentan-3-one (b) Benzaldehyde and Acetophenone.

Q2. Explain why ?

a) Aldehydes are more reactive than Ketones towards Nucleophilic addition reaction.

b) Chloroacetic acid is stronger than acetic acid.

Q3. Arrange the following compounds in increasing order of their reactivity in nucleophilic addition reactions.

(i) Ethanal, Propanal, Propanone, Butanone.

(ii) Benzaldehyde, *p*-Tolualdehyde, *p*-Nitrobenzaldehyde, Acetophenone.

Q4. Arrange the following compounds in increasing order of their (acid strength)

(a)  $\text{CH}_3\text{CH}_2\text{CH}(\text{Br})\text{COOH}$ ,  $\text{CH}_3\text{CH}(\text{Br})\text{CH}_2\text{COOH}$ ,  $(\text{CH}_3)_2\text{CHCOOH}$ ,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$

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

Q5. Give simple chemical tests to distinguish between the following pairs of compounds.

(i) Propanal and Propanone (ii) Acetophenone and Benzophenone

Q6. Distinguish between the following: (2 Marks each)

(i)  $\text{C}_6\text{H}_5\text{COCH}_3$  and  $\text{C}_6\text{H}_5\text{COCH}_2\text{CH}_3$

(ii) Benzoic acid and Phenol

(iii)  $\text{CH}_3\text{COCH}_2\text{CH}_3$  and  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$

(iv) Ethanal and Ethanoic acid

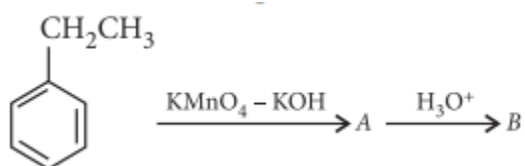
(v)  $\text{CH}_3\text{CH}_2\text{CHO}$  and  $\text{CH}_3\text{CH}_2\text{COCH}_3$

(vi)  $\text{CH}_3\text{COOH}$  and  $\text{HCOOH}$

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

$\text{CH}_3\text{CHO}$ ,  $\text{CH}_3\text{COOH}$ ,  $\text{CH}_3\text{CH}_2\text{OH}$

Q8. Write structures of compounds A and B in each of the following reactions.

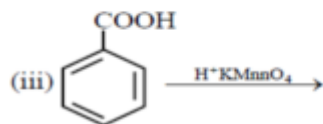
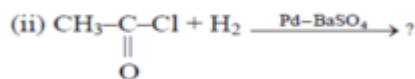
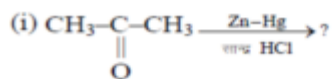


Q9. Aldehydes and ketones have lower boiling points than corresponding alcohols. Why?

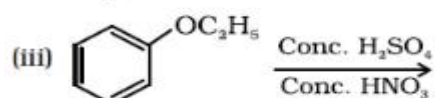
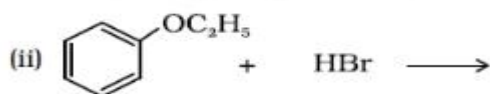
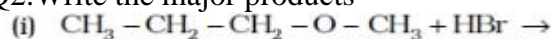
Q10. Give reasons : Chloroacetic acid is stronger than acetic acid.

## LONG ANSWERS TYPES QUESTIONS (3 MARKS)

Q1. Complete the reaction



Q2. Write the major products



Q3. An organic compound A with molecular formula  $\text{C}_8\text{H}_{16}\text{O}_2$  was hydrolysed with sulphuric acid to give a carboxylic acid B and an alcohol C. Oxidation of C with chromic acid produced B. C on dehydration gives but-1-ene. Write equations for the reactions involved.

Q4. Carry out the following conversions

(a) Propanone to Propene (b) Benzoic acid to Benzaldehyde (c) Ethanol to 3-Hydroxybutanal

Q5. Illustrate the following name reactions

giving a chemical equations in each case :

(i) Clemmensen reaction

(ii) Cannizzaro reaction

Q6. Account for the following :

(i)  $\text{CH}_3\text{CHO}$  is more reactive than  $\text{CH}_3\text{COCH}_3$  towards reaction with HCN.

(ii) There are two  $-\text{NH}_2$  groups in semicarbazide ( $\text{H}_2\text{NNHCONH}_2$ ).

However, only one is involved in the formation of semicarbazone.

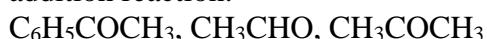
Q7. Give reasons :

(i) Electrophilic substitution in benzoic acid takes place at meta-position.

(ii) Carboxylic acids do not give the characteristic reactions of carbonyl group.

Q8. (a) Write the chemical reaction involved in Wolff-Kishner reduction.

(b) Arrange the following in the increasing order of their reactivity towards nucleophilic addition reaction.



(c) A and B are two functional isomers of compound  $\text{C}_3\text{H}_6\text{O}$ . On heating with NaOH and  $\text{I}_2$ , isomer B forms yellow precipitate of iodoform whereas isomer A does not form any precipitate. Write the formulae of A and B.

Q9. Account for the following :

(a) Aromatic carboxylic acids do not undergo Friedel-Crafts reaction.

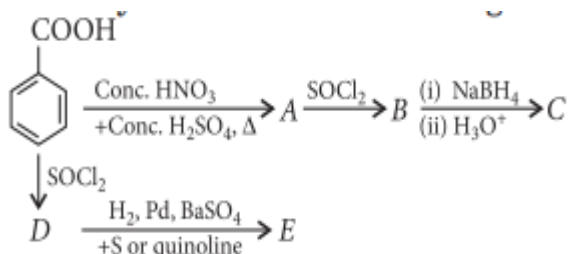
(b)  $\text{pK}_a$  value of 4-nitrobenzoic acid is lower than that of benzoic acid.

Q10. (i) How will you bring about the following conversions?

- (a) Ethanal to but-2-enal  
(b) Propanone to propene

### LONG ANSWERS TYPES QUESTIONS (5 MARKS)

Q1. Identify A to E in the following reactions :



Q2. An organic compound

- (A) on treatment with ethyl alcohol gives a carboxylic acid (B) and compound (C). Hydrolysis of (C) under acidified conditions gives (B) and (D). Oxidation of (D) with KMnO<sub>4</sub> also gives (B). (B) on heating with Ca(OH)<sub>2</sub> gives (E) having molecular formula C<sub>3</sub>H<sub>6</sub>O. (E) does not give Tollen's test and does not reduce Fehling's solution but forms 2, 4-dinitrophenyl hydrazone. Identify (A), (B), (C), (D) and (E).

### CASE-BASED/PASSAGE-BASED INTEGRATED QUESTIONS

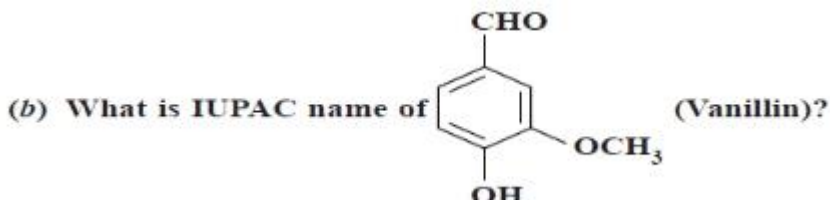
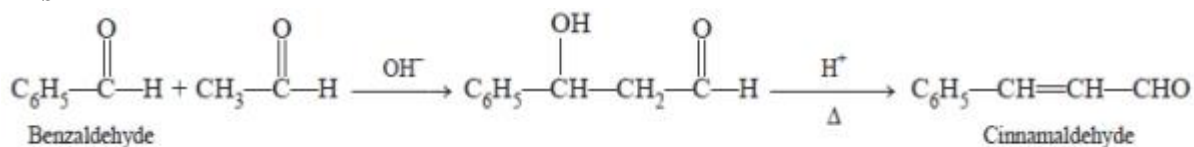
Read the given passage and answer the questions that follow.

Aldehydes, Ketones, Carboxylic acids and their derivatives are collectively called carboxyl compounds which are widely spread both in plants and animal kingdom. They play an important role in biological processes. They are responsible for fragrance and flavour of naturally occurring compounds *e.g.*, Vanilline (from vanilla beans), salicylaldehyde (from meadowsweet), cinnamaldehyde (from cinnamon) and isoamyl acetate (from banana) have pleasant flavour.

Acetone and acetic acid are widely used as solvents. Various carboxylic acids are used to prepare drugs (Analgesics, antipyretics etc.).

1. Convert benzaldehyde to Cinnamaldehyde?

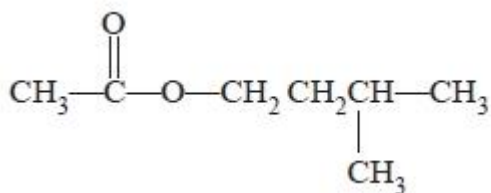
Ans:-



Ans :- 4-hydroxy-3-methoxy benzaldehyde

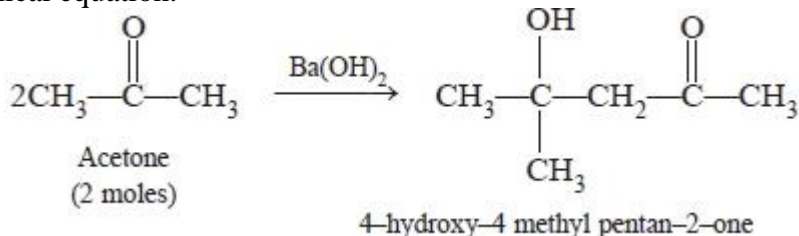
(c) Write the structural formula of Isoamyl acetate.





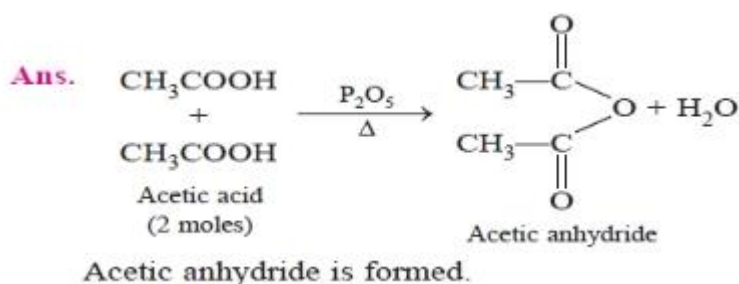
Ans:-

(d) What happens when 2 moles of acetone are condensed in presence of Ba(OH)<sub>2</sub>? Write chemical equation.



Ans:-

(e) What happens when acetic acid is heated with P<sub>2</sub>O<sub>5</sub>?



## COORDINATION COMPOUNDS

**Coordination compounds:** are those addition molecular compounds which retain their identity in solid state as well as in dissolved state. In these compounds the central metal atom or ion is linked by ions or molecules with coordinate bonds. e.g. K<sub>4</sub>[Fe(CN)<sub>6</sub>]

**Double Salts:** These are the addition molecular compounds which are stable in solid state but dissociate into constituent ions in the solution. e.g.,

Mohr's salt: FeSO<sub>4</sub>·(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>·6H<sub>2</sub>O get dissociated into Fe<sup>2+</sup>, NH<sub>4</sub><sup>+</sup> and SO<sub>4</sub><sup>2-</sup> ions.

### IMPORTANT TERMS:

**1. Complex ion or Coordination Entity:** It is an electrically charged species in which central metal atom is surrounded by number of ions or neutral molecules.

(i) Cationic complex entity It is the complex ion which carries positive charge.

e.g., [Pt(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup>

(ii) Anionic complex entity It is the complex ion which carries negative charge.

e.g., [Fe(CN)<sub>6</sub>]<sup>4-</sup>

**2. Central Atom or Ion:** The atom or ion to which a fixed number of ions or groups are bonded. It is also referred as Lewis acid. e.g. in [Ni(H<sub>2</sub>O)<sub>4</sub>], Ni is central metal atom.

**3. Ligands:** Ligands is electron donating species (ions or molecules) bonded to the Central atom. These may be charged or neutral.

### Ligands are of the following types:

(i) Unidentate It is a ligand, which has one donor atom. e.g., H<sub>2</sub>O, NH<sub>3</sub>.

- (ii) Bidentate It is the ligand. Which have two donor sites e.g.  $C_2O_4^{2-}$
- (iii) Polydentate It is the ligand, which have several donor sites. e.g.,  $[EDTA]^{4-}$  (ethylene diamine tetra acetate ion) is hexa dentate ligand.
- (iv) Ambidentate ligands- These are the mono dentate ligands which can ligate through two different sites. e.g.  $NO_2^-$ ,  $SCN^-$ , etc.
- (v) Chelating ligands- Di or Polydentate ligands cause cyclisation around the metal atom which are known as chelates, such ligands Uses two or more donor atoms to bind a single metal ion and are known as chelating ligands.

4. **Coordination Number:** It is defined as the number of coordinate bonds formed by central metal atom, with the ligands.

5. **Coordination Sphere:** The central ion and the ligands attached to it are enclosed in square bracket, which is known as coordination sphere.

### Colour in Coordination Compounds

- In complex compounds d-orbitals split in two sets  $t_{2g}$  (triply degenerate set) and  $e_g$  (doubly degenerate set). These have different energies. The difference in energies lies in visible region and electron jump from ground state  $t_{2g}$  level to higher state  $e_g$  level. This is known as d-d transition and it is responsible for colour of coordination compounds.
- d-d transition takes place in  $d^1$  to  $d^9$  ions, so the ions having  $d^1$  to  $d^9$  configuration are coloured. On the other hand, the ions  $d^0$  and  $d^{10}$  configuration do not show d-d transition.

## CASE-BASED/PASSAGE-BASED INTEGRATED QUESTIONS

### **I. Read the given passage and answer the questions that follow:**

Complex compounds play an important role in our daily life. Werner's theory of complex compounds says every metal atom or ion has primary valency (oxidation state) which is satisfied by negatively charged ions which are ionisable whereas secondary valency (coordination number) is non-ionisable, satisfied by ligands (+ve / -ve/ neutral) but having lone pair. Primary valency is non-directional, secondary valency is directional. Complex compounds are name according to IUPAC system. Valence bond theory helps in determining shapes of complexes based on hybridization, magnetic properties, outer or inner orbital complex. EDTA is used to treat lead poisoning, Cisplatin as anticancer agents. Vitamin B<sub>12</sub> is complex of cobalt. Hemoglobin, oxygen carrier is complex of  $Fe^{2+}$  and chlorophyll essential for photosynthesis is complex of  $Mg^{2+}$ .

### **Questions:**

(a) What is the oxidation state and coordination number of Ni in  $[Ni(CO)_4]$ ?

Ans. Zero and four

(b) One mole of  $CrCl_3 \cdot 6H_2O$  reacts with excess of  $AgNO_3$  to yield 2 mole of  $AgCl$ .

Write formula of complex. Write IUPAC name also.

Ans.  $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$ , Penta aqua chloride chromium (III) chloride

(c) Name the hexadentate ligand used for treatment of lead poisoning.

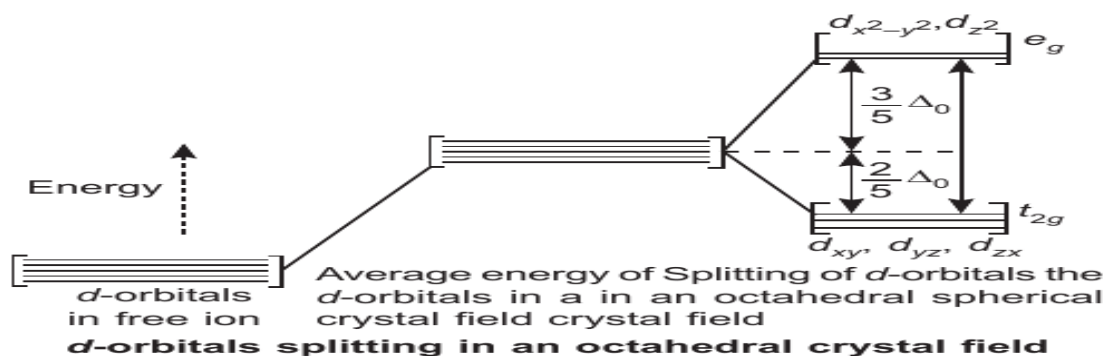
Ans.  $EDTA^{4-}$  (ethylene diamine tetra acetate)

(d) What is hybridization of  $[CoF_6]^{3-}$ ?  $[Co = 27]$ . Give its shape and magnetic properties. Ans.  $sp^3d^2$ , octahedral, paramagnetic. It is outer orbital complex.

(e) Out  $[Fe(CO)_5]$ ,  $[Fe(C_2O_4)_3]^{3-}$ ,  $[Fe(H_2O)_6]^{3+}$ ,  $[Fe(CN)_6]^{3-}$  which is most stable?

Ans.  $[Fe(CO)_5]$  is most stable because CO is strongest ligand.

II Observe the diagram of splitting of d-orbitals in octahedral field and answer the questions based on the diagrams and related studied concepts.



(a) What is crystal field splitting energy?

Ans: The energy difference between the two sets of d-orbitals is called crystal field splitting energy denoted by  $\Delta_0$

(b) Why  $d_{x^2-y^2}$ ,  $d_{z^2}$  have higher energy than  $d_{xy}$ ,  $d_{yz}$ ,  $d_{zx}$  orbitals in octahedral crystal field?

Ans: The orbitals  $d_{x^2-y^2}$ ,  $d_{z^2}$  lying in the direction of ligands, will experience greater repulsion and their energies will be raised relative to their positions in symmetrical field as compared to orbitals  $d_{xy}$ ,  $d_{yz}$ ,  $d_{zx}$  lying in between the axis away from the approach of ligand.

(c) What is relationship between (CFSE)  $\Delta_0$  and strength of ligand?

Ans. Greater the (CFSE)  $\Delta_0$ , more will be strength of ligand.

(d) What is electronic configuration of  $d^5$  ion if  $\Delta_0 < P$ ?

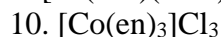
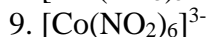
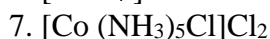
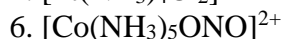
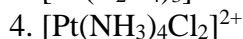
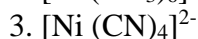
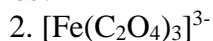
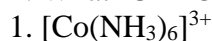
Ans.  $t_{2g}^3 e_g^2$

(e) What is spectrochemical series?

Ans. The series in which ligands are arranged in increasing order of magnitude of crystal field splitting energy ( $\Delta_0$ ) is called spectrochemical series.

### Topic:- Nomenclature of coordination compounds

1. What IUPAC names of following complexes?



Ans1. Hexammine cobalt (III) ion

Ans2. Trioxalato ferrate (III) ion

Ans3. Tetracyanido nickelate (II) ion

Ans4. Tetraammine dichlorido platinum (IV) ion

Ans 5. Tetrachloridonickelate (II) ion

Ans 6. Pentamminenitrito -O-cobalt (III) ion

Ans 7. Pentamminechlorido cobalt (III) Chloride

Ans 8. Pentaquacyanido chromium (III) ion

Ans9. Hexanitrito -N-cobaltate (III) ion

Ans 10. Tris(ethylenediamine) Cobalt (III) Chloride

**2. Write formula for the following compounds.**

1. Hexammine platinum (VI) Chloride

2. Potassium hexacyanido ferrate (III)

3. Diamminedichlorido platinum (III)

4. Tetramminedichlorido cobalt (III)

5. Amminechloridobis (ethane-1,2-diamine) cobalt (III)

6. Hexammine chromium (III) hexacyanido cobaltate (III)

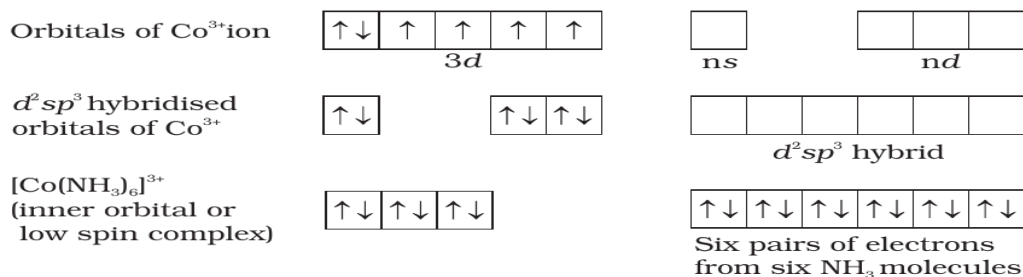
7. Pentamminenitro-N- Cobalt (III) Chloride.

8. Pentamminebromido cobalt (III) sulphate  
 9. Tri ammine di aquachlorido cobalt (III) Chloride  
 10. Tetrammine dichlorido platinum (IV) Bromide

- Ans1.  $[\text{Pt}(\text{NH}_3)_6]\text{Cl}_6$   
 Ans2.  $\text{K}_3[\text{Fe}(\text{CN})_6]$   
 Ans3.  $[\text{Pt}(\text{Cl}_2)(\text{NH}_3)_2]^+$   
 Ans4.  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$   
 Ans5.  $[\text{CoCl}(\text{en})_2(\text{NH}_3)]^{2+}$   
 Ans6.  $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$   
 Ans7.  $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$   
 Ans8.  $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$   
 Ans9.  $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})_2\text{Cl}]\text{Cl}_2$   
 Ans10.  $[\text{PtCl}_2(\text{NH}_3)_4]\text{Br}_2$

### TWO MARKS QUESTION

1. Explain that the complex  $[\text{Co}(\text{NH}_3)_6]^{3+}$  is diamagnetic on the basis of valence bond theory.  
 Ans. In  $[\text{Co}(\text{NH}_3)_6]^{3+}$  as all the electrons are paired so it is diamagnetic



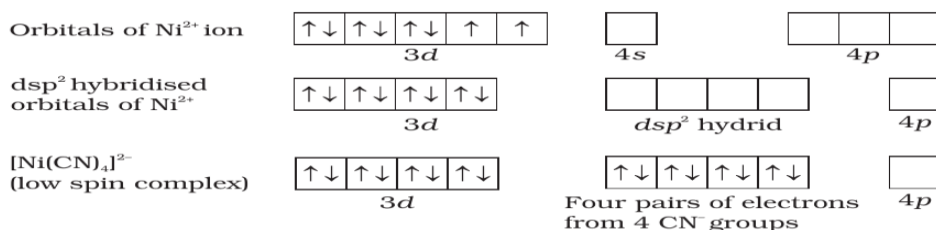
2. What are homoleptic and heteroleptic complex explain with suitable example?

Ans. Complexes in which the Central metal ion is bonded to only one kind of donor atoms or groups.

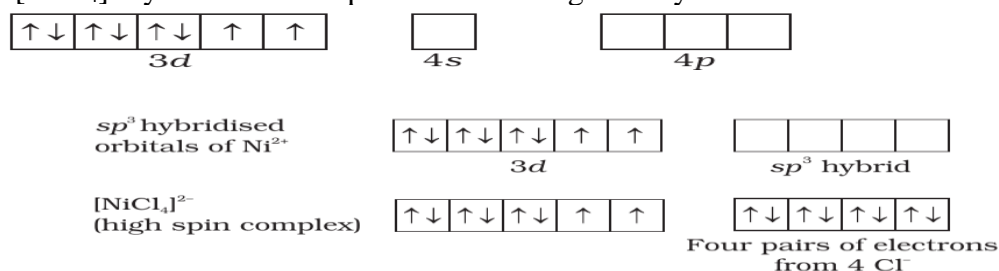
Example -  $\text{Co}(\text{NH}_3)_6]^{3+}$ , only ammonia is the ligand. Complexes in which the Central metal ion is bound to more than one kind of donor groups. Example-  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$

3.  $[\text{Ni}(\text{CN})_4]^{2-}$  is square planar whereas  $[\text{NiCl}_4]^{2-}$  is tetrahedral . Explain.

Ans. In  $[\text{Ni}(\text{CN})_4]^{2-}$  hybridization is  $dsp^2$  so square planar geometry

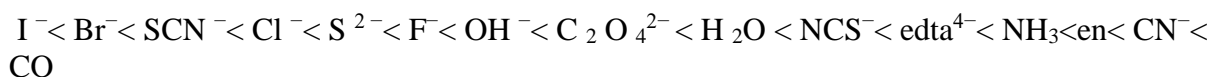


In  $[\text{NiCl}_4]^{2-}$  hybridization is  $sp^3$  so tetrahedral geometry Orbital's of  $\text{Ni}^{2+}$  ion



4. State crystal field theory.

- Ans: According to crystal field theory- (a). The metal ligand bond is ionic.  
 (b). Ligands are point charges in case of anions or dipoles in case of neutral molecules  
 (c). When the asymmetrical negative field of ligands surrounds the metal atom or ion, the degeneracy of its d- orbitals is lifted and they split into two sets.  
 (d). The pattern of splitting depends on the nature of crystal field.  
 (e). In general ligands can be arranged in a series in the order of increasing field strength called **spectro chemical series-**



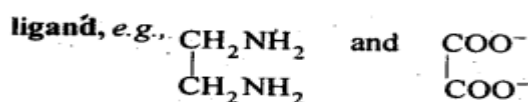
5. Why are complexes coloured? When is a coordination compound colourless?

Ans: The colour of complexes is due to d – d transitions of unpaired electron in d-orbitals  
 The complexes will be colourless if the configuration of metal ion or atom is  $d^{10}$  or  $d^0$

6. What is meant by Unidentate, Bidentate and ambidentate ligands? Give two examples for each.

Ans: A molecule or an ion which has only one donor atom to form one coordinate bond with the central metal atom is called Unidentate ligand, e.g.  $Cl^-$  and  $NH_3$ .

A molecule or ion which contains two donor atoms and hence forms two coordinate bonds with the central metal atom is called Bidentate

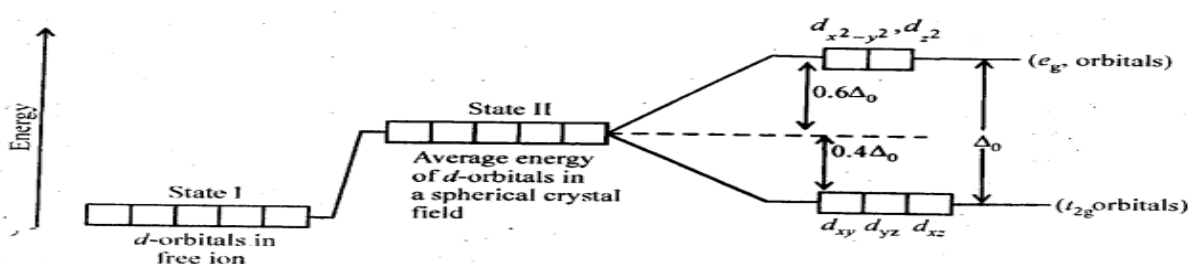


Ethylene diamine (en) Oxalate ion (ox)

A molecule or an ion which contains two donor atoms but only one of them forms a coordinate bond at a time with the central metal atom is called

**ambidentate ligand, e.g.  $:CN^-$  or  $NC^-$  and  $NO_2^-$  or  $ONO^-$**

7 Draw a figure to show the splitting of d orbital's in an octahedral crystal field.



### THREE MARKS QUESTION

1. What is crystal field splitting energy? How does the magnitude of  $\Delta_0$  decide the actual configuration of d orbitals in a coordination entity?

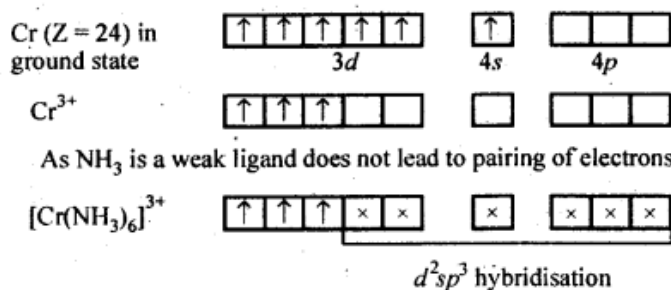
Ans- When the ligands approach a transition metal ion, the d-orbitals split into two sets, one with lower energy and the other with higher energy. The difference of energy between the two sets of orbitals is called crystal field splitting energy ( $\Delta_0$  for octahedral field). If  $\Delta_0 < P$  (pairing energy), the fourth electron enters one of the  $e_g$  orbitals giving the configuration  $t^3_2e^1_g$ , thus forming

high spin complexes. Such ligands for which  $\Delta_0 < P$  are called weak field ligands. If  $\Delta_0 > P$ , the fourth electron pairs up in one of the  $t_{2g}$  orbitals giving the configuration  $t_{2g}^4 e_g^1$  thereby forming low spin complexes. Such ligands for which  $\Delta_0 > P$  are called strong field ligands.

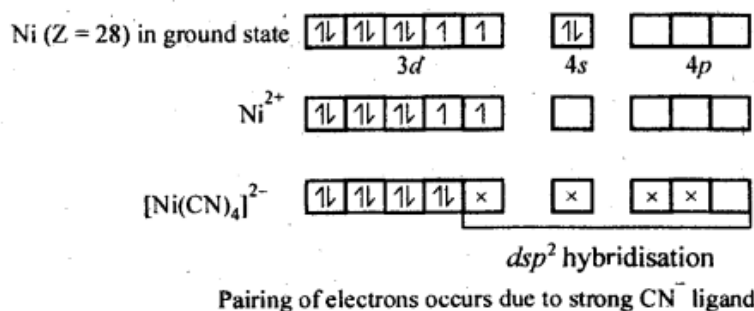
2.  $[\text{Cr}(\text{NH}_3)_6]^{3+}$  is paramagnetic while  $[\text{Ni}(\text{CN})_4]^{2-}$  is diamagnetic. Explain why?

Ans-

The presence of three unpaired electrons in  $[\text{Cr}(\text{NH}_3)_6]^{3+}$  explains its paramagnetic character.



$[\text{Ni}(\text{CN})_4]^{2-}$  is diamagnetic, since there is no unpaired electrons.



3. 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. Explain.

Ans- In  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ , Ni is in + 2 oxidation state and having  $3d^8$  electronic configuration, in which there are two unpaired electrons which do not pair in the presence of the weak  $\text{H}_2\text{O}$  ligand. Hence, it is coloured. The d-d transition absorbs red light and the complementary light emitted is green. In  $[\text{Ni}(\text{CN})_4]^{2-}$  Ni is also in + 2 oxidation state and having  $3d^8$  electronic configuration. But in presence of strong ligand  $\text{CN}^-$  the two unpaired electrons in the 3d orbitals pair up. Thus, there is no unpaired electron present. Hence, it is colourless.

4.  $[\text{Fe}(\text{CN})_6]^{4-}$  and  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  are of different colours in dilute solutions. Why?

Ans- In both the complexes, Fe is in + 2 oxidation state with  $d^6$  configuration. This means that it has four unpaired electrons. Both  $\text{CN}^-$  ion and  $\text{H}_2\text{O}$  molecules which act as ligands occupy different relative positions in the spectrochemical series. They differ in crystal field splitting energy ( $\Delta_0$ ). Quite obviously, they absorb radiations corresponding to different wavelengths/frequencies from the visible region of light. (VIBGYOR) and the transmitted colours are also different. This means that the complexes have different colours in solutions.

5. Explain the following:

- (i) The coordination-complexes are known for transition elements only.
- (ii) Nickel (II) does not form low spin octahedral complexes.
- (iii)  $[\text{Fe}(\text{CN})_6]^{4-}$  and  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  are of different colours in dilute solutions.

**Answer:**

(i) Transition metals have vacant d-orbitals which accept lone pair from ligands to form a bond and give pair of electron to molecular orbital of ligand forming  $d\pi - p\pi$  bond.

(ii)  $Ni^{2+}$  has unpaired electrons; therefore, forms high spin complex as pairing of electrons does not take place because after pairing only one d-orbital will be left which cannot be used in octahedral complex.

(iii) They absorb different wavelengths from visible light, undergo d-d transitions and radiate complementary colour.  $CN^-$  is stronger ligand than  $H_2O$ .

**FIVE MARKS QUESTION**

1. Give the oxidation state, d orbital occupation and coordination number of the central metal ion in the following complexes:

(i)  $K_3[Co(C_2O_4)_3]$

(ii)  $(NH_4)_2[CoF_4]$

(iii)  $cis-[Cr(en)_2Cl_2]Cl$

(iv)  $[Mn(H_2O)_6]SO_4$

**Ans:** (i)  $K_3[Co(C_2O_4)_3] \Rightarrow [Co(C_2O_4)_3]^{3-}$ .  $x + 3(-2) = -3$ . Oxidation state,  $x = +3$

Coordination number is also 6 as  $C_2O_4^{2-}$  is Bidentate.

$Co^{+3}$  is a case in which all electrons are paired

(ii)  $(NH_4)_2[CoF_4] = (NH_4)_2^{2+}[CoF_4]^{2-}$

$x - 4 = -2$ .

Oxidation state,  $x = +2$

Coordination number = 4.

$Co^{2+}$  is a  $d^5$  case, paramagnetic

(iii)  $cis-[Cr(en)_2Cl_2]^+Cl^-$

$x + 0 - 2 = +1$

Oxidation state,  $x = +3$

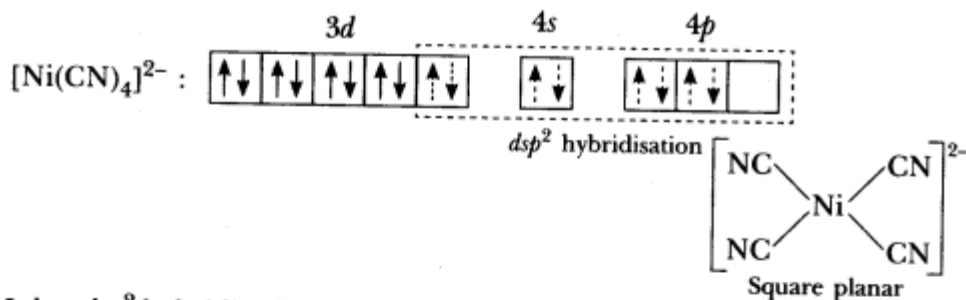
Coordination number is 6 as 'en' is Bidentate.  $Cr^{3+}$  is a  $d^3$  case, paramagnetic.

(iv)  $[Mn(H_2O)_6]^{2+}SO_4^{2-}$

$x + 0 = 2$  Oxidation state,  $x = +2$  Coordination number is 6.  $Mn^{+2}$  is a  $d^5$  case, paramagnetic

3. Compare the following complexes with respect to structural shapes of units, magnetic behaviour and hybrid orbitals involved in units:

(i)  $[Ni(CN)_4]^{2-}$  (ii)  $[NiCl_4]^{2-}$  (iii)  $[CoF_6]^{3-}$  [At. nos. : Ni = 28; Co = 27]

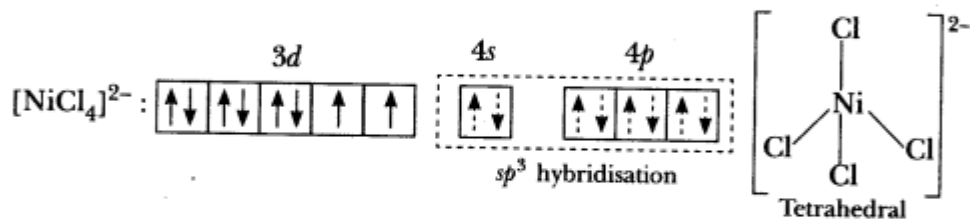


(ii) In  $[\text{NiCl}_4]^{2-}$ ,

Electronic configuration of Ni(28) :  $[\text{Ar}]4s^23d^8$

Electronic configuration of  $\text{Ni}^{2+}$  :  $[\text{Ar}]4s^03d^8$

$\text{Cl}^-$  is a weak field ligand, cannot cause pairing of electrons.

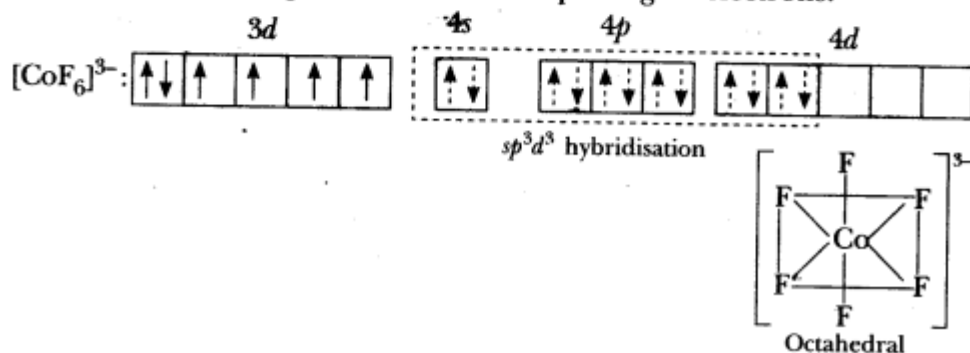


(iii) In  $[\text{CoF}_6]^{3-}$ ,

Electronic configuration of Co(27) :  $[\text{Ar}]4s^23d^7$

Electronic configuration of  $\text{Co}^{3+}$  :  $[\text{Ar}]4s^03d^6$

$\text{F}^-$  is a weak field ligand, cannot cause pairing of electrons.



Answer (i) \_

3. Compare the following complexes with respect to their molecular shape and magnetic behaviour :

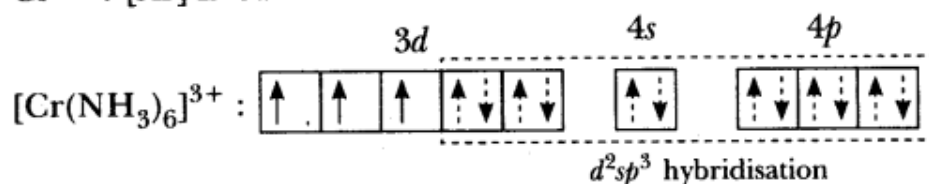
(i)  $[\text{Cr}(\text{NH}_3)_6]^{3+}$  (ii)  $[\text{Fe}(\text{CN})_6]^{4-}$  (iii)  $[\text{NiCl}_4]^{2-}$

(At. No. : Cr = 24, Fe = 26, Ni = 28)



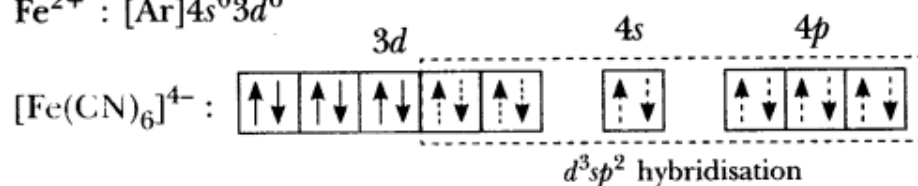
Ans-

- (i) In  $[\text{Cr}(\text{NH}_3)_6]^{3+}$   
 $\text{Cr}(24) : [\text{Ar}]4s^13d^5$   
 $\text{Cr}^{3+} : [\text{Ar}]4s^03d^3$



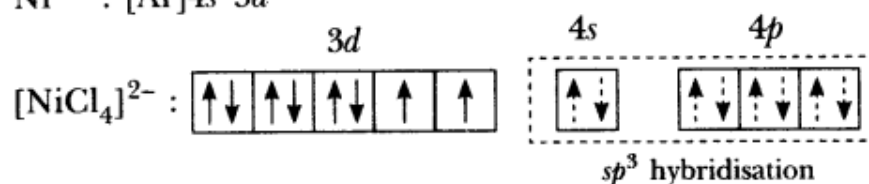
It has  $d^2sp^3$  hybridisation, octahedral shape, paramagnetic in nature.

- (ii) In  $[\text{Fe}(\text{CN})_6]^{4-}$   
 $\text{Fe}(26) : [\text{Ar}]4s^23d^6$   
 $\text{Fe}^{2+} : [\text{Ar}]4s^03d^6$



It has  $d^3sp^2$  hybridisation, octahedral shape, diamagnetic in nature.

- (iii) In  $[\text{NiCl}_4]^{2-}$   
 $\text{Ni}(28) : [\text{Ar}]4s^23d^8$   
 $\text{Ni}^{2+} : [\text{Ar}]4s^03d^8$



It has  $sp^3$  hybridisation, tetrahedral shape, paramagnetic in nature.

DAV CENTENARY PUBLIC SCHOOL, PASCHIM ENCLAVE, NEW DELHI-87

**XII CHEMISTRY BLUE PRINT**

**TERM – II**

**2021-22**

S.No	UNIT	SECTION-A (2 MARKS)	SECTION-B (3 MARKS)	SECTION-C (5 MARKS)	TOTAL
1	ELECTROCHEMISTRY	1(2)	1(3)	-	2(5)
2	CHEMICAL KINETICS	-	-	1(5)	1(5)
3	SURFACE CHEMISTRY	-	1(3)	-	1(3)
4	d- & f- BLOCK ELEMENTS	-	2(6)	-	2(6)
5	COORDINATION COMPOUNDS	-	1(3)	-	1(3)
6	ALDEHYDES, KETONES & CARBOXYLIC ACIDS	2(4)	1(3)	-	3(7)
7	AMINES	-	2(6)	-	2(6)
	<b>TOTAL NO OF QUESTIONS</b>	<b>3(6)</b>	<b>8(24)</b>	<b>1(5)</b>	<b>12(35)</b>

# IN 3 MARKS QUESTIONS 4 INTERNAL CHOICES MAY BE GIVEN.

# IN 5 MARKS QUESTION INTERNAL CHOICE MAY BE GIVEN IN (d) SUB PART.

MM:35

Time: 2 Hours

GENERAL INSTRUCTIONS:

Read the following instructions carefully.

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2. **SECTION A - Q. No. 1 to 3** are very short answer questions carrying 2 marks each.
3. **SECTION B - Q. No. 4 to 11** are short answer questions carrying 3 marks each.
4. **SECTION C- Q. No. 12** is case based question carrying 5 marks.
5. All questions are compulsory.
6. Use of log tables and calculators is not allowed

**SECTION A**

1. Give the answer of following questions; (1x2=2)
  - (a) Following reactions can occur at cathode during the electrolysis of aqueous silver nitrate solution using pt electrode  
$$\text{Ag}^+_{(\text{aq})} + \text{e}^- \longrightarrow \text{Ag}_{(\text{s})}; E^0 = 0.80\text{V}$$
$$\text{H}^+_{(\text{aq})} + \text{e}^- \longrightarrow 1/2 \text{H}_{2(\text{g})}; E^0 = 0.00\text{V}$$
On the basis of the standars electrode potential values, which reaction is feasible at cathode and why ?
  - (b) Why on dilution the  $\Lambda_m$  of  $\text{CH}_3\text{COOH}$  increases electrolytically while what of  $\text{CH}_3\text{COONa}$  increases gradually.
2. Give the answer of following questions; (any two) (1x2=2)
  - (a) Explain why Dialkylcadmium is considered superior to Grignard reagent for the preparation of a Ketone from an acid chloride
  - (b) Benzaldehyde reduce tollens reagent but not the fehlings are Benedict 's solution explain
  - (c) Why carboxylic acid do not give the characteristic reaction of carbonyl group.
3. Give the answer of following questions; (1x2=2)
  - (a) write a test to differentiate between pentan -2-one and pentan-3- one.
  - (B) What will be happen when nitriles react with stannous chloride in the presence of hydrochloric acid.

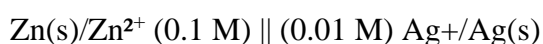
## SECTION B

4. Write the answer of following questions; (1x3=3)

(a) Define molar conductivity .

(b) Define electrochemical cell. What happens if External potential applied because greater than  $E^0_{\text{Cell}}$  of electrochemical cell ?

(c) Calculate emf of the following cell:



$$\text{Given } E^0_{\text{Zn}^{2+}/\text{Zn}} = -0.76\text{V}$$

$$E^0_{\text{Ag}^+/\text{Ag}} = +0.80\text{V} \quad [\text{Given, } \log 10 = 1]$$

5. Answer the following questions; (1x3=3)

(a) Justify the use of gelatin as protective colloids.

(b) What happens when a freshly precipitated  $\text{Fe}(\text{OH})_3$  is shaken with little amount of dilute solution of  $\text{FeCl}_3$ .

(c) What is mean by shape selective catalysis?

6. Explain briefly how +2 state becomes more and more stable in the first half of the first row transition elements with increasing atomic number ? (1x3=3)

7. On the basis of crystal field theory, explain why  $\text{Co}(\text{III})$  forms paramagnetic octahedral Complex with weak field ligand whereas it forms diamagnetic octahedral Complex with strong field ligands

OR

What is the relationship between observed colour of the complex and the wavelength of light absorbed by the complex ? (1x3=3)

8. How will you convert (any three) (1x3=3)

(i)  $\text{HCHO}$  into urotropine

(ii) Benzene to acetophenone

(iii) Ethanal to 2 hydroxy-3- butenoic acid

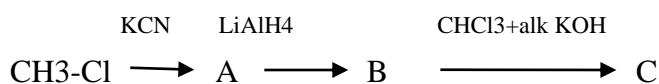
(v) Acetophenone to benzoic acid

9. Answer the following questions; (1x3=3)

(a) Are the following in the increasing order of their basic strength



(b) Write the structure of A, B and C in the following



(c) Write the structure of the following compounds

(i) N,N diethyl butane-1-amine

(ii) Butanamide

10. Answer the given questions; (1+2=3)

(a) The presence of a base is needed in the ammonolysis of alkyl halides. Explain.

OR

How will you convert 4-nitrotoluene to 2-bromo benzoic acid

(b) Give one chemical test to distinguish between the following pair of compounds

(i) Methylamine and dimethylamine

(ii) Secondary and tertiary amine

11. Give the answer of the following questions; (1x3=3)

(i) 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

(ii) Although fluorine is more electronegative than oxygen but the ability of oxygen to stabilise higher oxidation state exceeds that of fluorine. Why?

(iii) Predict which of the following will be coloured in aqueous solution:  $\text{Ti}^{3+}, \text{V}^{3+}, \text{Cu}^+, \text{Sc}^{3+}, \text{Mn}^{2+}, \text{Fe}^{3+}$  and  $\text{Co}^{2+}$ . Give reasons for each.

### SECTION C

12. Read the following and answer the questions from (i) to (iv) given below (1x5=5)

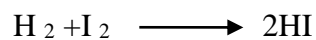
The rate of a chemical reaction at a given temperature may depend on the concentration of one or more reactants and sometimes even on the concentration of products or some foreign substances. The representation of rate of a reaction in terms of the concentration of the reactants is called rate law.

The rate law for a given reaction has to be established by experimental study of the rate of reaction over a wide range of concentration of the reactants and products. The rate law thus

established is also called differential rate equation or rate expression.

(i) The reaction  $2A+B+C \longrightarrow 2E$  is found to be first order in A, second order in B and zero order in C, then write the rate expression.

(ii) Express the rate of the following reaction



(iii) Why does the rate of a reaction not remain constant throughout the reaction process?

(iv) The reaction  $A+B \longrightarrow C$  has zero order. Write rate equation.

.....

TERM – II  
CHEMISTRY THEORY (043)

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MM:35

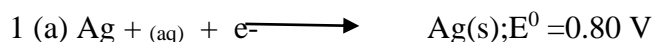
Time: 2 Hours

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6. Use of log tables and calculators is not allowed

**SECTION A**



Reaction is feasible at cathode because it has higher reduction potential 1

(b) In the case of  $\text{CH}_3\text{COOH}$  which is a weak electrolyte the number of ions increase on dilution due to an increase in degree of dissociation.  $\text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}_3\text{O}^+$  In the case of strong electrolyte the number of ions remains the same but the inter ionic attraction decreases. 1

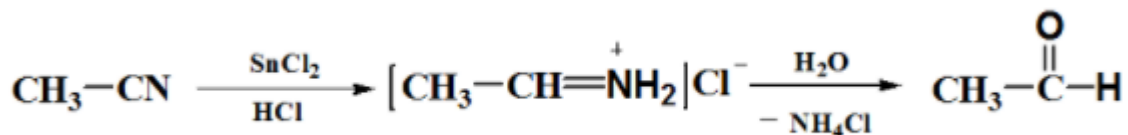
2. (a) Dialkyl cadmium is considered superior to grignard's reagent for preparation of ketones. This is so because dialkyl cadmium can only reduce acids to ketones, but grignard's reagent reduces ketones further to tertiary alcohols. because grignard reagent will react further with ketones to give tertiary alcohols 1

(b) Benzaldehyde reduces Tollens' reagent but not the Fehling's or the Benedict's solution. The electron-donating resonance effect (+R-effect) of the benzene ring increases the electron density in the carbonyl group of benzaldehyde. This, in turn, increases the electron density in the C-H bond of the aldehyde group 1

(c) Carboxylic acids do not give characteristic reaction of carbonyl group. This is because the lone pairs on oxygen atom attached to hydrogen atom in the  $-\text{COOH}$  group are involved in resonance thereby making the carbon atom less electrophilic. Hence, carboxylic acids do not give characteristic reaction of carbonyl group 1

3. (a) Iodoform test is performed to differentiate between pentan-2- one and pentan-3-one. the one with a ketonic group that is pentan-2- one will give iodoform test and pentan-3-one won't give it. iodoform tests are performed by compounds that have methyl ketones 1

(b) An example where the Stephan reaction is used is when acetaldehyde is produced from methyl cyanide as shown below. 1



As shown above, there is an imine intermediate formed when the nitrile undergoes reduction with stannous chloride and hydrogen chloride gas (in ethyl acetate solvent). This imine intermediate is subjected to hydrolysis to yield the corresponding aldehyde. 2

## SECTION B

4. (a) Molar conductivity of a solution is the conductance of that volume of solution containing one mole of electrolyte, kept between two electrodes having unit length joining them and large cross sectional areas so as to contain the electrolyte. 1

(b) Electrochemical cell is a device used for the production of electricity from energy released during spontaneous chemical reaction and use electrical energy to bring about the chemical change. If the external potential applied become greater than  $E^\circ_{\text{cell}}$  of electrochemical cell the reaction gets reversed. 1

(c) Using Nernst equation,  $E_{\text{cell}} = E^\circ_{\text{cell}} - 0.059 \log K$  1/2

$$E^\circ_{\text{cell}} = E^\circ_{\text{Ag}^+/\text{Ag}} - E^\circ_{\text{Zn}^{2+}/\text{Zn}}$$

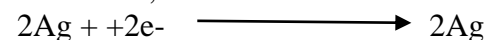
$$= 0.80 - (-0.76)$$

$$= 0.80 + 0.76 = 1.56\text{V}$$

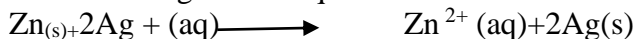
At anode,



At cathode,



On combining the net equation is



$$E_{\text{cell}} = 1.56 - 0.059/2 \log [\text{Zn}^{2+}] / [\text{Ag}^+]^2$$

1/2



6. +2 state becomes more and more stable in the first half of the first row transition elements with increasing atomic number as 3d orbitals acquire only one electron in each of five 3d orbitals (remain half-filled) and the electronic repulsion is least and the nuclear charge increases. In the second half of the first row transition series, electrons pair up in 3d orbitals. This increases the electronic repulsion.

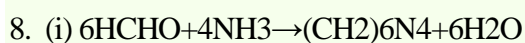
1x3

7. With weak field ligands;  $\Delta_0 < p$ , the electronic configuration of Co (III) will be  $t_{2g}^4 e_g^2$  and it has 4 unpaired electrons and is paramagnetic. With strong field ligands,  $\Delta_0 > p$ , the electronic configuration will be  $t_{2g}^6 e_g^0$ . It has no unpaired electrons and is diamagnetic.

1x3

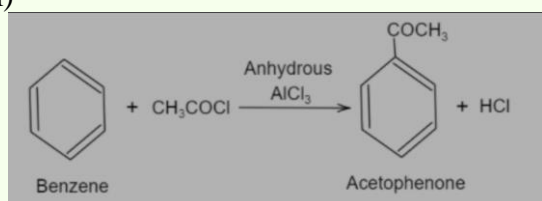
7. When white light falls on the complex, some part of it is absorbed. Higher the crystal field splitting, the lower will be the wavelength absorbed by the complex. The observed colour of the complex is the color generated from the wavelength left over.

1x3



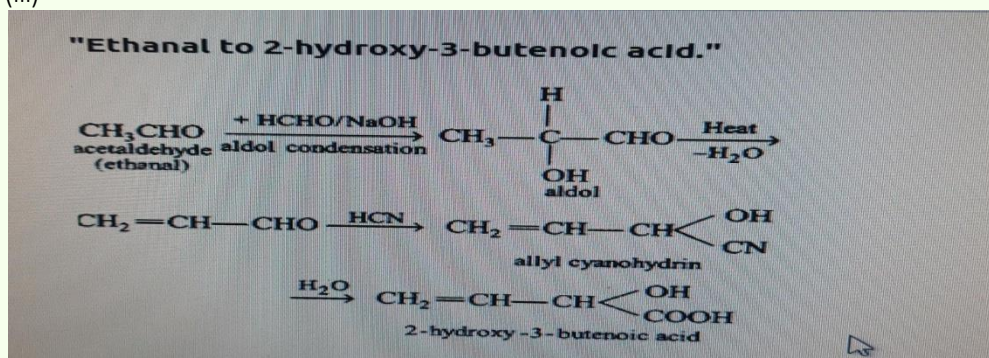
1

(ii)

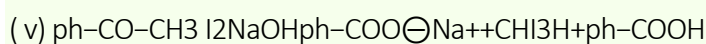


1

(iii)



1



Benzoic acid

Acetophenone

Acetophenone has  $\text{ph}-\text{OC}-\text{CH}_3$  group which can be converted to carboxylate ion in iodoform test. The formed carboxylate ion can be converted to acid by addition of  $\text{H}^+$ .

9. (a)  $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$ , N is not directly attached to the benzene ring. Thus, its lone pair is not delocalized over the benzene ring. Therefore, the electrons on the N atom are more easily available for protonation in  $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$  than in  $\text{C}_6\text{H}_5\text{NH}_2$  i.e.,  $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$  is more basic than  $\text{C}_6\text{H}_5\text{NH}_2$ .

1

(b) A = CH<sub>3</sub>-CN B = CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>, C = CH<sub>3</sub>CH<sub>2</sub>NC

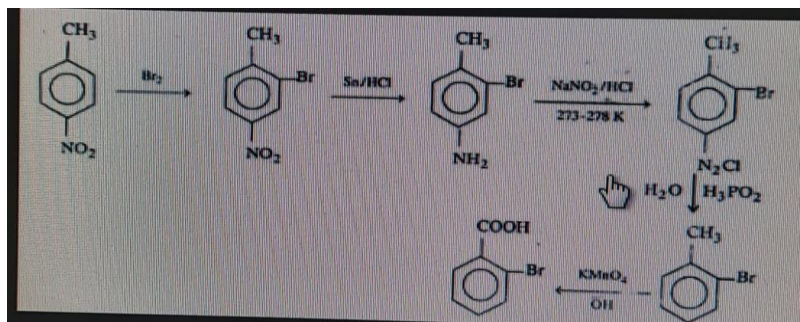
1

(c) (i) (CH<sub>3</sub>)<sub>2</sub>N(CH<sub>2</sub>)<sub>3</sub>-CH<sub>3</sub> (ii) CH<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub>CO NH<sub>2</sub>

½x2=1

10. (a) During ammonolysis of alkyl halides, the acid liberated during the reaction combines with the amine and forms amine salt. To liberate free amine from the amine salt, a base is needed. The base used is excess of alcoholic NH<sub>3</sub> which serves both as a nucleophile as well as a base 1

10.(a)



10(b) (i) Methylamine and dimethylamine can be distinguished by the carbylamine test 1

(ii) Secondary and tertiary amines can be distinguished by reacting them with Hinsberg's reagent which is also called benzenesulphonyl chloride. 1

11.(i) Electronic configuration of Ce:

Ce:  $2S^2 P^6 3S^2 3P^6 3d^{10} 4S^2 4P^6 4d^{10} 5S^2 5P^6 4f^1 5d^1 6S^2$

∴ Electronic configuration of Ce<sup>+3</sup> using Hund's rule is,

Ce<sup>+3</sup>:  $1S^2 2S^2 P^6 3S^2 3P^6 3d^{10} 4S^2 4P^6 4d^{10} 5S^2 5P^6 4f^1$

or, Ce<sup>+3</sup>:  $54[Xe]4f^1$

No. of unpaired electrons in Ce<sup>+3</sup> = 1 = n

∴ Magnetic moment,  $\mu = n(n+2)$  B.M

⇒  $\mu = 1(1+2)$  B.M

⇒  $\mu = 3$  B.M

⇒  $\mu = 1.73$  B.M

1

11. (i) Oxygen can form multiple bonds with metals, while fluorine can't form multiple bonds with metals. Hence, oxygen has more ability to stabilize higher oxidation state rather than fluorine.

(ii) Transition metal ions with incompletely filled d orbitals are colored and those with completely filled d orbitals (or vacant d orbitals) are colorless.

Ti<sup>3+</sup>, V<sup>3+</sup>, Mn<sup>2+</sup> and Co<sup>2+</sup> are colored due to d-d transition in incompletely filled d orbitals.

Cu<sup>+</sup>, Sc<sup>3+</sup> are colorless due to completely filled and empty d orbitals respectively.

1

## SECTION C

- 12 (i) .Rate =  $k[A]^1[B]^2[C]^0$  1
- (ii) Rate =  $-d[H_2]/dt = -d[I_2]dt = + 1/2d[HI]dt$  1
- (iii) Rate = k Change in concentration / time
- The rate of a reaction decreases as time progressed as it is inversely proportional to time 2
- (iv) For the zero order reaction rate equation =  $k[A]^0[B]^0$  1

**GENERAL INSTRUCTIONS:**

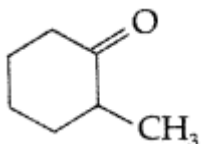
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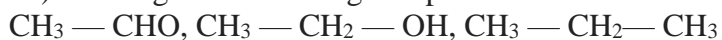
**SECTION A**

1. The conductivity of 0.20 M solution of KCl at 298 K is  $0.025 \text{ S cm}^{-1}$ . Calculate its molar conductivity.

2.a) Write the IUPAC name of the following :



b) Rearrange the following compounds in the increasing order of their boiling points:



3. Give reasons :

- (i) Electrophilic substitution in Benzoic acid takes place at meta position.
- (ii) Carboxylic acids do not give characteristic reactions of carbonyl group.

**SECTION B**

4. Explain what is observed when

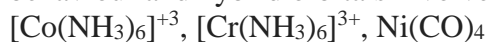
- (i) an electric current is passed through a colloidal sol.
- (ii) a beam of light is passed through a colloidal sol
- (iii) an electrolyte (say NaCl) is added to ferric hydroxide sol

**OR**

4. Explain the following:

- (i) Deltas are formed when river and sea water meet.
- (ii) Artificial rain is caused by spraying salt over clouds.
- (iii) Physisorption is multi-layered, while chemisorption is mono-layered.

5. Compare the following complexes with respect to structural shapes of units, magnetic behaviour and hybrid orbitals involved in unit:



(At. nos. : Co = 27, Cr = 24, Ni = 28)

**OR**

5.a) Explain why the Low spin octahedral complexes of nickel are not known.

b) Using IUPAC norms write the formulae for the following:

(i) Sodium dicyanido aurate (I)

(ii) Tetra ammine chlorido nitrito-N-platinum (IV) sulphate

6. Calculate the EMF of the following cell at 298 K:

$\text{Fe(s)} \mid \text{Fe}^{2+} (0.001 \text{ M}) \parallel \text{H}^+ (1\text{M}) \mid \text{H}_2(\text{g}) (1 \text{ bar}), \text{Pt(s)}$  (Given  $E^\circ_{\text{cell}} = +0.44\text{V}$ )

7. An organic compound with molecular formula  $\text{C}_5\text{H}_{10}\text{O}$  does not reduce Tollen's reagent but forms an addition compound with sodium hydrogen sulphite and gives a positive iodoform test. On vigorous oxidation, it gives ethanoic acid and propanoic acid. Identify the compound and write all chemical equations for the reactions.

8.a) What is lanthanoid contraction? What are the consequences of lanthanoid contraction?

b)  $\text{Cu}^+$  is unstable in an aqueous solution. Why?

9 Give reasons for the following:

(i) Silver atom has completely filled d-orbitals ( $4d^{10}$ ) in its ground state, yet it is regarded as a transition element..

(ii)  $\text{MnO}$  is basic while  $\text{Mn}_2\text{O}_7$  is acidic.

(iii) Calculate the magnetic moment of a divalent ion in aqueous medium if its atomic no is 26.

**OR**

9. Explain the following observations giving an appropriate reason for each.

(i) The enthalpies of atomization of transition elements are quite high.

(ii) Most of the transition metal ions exhibit characteristic colours in aqueous solutions.

(iii)  $\text{Mn}^{2+}$  is much more resistant than  $\text{Fe}^{2+}$  towards oxidation.

10.a) Give the chemical tests to distinguish between the following pairs of compounds :

(i) Methyl amine and Dimethylamine

(ii) Secondary and tertiary amines

b) Convert-Nitromethane to dimethylamine

11. Give reasons for the following:

(a) Acetylation of aniline reduces its activation effect.

(b)  $\text{CH}_3\text{NH}_2$  is more basic than  $\text{C}_6\text{H}_5\text{NH}_2$ .

(c) Although  $-\text{NH}_2$  is o/p directing group, yet aniline on nitration gives a significant amount of m-nitroaniline.

**OR**

11. An aromatic compound 'A' on treatment with aqueous ammonia and heating forms compound 'B' which on heating with  $\text{Br}_2$  and  $\text{KOH}$  forms a compound 'C' of molecular formula  $\text{C}_6\text{H}_7\text{N}$ . Write the structures and IUPAC names of compounds A, B and C.

## SECTION C

12. Read the passage given below and answer the questions that follow:-

### What is the Order of a Reaction?

The mathematical expression showing the dependence of rate on the concentration(s) of reactant(s) is known as rate-law or rate-expression of the reaction and sum of the indices (powers) of the concentration terms appearing in the rate law as observed experimentally is called order of reaction.

The order of a reaction in some species seems an obvious, trivial concept that all chemists master. However, in complex situations such as catalytic systems, the order of a reaction is not always that simple: it can be partial, negative and function of other parameters. In order to analyze rate laws and experimental orders of complex reaction networks, it is necessary to have a proper mathematical description of what the order of a reaction is. In general, chemists working in catalysis are unaware that such a mathematical description exists and therefore they are restricted to analyzing only extreme limit cases of rate laws. This manuscript offers a description and a simple demonstration of this concept, known as elasticity coefficient or normalized sensitivity. It also presents several examples of applications on classic and usual catalytic scenarios. Kinetic studies of catalytic reactions are an essential part of experimental mechanistic studies, performed to understand these reactions at a molecular level. Kinetic studies reveal how much each parameter affects the rate of a reaction at each time. This information is useful from a practical point of view, and it also allows discerning between different mechanistic proposals. Each mechanistic proposal has a different rate law, which is the equation that indicates the expected effect of each parameter on the rate of a reaction. However, this information is not always easy to extract and interpret for catalytic reactions due to the inherent complexity of their rate laws. (Jordi Bures) Published online: 9 May 2017

- a) For a reaction  $R \rightarrow P$ , half-life ( $t_{1/2}$ ) is observed to be independent of the initial concentration of reactants. What is the order of reaction?
- b) A reaction is found to be zero order. Will its molecularity be equal to zero?
- c) What is the order of the reaction whose rate constant has same units as the rate of reaction?
- d) A reaction is of second order with respect to a reactant. How will the rate of reaction be affected if the concentration of this reactant is i) reduced to half ii) doubled?

**OR**

- d) i) The thermal decomposition of HI on gold surface belongs to which order of reaction?
  - ii) Does the catalyst change the equilibrium constant of a reaction?
-

**MARKING SCHEME (2021-22)**  
**TERM – II CLASS -XII**  
**CHEMISTRY THEORY (043)**  
**SECTION A**

1.  $\Lambda_m = k \cdot 1000$

$= 0.025 \cdot 1000 / .20 = 125 \text{ S cm}^2 \text{ mol}^{-1}$

1

$\Lambda_m = 125 \text{ S cm}^2 \text{ mol}^{-1}$

1

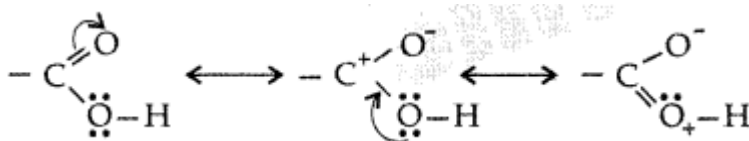
2.a) IUPAC name : 2-Methylcyclohexanone 1

b)  $\text{CH}_3\text{CH}_2\text{CH}_3 < \text{CH}_3\text{CHO} < \text{CH}_3\text{CH}_2\text{OH}$

1

3.(i) Since the — COOH group in benzene is an electron withdrawing group, therefore it is meta directing group. 1

(ii) The carboxylic carbon is less electrophilic than carbonyl carbon because of the possible resonance structure.



**SECTION B**

4. (i) When electric current is passed through a colloidal solution, the positively charged particles move towards cathode while negatively charged particles move towards anode where they lose their charge and get coagulated. The phenomenon is known as Electrophoresis. 1

(ii) When a beam of strong light is passed through a colloidal solution, scattering of light occurs by colloidal particles and the path of light becomes visible and the phenomenon is known as Tyndall effect. 1

(iii) When NaCl is added to hydrated ferric oxide solution, then coagulation will take place. 1

**OR**

4. (i) River water is a colloidal solution. 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 deltas. 1

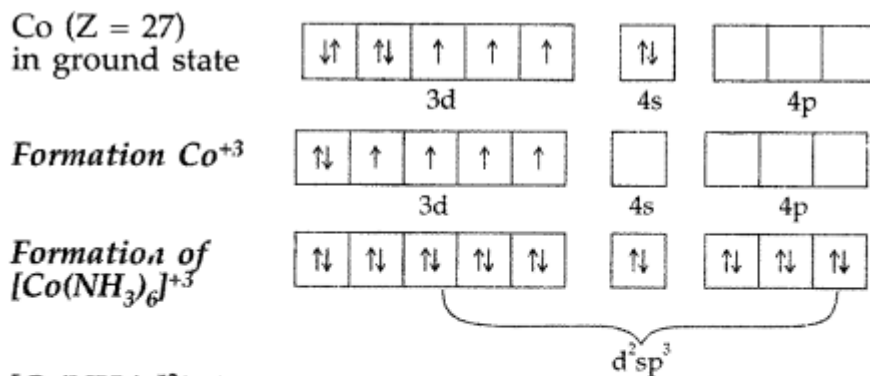
(ii) Clouds are colloidal dispersion of water particles in air carrying some charge over them. It is possible to cause artificial rain by throwing electrified sand or spraying a sol carrying charge opposite to the one on clouds from an aeroplane. The colloidal water particles present in the clouds will get neutralized and as result they will come closer and grow in size to form bigger water drops and ultimately cause artificial rain. 1

(iii) In physical adsorption, layers of the gas can be adsorbed one over the other by vander Waals forces. Multi-molecular layers are formed under high pressure. In chemical adsorption, chemical bond can be formed only with the layer of molecules coming in direct contact with the surface of the adsorbent, hence this type of adsorption is mono-layered. 15) 1+1+1

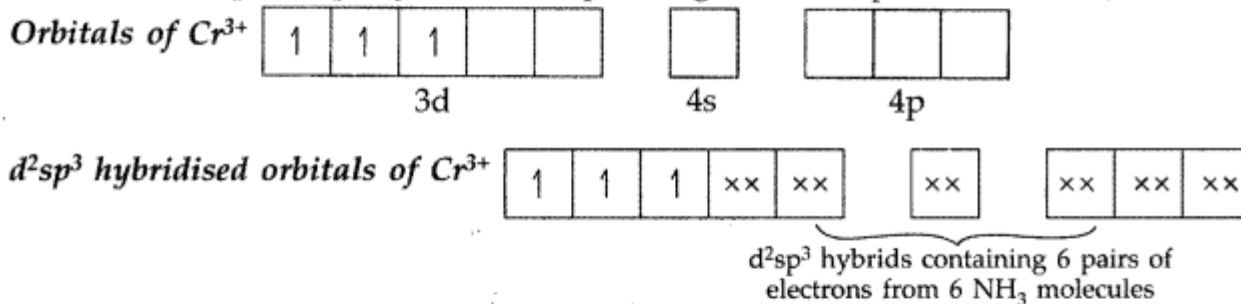
(i)  $[\text{Co}(\text{NH}_3)_6]^{+3} \rightarrow$  Octahedral shape,  $d^2sp^3$  hybridisation, diamagnetic

Formation of  $[\text{Co}(\text{NH}_3)_6]^{+3} \rightarrow$  oxidation state of Co is

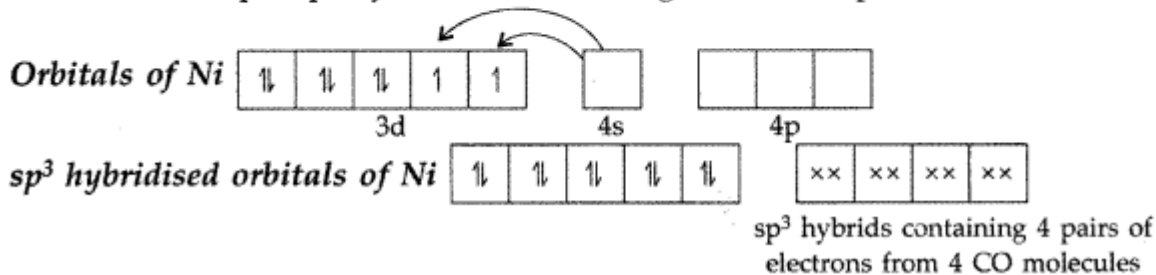
+3.



(ii)  $[Cr(NH_3)_6]^{3+}$   
Octahedral shape,  $d^2sp^3$  hybridisation paramagnetic (3 unpaired electrons)



(iii)  $[Ni(CO)_4]$   
Tetrahedral shape,  $sp^3$  hybridisation, diamagnetic (no unpaired electrons)



OR

5. a) The electronic configuration of Ni is  $[Ar] 3d^8 4s^2$  in which two inner d orbital's are not available which are required to form  $d^2sp^3$  hybridization. 1

b)(i)  $Na[Au(CN)_2]$

(ii)  $[Pt(NH_3)_4 Cl (NO_2)] (SO_4)$  1+1

6. As  $Fe + 2H^+ \rightarrow Fe^{2+} + H_2$  (n = 2) 1

According to Nernst equation

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.0591}{2} \log \frac{[Fe^{2+}]}{[H^{+2}]^2}$$

$$\Rightarrow E_{\text{cell}} = 0.44 - \frac{0.0591}{2} \log \frac{10^{-3}}{1^2}$$

$$\therefore E_{\text{cell}} = 0.44 - \frac{0.0591}{2} \times (-3) \\ = 0.44 + 0.0887 = 0.529 \text{ V}$$

1+1

7. (i) Molecular formula of compound :  $C_5H_{10}O$ .

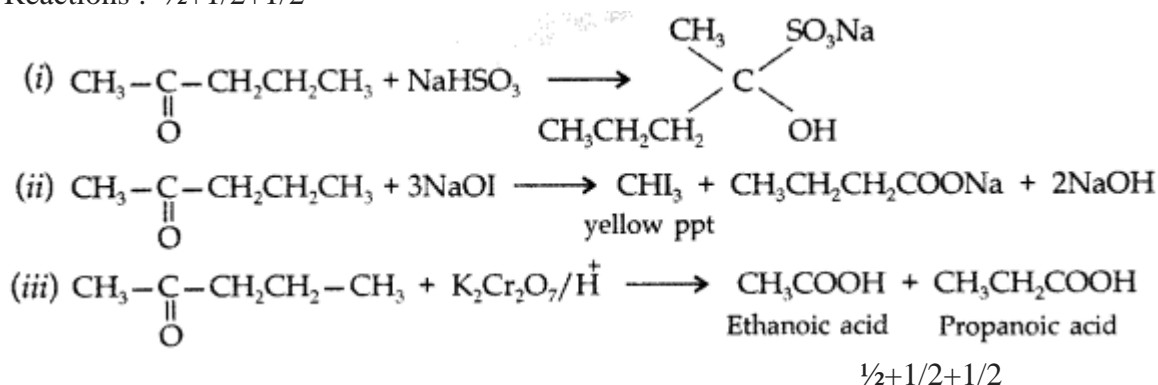
(ii) It gives an addition product with  $NaHSO_3$  so it must be either an aldehyde or methyl ketone.

(iii) It does not reduce Tollen's reagent so it is not an aldehyde.



- (iv) It gives +ve iodoform test, therefore it is methyl ketone.  
 (v) On oxidation it gives a mixture of ethanoic acid and propanoic acid  
 Therefore, possible structure is pentan-2-one.

Reactions :  $\frac{1}{2}+1/2+1/2$



8 a) Lanthanoid contraction: The overall decrease in atomic and ionic radii with increasing atomic number from La to Lu due to imperfect shielding of 4f-orbital is known as lanthanoid contraction.

### Consequences :

(i) Due to small change in atomic radii, the chemical properties of lanthanoids are very similar due to which separation of lanthanoids becomes very difficult.

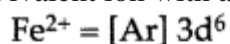
(ii) There is similarity in size of elements belonging to same group of second and third transition series.  $1+1/2+1/2$

b)  $\text{Cu}^+$  is unstable in an aqueous solution because  $\text{Cu}^+$  undergoes disproportionation reaction as follows:  $2\text{Cu}^+ \rightarrow \text{Cu}^{2+} + \text{Cu}$  1

9. (i) Because silver has incomplete d-orbital ( $4d^9$ ) in its +2 oxidation state, hence it is a transition element. 1

(ii)  $\text{MnO}$  is basic while  $\text{Mn}_2\text{O}_7$  is acidic because the basic nature decreases as the oxidation state or number of oxygen atoms increases i.e.  $\text{MnO}$  (+4) and  $\text{Mn}_2\text{O}_7$  (+7). 1

(iii) Divalent ion with atomic number 26 is  $\text{Fe}^{2+}$



$$\mu = \sqrt{n(n+2)} \text{ B.M.} \Rightarrow \mu = \sqrt{4(4+2)} \text{ B.M.}$$

$$\Rightarrow \mu = 4.90 \text{ B.M.}$$

1

### OR

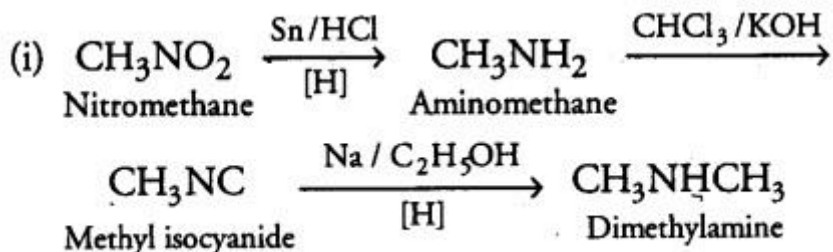
9.(i) In transition elements, there are large number of unpaired electrons in their atoms, thus they have a stronger inter atomic interaction and thereby stronger bonding between the atoms. Due to this they have high enthalpies of atomization. 1

(ii) Due to the presence of unpaired electrons in d-orbital, transition metal exhibits colours in aqueous solution or due to d-d transition 1

(iii) The 3d orbital in  $\text{Mn}^{2+}$  is half-filled and is more stable compared to  $\text{Fe}^{2+}$  has 6 electrons in the 3d orbital.  $\text{Mn}^{2+}$  prefer to lose an electron or get oxidised whereas  $\text{Fe}^{2+}$  will readily loose one electron or get oxidised. Therefore,  $\text{Mn}^{2+}$  is much more resistant than  $\text{Fe}^{2+}$  towards oxidation. 1

10. (i) Methylamine and Dimethyl amine : By Carbylamine test: Methylamine being a primary amine gives this test but Dimethylamine being a secondary amine does not. 1

ii) Hinsberg test Secondary amine forms alkyl sulphonamide which does not form salt with alkali and hence remains insoluble (solid) in alkali solution. Tertiary amines does not react with Hinsberg's reagent. 1  
b) 1



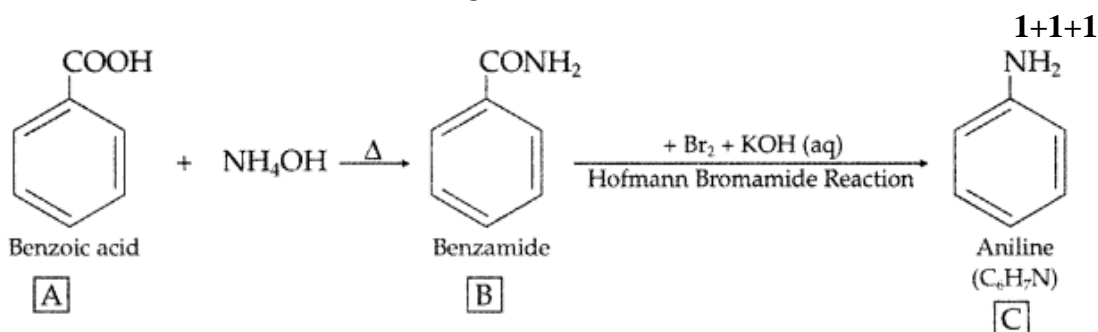
11(i) Acetylation of aniline reduces its activation effect because acetyl group being electron withdrawing group attracts the lone pair of electrons of the N-atom towards carboxyl group and the lone pair of electrons on N is less available for donation to benzene ring by resonance.

(ii)  $\text{CH}_3\text{NH}_2$  is more basic than aniline due to availability of lone pair of electrons for donation while in aniline lone pair of electrons on the nitrogen atom is delocalised over benzene ring and thus less available for donation.

(iii) Because of nitration in an acidic medium, aniline gets protonated to give anilinium ion which is meta directing. 1+1+1

OR

11 .



Thus,

A → Benzoic acid, B → Benzamide, C → Aniline

### SECTION C

12. a) first order reaction 1  
 b) No, the molecularity can never be zero. 1  
 c) zero order reaction 1  
 d) i) reaction will reduced to 1/4 th of initial rate ii) rate will increase 4 times 1+1

OR

- d) i) zero order reaction 1  
 ii) No, catalyst does not alter the equilibrium constant of a reaction. 1