



केन्द्रीय विद्यालय संगठन
Kendriya Vidyalaya Sangathan

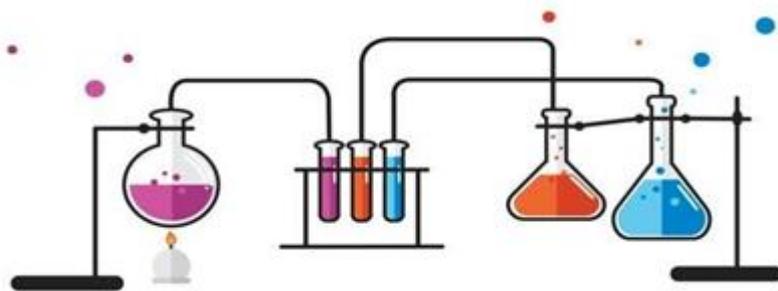
Chemistry (043) / XII / TERM-2 / 2021-22



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केन्द्रीय विद्यालय संगठन

KENDRIYA VIDYALAYA SANGATHAN AHMEDABAD REGION
STUDENT SUPPORT MATERIAL TERM-2
CLASS- XII

SUBJECT- CHEMISTRY(043) SESSION- 2021-22



INSPIRATION



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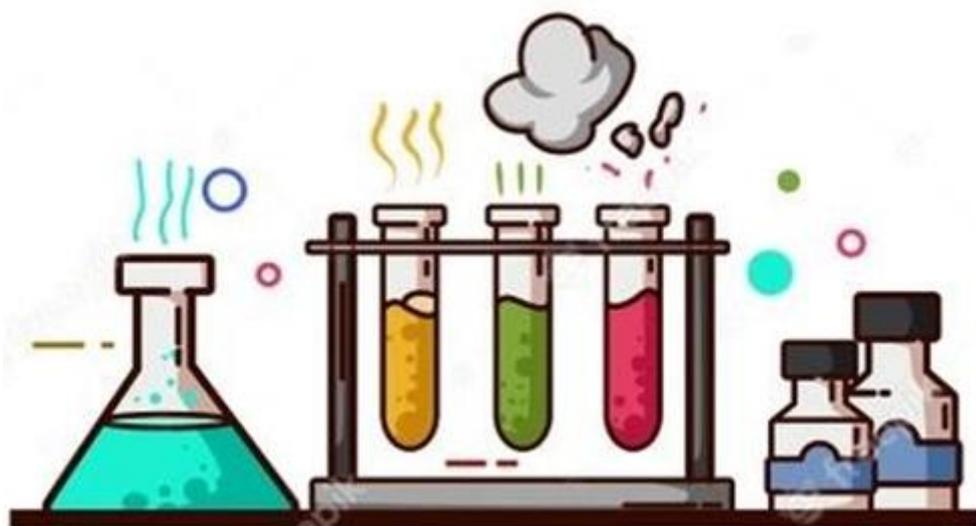
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SYLLABUS FOR SESSION 2021-22

CLASS XII - Term-II

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

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

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

Surface Chemistry: Adsorption - physisorption and chemisorption, factors affecting adsorption of gases on solids, colloidal state: distinction between true solutions, colloids and suspension; lyophilic, lyophobic, multi-molecular and macromolecular colloids; properties of colloids; Tyndall effect, Brownian movement, electrophoresis, coagulation.

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

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

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

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

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

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

PRACTICALS

TERM-II Evaluation Scheme

S. No	Practical	Marks
1.	Volumetric Analysis	4
2.	Salt Analysis	4
3	Content Based Experiment	2
4	Project Work and Viva (Internal and External Both)	5
	TOTAL	15

1) Volumetric analysis (4 marks)

Determination of concentration/ molarity of KMnO_4 solution by titrating it against a standard solution of:

- i. Oxalic acid,
- ii. Ferrous Ammonium Sulphate

(Students will be required to prepare standard solutions by weighing themselves).

2) Salt analysis (Qualitative analysis) (4 marks)

Determination of one cation and one anion in a given salt.

Cations- Pb^{2+} , Cu^{2+} , As^{3+} , Al^{3+} , Fe^{3+} , Mn^{2+} , Ni^{2+} , Zn^{2+} , Co^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , Mg^{2+} , NH_4^+ Anions - $(\text{CO}_3)^{2-}$, S^{2-} , NO_2^- , SO_3^{2-} , SO_4^{2-} , NO_3^- , Cl^- , Br^- , I^- , PO_4^{3-} , $\text{C}_2\text{O}_4^{2-}$, CH_3COO^- (Note: Insoluble salts excluded)

3) **Content based experiment**

A. Preparation of Inorganic Compounds

Preparation of double salt of Ferrous Ammonium Sulphate or Potash Alum. Preparation of Potassium Ferric Oxalate.

B. Tests for the functional groups present in organic compounds:

Unsaturation, alcoholic, phenolic, aldehydic, ketonic, carboxylic and amino (Primary) groups.

General Instructions for Investigatory Project

In Chemistry the students of class XI and XII are supposed to conduct a scientific investigations involving laboratory testing and collecting information from other sources. This project is assessed as a part of practical examination at the end of year.

At the outset, teachers must map appropriate competencies or learning outcomes with real world problems (projects) that are age appropriate for their students. Students in consultation with their teacher finally determine the project question for them depending upon their interest and proclivity. A project should ideally arise out of the need felt by the student. Students explore their areas of interest and narrow down their ideas to a testable hypothesis or problem question.

For example: Abdul waits for summers as his favorites fruit watermelon is available in plenty. This year he noticed that every time he bought a watermelon its colour was dark red and was exceptionally sweet from inside. This never happened in earlier years. Some watermelons would be sweet some would not. Abdul were surprised by this observation and worried if the fruit was adulterated. He thought of conducting a test to find out if fruits and vegetables available in his locality were adulterated. He reviewed articles and papers on adulteration and found out simple tests to check adulteration at home. Abdul conducted the test and shared his results with his friend and teacher. He developed a small manual to help other check adulteration in fruits.

There are many issues in our immediate surroundings which need to be addressed. Keen observation will help identify the problem.

Before developing a problem question, students must do research on topics and find out what other people have already done in the selected area to avoid repetition. During this phase, students should be encouraged to record the reference of every bit of information they got from different sources. After developing problem question, students should write down precise testable

hypothesis and design an experiment or procedure to test their hypothesis by collecting and analysing the data followed by writing conclusion and limitation of the study. Students must also develop a timeline and checklist about accessibility to resources required, safety of experiment/procedure, harmlessness of experiments to environment, organisms and other people. Teacher must ensure that it is doable within a specified period of time and available resources and is appropriately challenging to a particular student (neither be very complex or longer nor be very easy and short). It should not culminate into finding information from a book or website.

A project could have the following outline:

1. **Statement of Problem-** A clear statement of the problem.
2. **Objectives-**General and specific objectives of topic.
3. **Introduction-**The introduction should describe the relevance of problem or why the problem is the most appropriate for your inquiry. It should also describe previously known facts about your problem question with proper bibliography. Introduction towards end briefly includes hypothesis your hypothesis and the method to test it.
4. **Problem question-** (specific, concrete questions to which concrete answers can be given) and/ or hypotheses
5. **Methods/Procedures-**Methodology (will your research be based on survey, an experimental investigation, historical study, ethnographic study or content analysis).Methods describe the experiments proposed or the observations planned to make and the detailed process of analysis of data/observations. Methods proposed should be feasible and be able to adequately answer problem question.
6. **Materials/Resources required**
7. **Observations/Data gathered**

Using the procedures mentioned in introduction, experiments should be conducted and data should be recorded. Interesting things that happened during the conduct of experiments should also be recorded.
8. **Analysis of data and discussion of result**

Data should be interpreted in terms of proposed hypothesis. Data should be tabulated and interpreted with the help of graphs. The interpretation should be done in an honest manner even if it does not support proposed hypothesis.
9. **Conclusion Reporting and writing up the report**

Discussion of new learning from the study may be covered under

conclusion. This may have possible suggestions for future studies.

10. Limitation of the study

The limitations of the study are those features of design or procedure that might have affected the interpretation of the results of study. The limitations are alternatively interpreted as flaws or shortcomings due to flawed methodology, observations, small number of experiments or non-peer reviewed nature of study etc.

11. Bibliography

Rubric for Assessment of Project

PARAMETER	Exemplary (4)	Accomplished (3)	Developing (2)	Beginner (1)
Factual information	Content covers the research well	Content from all eras but has few inaccuracies	Content does not cover all eras and has few inaccuracies	Content does not cover all eras and is historically Inaccurate
Sources	Multiple sources (6 or more) used (library, books, interview with people, different websites, blogs etc.)	Many sources (4-5) used (Books, websites, blogs)	Few sources used (2-3)	Relied on only one source
Data collection	Collected data from a large random sample (50 people or more from different age group, gender, social status) OR collected data for different samples and at least 5 reading for each set of experiment	Collected data from a fairly large random sample (30 - 50 people from different age group, gender, social status) OR collected data for different samples and 3 reading for each set of experiment	Collected data from a small random sample (20 people from different age group, gender, social status) OR collected data for one sample and 3-5 readings	Collected data from a small sample (10 or less people) OR collected data for one sample and 1-2 readings

Interpretations and conclusion	In correlation with data and aim of the project. Clear conclusions based on findings	In correlation with data and aim of the project. Conclusions not based on findings	Not in correlation with data but in correlation with the aim Random conclusions	Not in correlation with data and aim, No conclusions
Journal	Daily entries with details of discussions and brainstorming sessions with the teacher.	Most of the entries done with details of discussions with the teacher	Daily entries without details	Random entries
Project report	Exceptionally attractive, organized sequentially and logically, creatively presented with data and clear conclusions	Attractive, organized sequentially and logically, presented some data and conclusions	Information is organized sequentially and logically but not in an attractive manner. Random Data without conclusions	Presentation is confusing. There is no sequence.
Academic Honesty	Sites all sources and gives due credits	Most of the sources cited	Few sources cited	Uses other people's ideas without giving Credit

CHAPTER -1

ELECTROCHEMISTRY

- Electrochemical cells (Galvanic cells) produce electricity as a result of chemical reaction, while in electrolytic cells electricity is used to produce a non-spontaneous chemical change at the electrodes.
- In Galvanic Cells, oxidation occurs at -ve electrode called anode whereas reduction occurs at +ve electrode called cathode.
- **ELECTRODE POTENTIAL OF A CELL $E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$**
(in terms of reduction potential)
- **FREE ENERGY CHANGE FOR THE REACTION $\Delta G^{\circ} = -nF E^{\circ}_{\text{cell}}$**
- $E^{\circ}_{\text{cell}} = \frac{0.059}{n} \log K_c$ (At 298 K) K_c is EQUILIBRIUM CONSTANT
- $\Delta G^{\circ} = -nF \frac{2.303 RT}{nF} \log K_c$ or
- $\Delta G^{\circ} = -2.303 RT \log K_c$
- For an electrochemical cell if $\Delta G^{\circ} < 0$ then cell will work
- E°_{cell} is > 0 for spontaneous process.
- As per E° values, a metal having more negative reduction potential is stronger reducing agent than hydrogen while a metal having more positive reduction potential is weaker reducing agent than hydrogen.

- **NERNST EQUATION**

$$E = E^{\circ} - \frac{0.0591}{n} \log \frac{1}{[M^{n+}_{(aq)}]}$$

- **Mass of substance deposits at electrode $m = Z I(\text{amp}) t(\text{s})$ (FARADAYS I LAW OF ELECTROLYSIS)**

- Charge on one mole of electrons is equal to $96487 \approx 96500 \text{ C/mol} = 1F$.

- **KOHLRAUSCH LAW** $\Lambda_m^{\infty} = x \times \Lambda_{\text{cation}}^{\infty} + y \times \Lambda_{\text{anion}}^{\infty}$

- SHE (Standard Hydrogen Electrode) is represented by

Pt/H₂ (g, 1 bar)/ H⁺ (1M) and it is used as a reference half-cell.



- **Conductance (G)** is inverse of resistance (R). Unit : Ohm^{-1} or S. $G = 1/R$
- **Conductivity (specific conductance)** denoted by κ , is reciprocal of resistivity and is expressed in S cm^{-1} . $\rho = 1/\kappa$
- **Conductivity (κ) = Conductance (G) x cell constant(I/A)**
(Cell constant unit is cm^{-1} or m^{-1}).
- **Molar conductance (λ_m)** is conductance of solution containing 1 mol of solute in a given volume. Unit $\text{Scm}^2\text{mol}^{-1}$
- **MOLAR CONDUCTANCE (λ_m) = $\kappa \times 1000/C$**
- **Degree of dissociation (α) = $\lambda_m / \lambda_m^{\circ}$**
- **$K = C \alpha^2 / (1 - \alpha)$**
- Conductivity decreases but molar conductivity increases with decrease in concentration.
- In electrochemical process, the voltage required for a reaction is sometimes much greater than that indicated by the electrode potentials. The additional voltage required to cause electrolysis is called **overvoltage**.

QUESTIONS - ANSWERS

QUESTIONS – 2MARKS	
1	<p>Suggest a way to determine Λ°_m of water.</p> <p>Ans: $\Lambda^{\circ}_m(\text{H}_2\text{O}) = \Lambda^{\circ}(\text{H}^+) + \Lambda^{\circ}(\text{OH}^-)$ $= \Lambda^{\circ}(\text{H}^+) + \Lambda^{\circ}(\text{OH}^-) + \Lambda^{\circ}(\text{Na}^+) - \Lambda^{\circ}(\text{Na}^+) + \Lambda^{\circ}(\text{Cl}^-) - \Lambda^{\circ}(\text{Cl}^-)$ $= [\Lambda^{\circ}(\text{H}^+) + \Lambda^{\circ}(\text{Cl}^-)] + [\Lambda^{\circ}(\text{OH}^-) + \Lambda^{\circ}(\text{Na}^+)] - [\Lambda^{\circ}(\text{Na}^+) + \Lambda^{\circ}(\text{Cl}^-)]$ $\Lambda^{\circ}_m(\text{H}_2\text{O}) = \Lambda^{\circ}_m(\text{HCl}) + \Lambda^{\circ}_m(\text{NaOH}) - \Lambda^{\circ}_m(\text{NaCl})$</p> <p>Thus the molar conductance of water can be determined.</p>
2	<p>Al_2O_3 is reduced by electrolysis at low potentials and high currents. If 4.0×10^4 A of current is passed through molten Al_2O_3 for 6 hrs, how much Al is produced?</p> <p>Ans: Aluminium is in +3 oxidation state so the production of 1 mol of Al requires 3 mol of electrons. i.e $3F = 3 \times 96500 \text{ C}$ Total charge passed = $4.0 \times 10^4 \text{ A} \times 6 \times 60 \times 60 = 8.64 \times 10^8 \text{ C}$ Mass of Al produced = $8.64 \times 10^8 \times 27 / 3 \times 96500$ $= 8.06 \times 10^4 \text{ g}$</p>
3	<p>On the basis of following data given identify the strongest oxidising agent Fe^{2+} or Fe^{3+} or $[\text{Fe}(\text{CN})_6]^{4-}$ or $[\text{Fe}(\text{CN})_6]^{3-}$ $[\text{Fe}(\text{CN})_6]^{4-} \rightarrow [\text{Fe}(\text{CN})_6]^{3-} + e^- \quad E^{\circ} = -0.35 \text{ V}$ $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + e^- \quad E^{\circ} = -0.77 \text{ V}$</p> <p>Ans: The species which have higher reduction potential can act as oxidising agent. Among these only Fe^{3+} (0.77V) and $[\text{Fe}(\text{CN})_6]^{3-}$ (0.35 V) have positive reduction potential. Fe^{3+} is stronger oxidising agent as Reduction potential of Fe^{3+} is higher than $[\text{Fe}(\text{CN})_6]^{3-}$</p>
4	<p>Λ°_m for NaCl, HCl and CH_3COONa are 126.0, 426, 1000 Scm^2/mol respectively. If the conductance of 0.001 M CH_3COOH is $5 \times 10^{-5} \text{ S/cm}$, calculate the degree of dissociation of CH_3COOH.</p> <p>Ans: $\Lambda^{\circ}_m \text{CH}_3\text{COOH} = \Lambda^{\circ}_m \text{CH}_3\text{COONa} + \Lambda^{\circ}_m \text{HCl} - \Lambda^{\circ}_m \text{NaCl}$ $\Lambda^{\circ}_m \text{CH}_3\text{COOH} = 100 + 426 - 126 = 400 \text{ Scm}^2/\text{mol}$ $\Lambda^c_m = 1000 \kappa / M = 1000 \times 5 \times 10^{-5} / 0.001 = 50 \text{ Scm}^2/\text{mol}$ $\alpha = \Lambda^c_m / \Lambda^{\circ}_m = 50 / 400 = 0.125$ or $\alpha = 0.125 \times 100 = 12.5\%$</p>
5	<p>The molar conductance of an M/32 solution of weak monobasic acid is 8 mho cm^2 and that at infinite solution is 400 mho cm^2. Find the dissociation constant of the acid?</p> <p>Ans: $\alpha = \lambda_m / \lambda_m^{\circ} = 8 \text{ mho cm}^2 / 400 \text{ mho cm}^2 = 0.02$ $K_a = c \alpha^2 / (1 - \alpha) = (1/32) \times (0.02)^2 / (1 - 0.02)$ $K_a = 1.25 \times 10^{-5}$</p>
6	<p>A galvanic cell has two hydrogen electrodes one is immersed in a solution with $[\text{H}^+] = 1 \text{ M}$ and other is immersed in 0.85 M KOH. Determine E_{cell}.</p> <p>Ans: The galvanic cell is $\text{Pt}/\text{H}_2(\text{g}, 1 \text{ bar})/\text{H}^+(\text{xM})//\text{H}^+(1 \text{ M})/\text{H}_2(\text{g}), \text{Pt}$ Where $x = K_w / [\text{OH}^-]$ $= 1 \times 10^{-14} / 0.85$ $= 1.18 \times 10^{-14}$ $E_{\text{cell}} = -0.0592 \log x$ $= 0.0592 \times 1.18 \times 10^{-14}$ $= 0.82 \text{ v}$</p>
7	<p>Assess whether the following reaction is spontaneous or not? $2\text{KMnO}_4 + 3\text{H}_2\text{SO}_4 + 5 \text{H}_2\text{C}_2\text{O}_4 \rightarrow 2\text{MnSO}_4 + \text{K}_2\text{SO}_4 + 10\text{CO}_2 + 8\text{H}_2\text{O}$</p> <p>Ans: Separate the reactions in to oxidation and reduction half reactions. $\quad \quad \quad +3 \quad \quad \quad +4$</p>

	<p>i) $[Al(s) \rightarrow Al^{3+}(aq) + 3e^-] \times 2$ $[Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)] \times 3$</p> <hr/> $2Al(s) + 3 Cu^{2+}(aq) \rightarrow 2Al^{3+} (aq) + 3Cu (s) \quad n= 6$ <hr/> <p>Substituting in Nernst equation</p> $E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{n} \log \frac{[Al^{3+}]^2}{[Cu^{2+}]^3}$ $1.98 V = E^{\circ}_{cell} - \frac{0.0591}{6} \log \frac{[0.01]^2}{[0.01]^3}$ $E^{\circ}_{cell} = 1.98 + 0.0197$ $= 1.9997 V$ <p>ii) No, we cannot store copper sulphate solution in aluminium container. Because as per above reaction Al will displace Cu^{2+} from its solution.</p>
14	<p>One half cell in a voltaic cell is constructed from a silver nitrate solution of unknown concentration. The other electrode consists of a zinc electrode in a 0.10 M solution of zinc nitrate. A voltage of 1.48 V is measured for this cell. Use this information to calculate the concentration of silver ions in the solution.</p> <p>Given that $E^{\circ}_{Zn^{2+}/Zn} = -0.763V$ and $E^{\circ}_{Ag^+/Ag} = +0.80V$</p> <p>Ans: Electro chemical cell formed is $Zn(s)/Zn^{2+} (0.010M) // Ag^+ (x M) / Ag(s)$</p> $E^{\circ}_{cell} = E^{\circ}_{cathode} - E^{\circ}_{anode}$ $= 0.80 - (-0.763) V = 1.563 V$ <p>Nernst equation for the reaction</p> $E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{n} \log \frac{[Zn^{2+}]}{[Ag^+]^2}$ $1.48 V = 1.563 V - \frac{0.0591}{2} \log \frac{[0.10]}{[Ag^+]^2}$ $\log \frac{[0.10]}{[Ag^+]^2} = 0.083 / 0.02955 = 2.8087$ $\frac{[0.10]}{[Ag^+]^2} = A. \log(2.8087) = 643.7$ $[Ag^+] = 1.247 \times 10^{-2} M$
15	<p>Calculate the cell potential of galvanic cells in which the following reactions take place. Also calculate equilibrium constant and ΔG° of the reaction.</p> $2Cr (s) + 3Cd^{2+} (aq) \rightarrow 2Cr^{3+}(aq) + 3 Cd(s)$ <p>Given $E^{\circ}_{Cd^{2+}/Cd} = -0.40V$, $E^{\circ}_{Cr^{3+}/Cr} = -0.74 V$</p> <p>Ans: $E^{\circ}_{cell} = E^{\circ}_{Cd^{2+}/Cd} - E^{\circ}_{Cr^{3+}/Cr} = -0.40 - (-0.74) V = 0.34 V$</p> $\Delta G^{\circ} = -nF E^{\circ}_{cell} = -6 \times 96500 \times 0.34 = -196.86 kJ/mol$ $= 196.86 \times 10^3 J/mol$ $\Delta G^{\circ} = -2.303 RT \log K$ $\log K = \Delta G^{\circ} / 2.303 RT$ $= 196.86 \times 10^3 / 2.303 \times 8.314 \times 298 = 34.5014$ $K = A. \log (34.5014)$ $= 3.16 \times 10^{34}$
16	<p>In the Edison storage cell $Fe(s)/KOH(aq) // Ni_2O_3(s) / Ni$, the half cell reaction are as follows.</p> $Ni_2O_3(s) + H_2O(l) + 2e^- \rightarrow 2NiO(s) + 2OH^- \quad E^{\circ} = +0.40V$ $FeO (s) + H_2O(l) + 2e^- \rightarrow Fe(s) + 2OH^- \quad E^{\circ} = -0.87V$ <p>i) What is the cell reaction? ii) What is the emf of the cell? How it depends upon the concentration of KOH? iii) What is the maximum amount of electrical energy obtained from the cell?</p> <p>Ans: i) The cell reaction is $Fe(s) + Ni_2O_3(s) \rightarrow FeO (s) + 2NiO(s)$</p> <p>ii) $E^{\circ}_{cell} = E^{\circ}_{Ni_2O_3/NiO} - E^{\circ}_{FeO/Fe} = 0.40 - (-0.87) V = 1.27 V$</p> <p>iii) The consumption of 1mol of Ni_2O_3 will deliver $2F$ charge across the electrodes under a potential difference of 1.27 V.</p>

	<p>Maximum amount of electrical energy available from the cell can be calculated from the relation $\Delta G^0 = -w$ or $w = -\Delta G^0 = nF E^0_{\text{cell}}$</p> $= 2 \times 96500 \times 1.27$ $= 245110 \text{ J} = 245.11 \text{ kJ}$ <p>Maximum amount of electrical energy available from the cell is 245.11 kJ</p>
17	<p>The emf of hydrogen-oxygen fuel cell is 1.23 V at 25°C. What is the equilibrium constant for the reaction $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \leftrightarrow 2\text{H}_2\text{O}(\text{l})$</p> <p>Ans: Half cell reaction in hydrogen-oxygen fuel cell are as follows Oxidation: $\text{H}_2(\text{g}) + 2\text{H}_2\text{O} \rightarrow 2\text{H}_3\text{O}^+ + 2\text{e}^-$ Reduction: $\text{O}_2(\text{g}) + 4\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$ Over all cell reaction is $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \leftrightarrow 2\text{H}_2\text{O}(\text{l})$ which involves 4 F. At 25°C $E^0_{\text{cell}} = \frac{0.0591}{n} \log K$ or $\log K = n E^0_{\text{cell}} / 0.0591$</p> $\log K = 4 \times 1.23 / 0.0591 = 83.1081$ $K = \text{antilog}(83.1081) = 1.26 \times 10^{83}$
18	<p>Two students use the same stock of solution of ZnSO_4 and a solution of CuSO_4. The emf of one cell is 0.03V higher than the other cell. The concentration of CuSO_4 in the cell with higher emf is 0.5 M. Find the concentration of CuSO_4 in the other cell.</p> <p>Ans: Let the concentration of the stock of ZnSO_4 solution be C and concentration of CuSO_4 solution be C_1 and C_2 (where $C_2 > C_1$) The emf of the two cells be E_1 and E_2</p> $E_1 = E^0_{\text{cell}} - \frac{0.0591}{n} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$ so $E_1 = E^0_{\text{cell}} - \frac{0.0591}{2} \log \frac{[C]}{[C_1]}$ $E_2 = E^0_{\text{cell}} - \frac{0.0591}{n} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$ so $E_2 = E^0_{\text{cell}} - \frac{0.0591}{2} \log \frac{[C]}{[C_2]}$ $E_2 - E_1 = \frac{0.0591}{2} \log \frac{[C_2]}{[C_1]}$ But $E_2 - E_1 = 0.03 \text{ V}$ as given. $0.03 = 0.0296 \log \frac{[C_2]}{[C_1]}$ so $1 = \log \frac{[C_2]}{[C_1]}$ or $\log \frac{[C_2]}{[C_1]} = A. \log(1) = 10$ $\frac{[C_2]}{[C_1]} = 10$ $C_1 = C_2 / 10 = 0.05 \text{ M}$
19	<p>Calculate the emf of the following cell when 99.99% of Cu^{2+} ion is consumed. $\text{Zn}(\text{s}) / \text{Zn}^{2+} (1\text{M}) // \text{Cu}^{2+} (1\text{M}) / \text{Cu}(\text{s})$ $E^0_{\text{cell}} = 1.10 \text{ V}$</p> <p>Ans: When 99.99% Cu^{2+} ion is consumed, its concentration decreases by 0.9999M and Zn^{2+} ion concentration increases by 0.9999 M. Final concentration of Cu^{2+} ion = 0.0001M and Zn^{2+} ion = 1.9999M</p> $E_{\text{cell}} = E^0_{\text{cell}} - \frac{0.0591}{n} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$ $E_{\text{cell}} = 1.10 - \frac{0.0591}{2} \log \frac{1.9999}{0.0001}$ $E_{\text{cell}} = 1.10 - \frac{0.0591}{2} \log (.9999 \times 10^4)$ $E_{\text{cell}} = 0.97 \text{ V}$
20	<p>The emf of the cell corresponding to the reaction $\text{Zn}(\text{s}) + 2\text{H}^+(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}, 0.1\text{M}) + \text{H}_2(\text{g}, 1 \text{ atm})$ Given $E_{\text{cell}} = 0.28\text{V}$ Write the half cell reaction and calculate the pH of the solution. Given $E^0_{\text{Zn}^{2+}/\text{Zn}} = -0.76\text{V}$, $E^0_{\text{H}^+/\text{H}_2} = 0 \text{ V}$</p> <p>Ans: Anode reaction $\text{Zn}(\text{s}) \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^-$ Cathode reaction $2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$</p> <p>Nernst equation for the above reaction</p> $E_{\text{cell}} = E^0_{\text{cell}} - \frac{0.0591}{n} \log \frac{\text{pH}_2 [\text{Zn}^{2+}]}{[\text{H}^+]^2}$ $E_{\text{cell}} = 0.76 \text{ V} - \frac{0.0591}{2} \log \frac{1 \text{ atm} [0.1]}{[\text{H}^+]^2}$ $E_{\text{cell}} = 0.76 \text{ V} - \left\{ \frac{0.0591}{2} \log (1 \times 0.1) - \frac{0.0591}{2} \log [\text{H}^+]^2 \right\}$ $0.28 = 0.76 \text{ V} - \left\{ \frac{0.0591}{2} \log (1 \times 0.1) - 2 \times \frac{0.0591}{2} \log [\text{H}^+] \right\}$ $0.28 = 0.76 - (-0.03) - 0.0591 \text{pH}$ $0.28 = 0.79 - 0.0591 \text{pH}$ $\text{pH} = (0.79 - 0.28) / 0.0591 = 8.6$

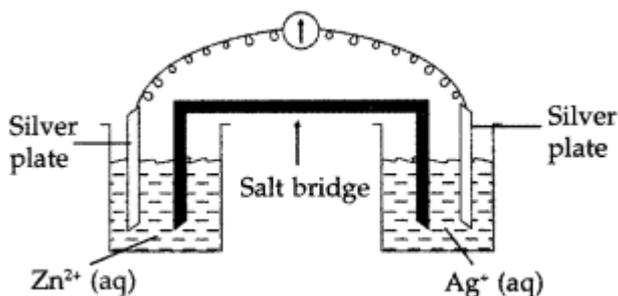
QUESTIONS- 5 MARKS

- 21 (a) What is limiting molar conductivity? Why there is steep rise in the molar conductivity of weak electrolyte on dilution?
 (b) Calculate the emf of the following cell at 298 K :
 $\text{Mg (s) | Mg}^{2+} (0.1 \text{ M}) || \text{Cu}^{2+} (1.0 \times 10^{-3} \text{ M}) | \text{Cu (s)}$
 [Given $E_0 \text{ Cell} = 2.71 \text{ V}$].

Ans: (a) The molar conductivity of a solution at infinite dilution is called limiting molar conductivity and is represented by the symbol Λ° . There is steep rise in the molar conductivity of weak electrolyte on dilution because as the concentration of the weak electrolyte is reduced, more of it ionizes and thus rapid increase in the number of ions in the solution.

<p>(b) $\text{Mg (s) Mg}^{2+} (0.1 \text{ M}) \text{Cu}^{2+} (1.0 \times 10^{-3} \text{ M}) \text{Cu (s)}$</p> <p>Given: $E_{\text{Cell}}^0 = 2.71 \text{ V}$</p> <p>Applying Nernst equation</p> $\text{Mg} + \text{Cu}^{2+} \longrightarrow \text{Mg}^{2+} + \text{Cu}$ $E_{\text{Cell}} = E_{\text{Cell}}^0 - \frac{0.0591}{n} \log \frac{[\text{Mg}^{2+}]}{[\text{Cu}^{2+}]}$	$= 2.71 - \frac{0.0591}{2} \log \frac{0.1}{1 \times 10^{-3}}$ $= 2.71 - \frac{0.0591}{2} \log \frac{0.1}{0.001}$ $= 2.71 - 0.02955 \log 100$ $= 2.71 - 0.02955 \times 2$ $= 2.71 - 0.0591$ $\therefore E_{\text{Cell}} = 2.65 \text{ V}$
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- 22 Consider the figure given and answer the following questions :
- (i) What is the direction of flow of electrons?
 (ii) Which is anode and which is cathode?
 (iii) What will happen if the salt bridge is removed?



- (iv) How will concentration of Zn^{2+} and Ag^+ ions be affected when the cell functions?
 (v) How will concentration of these ions be affected when the cell becomes dead?

Ans: (i) Electrons flow from anode (Zinc plate) to cathode (Silver plate).
 (ii) Zinc plate where oxidation occurs acts as anode and silver plate where reduction occurs acts as cathode.
 (iii) If the salt bridge is removed then electrons from zinc electrode will flow to the silver electrode where they will neutralize some of Ag^+ ions and the SO_4^{2-} ions will be left and the solution will acquire a negative charge. Secondly the Zn^{2+} ions from zinc plate will enter into ZnSO_4 solution producing positive charge. Thus due to accumulation of charges in two solutions, further flow of electrons will stop and hence the current stops flowing and the cell will stop functioning.

(iv) As silver from silver sulphate solution is deposited on the silver electrode and sulphate ions migrate to the other side, the concentration of Ag_2SO_4 solution decreases and of ZnSO_4 solution increases as the cell operates.

(v) When the cell becomes dead, the concentration of these ions become equal due to attainment of equilibrium and zero EMF.

23	<p>(a) Calculate E°_{cell} for the following reaction at 298 K: $2\text{Al(s)} + 3\text{Cu}^{2+} (0.01\text{M}) \rightarrow 2\text{Al}^{3+} (0.01\text{M}) + 3\text{Cu(s)}$ Given: $E_{\text{cell}} = 1.98 \text{ V}$</p> <p>(b) Using the E° values of A and B, predict which is better for coating the surface of iron [$E^{\circ}(\text{Fe}^{2+}/\text{Fe}) = -0.44 \text{ V}$] to prevent corrosion and why? Given: $E^{\circ}(\text{A}^{2+}/\text{A}) = -2.37 \text{ V}$; $E^{\circ}(\text{B}^{2+}/\text{B}) = -0.14 \text{ V}$ (All India 2016)</p> <p>Ans: (a) For the reaction $2\text{Al(s)} + 3\text{Cu}^{2+} (0.01\text{M}) \rightarrow 2\text{Al}^{3+} (0.01\text{M}) + 3\text{Cu(s)}$ Given: $E_{\text{cell}} = 1.98 \text{ V}$ $E^{\circ}_{\text{cell}} = ?$ Nernst equation for the reaction is</p> $E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0591}{n} \log \frac{[\text{Al}^{3+}]^2}{[\text{Cu}^{2+}]^3}$ <p>or $1.98 \text{ V} = E^{\circ}_{\text{cell}} - \frac{0.0591}{6} \log \frac{(0.01)^2}{(0.01)^3}$</p> $\left[\begin{array}{l} \because \log 100 = 2 \log 10 \\ \log 10 = 1 \end{array} \right]$ <p>or $1.98 \text{ V} = E^{\circ}_{\text{cell}} - 0.00985 \log 100$ or $1.98 \text{ V} = E^{\circ}_{\text{cell}} - 0.00985 \times 2$ $1.98 \text{ V} = E^{\circ}_{\text{cell}} - 0.0197$ $\therefore E^{\circ}_{\text{cell}} = 1.98 \text{ V} + 0.0197$ $\therefore E^{\circ}_{\text{cell}} = 1.9997 \text{ V}$</p> <p>(a) Element A will be better for coating the surface of iron than element B because its E° value is more negative.</p>
24	<p>One half-cell in a voltaic cell is constructed from a silver wire dipped in silver nitrate solution of unknown concentration. Its other half-cell consists of a zinc electrode dipping in 1.0 M solution of $\text{Zn}(\text{NO}_3)_2$. A voltage of 1.48 V is measured for this cell. Use this information to calculate the concentration of silver nitrate solution used.</p> <p>($E^{\circ}_{\text{Zn}^{2+}/\text{Zn}} = -0.76 \text{ V}$, $E^{\circ}_{\text{Ag}^+/\text{Ag}} = +0.80 \text{ V}$)</p> <p>Ans: In this silver electrode act as cathode and zinc electrode act as anode. Half cell reactions take place at silver and zinc electrode are as follows</p> <p><i>At cathode:</i> $2\text{Ag}^+(\text{aq}) + 2\text{e}^- \rightarrow 2\text{Ag(s)}$</p> <p><i>At anode:</i> $\text{Zn(s)} \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^-$</p> <p>The cell can be represented as $\text{Zn(s)} \text{Zn}^{2+}(\text{aq}) \text{Ag}^+(\text{aq}) \text{Ag(s)}$</p> <p>The cell reaction is $\text{Zn(s)} + 2\text{Ag}^+(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{Ag(s)}$</p> <p>$\therefore E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$ $= 0.80 - (-0.76) = 1.56 \text{ V}$</p> <p>$\therefore E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.059}{n} \log \frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2}$</p> <p>$1.48 = 1.56 - \frac{0.059}{2} \log \frac{1}{[\text{Ag}^+]^2}$</p> <p>$\frac{0.059}{2} \log \frac{1}{[\text{Ag}^+]^2} = 1.56 - 1.48 = 0.08$</p> <p>$\log \frac{1}{[\text{Ag}^+]^2} = \frac{0.08 \times 2}{0.059}$</p> <p>or $-2 \log [\text{Ag}^+] = \frac{0.16}{0.059}$</p> <p>$\therefore \log [\text{Ag}^+] = -1.356 = -1 - 0.356 = -1 + 1$ $= -2 + (1 - 1.356)$ $[\text{Ag}^+] = 2.644 \therefore [\text{Ag}^+] = 4.406 \times 10^{-2} \text{ M}$</p>
25	<p>a) A current was passed for 5 hours through two electrolytic cells connected in series. The first cell contains AuCl_3 and second cell CuSO_4 solution. If 9.85 g of gold was deposited in the first cell, what amount of copper gets deposited in the second cell? Also calculate magnitude of current in ampere. Given: Atomic mass of Au = 197 g/mol and Cu = 63.5 g/mol)</p> <p>b) Two half-reactions of an electrochemical cell are given below :</p> <p>$\text{MnO}_4^- (\text{aq}) + 8\text{H}^+ (\text{aq}) + 5\text{e}^- \rightarrow \text{Mn}^{2+} (\text{aq}) + 4\text{H}_2\text{O} (\text{l}), E^{\circ} = 1.51 \text{ V}$ $\text{Sn}^{2+} (\text{aq}) \rightarrow \text{Sn}^{4+} (\text{aq}) + 2\text{e}^-, E^{\circ} = +0.15 \text{ V}.$</p> <p>Construct the redox reaction equation from the two half-reactions and calculate the cell potential from the standard potentials and predict if the reaction is reactant or product favoured.</p>

Ans: a) According to Faraday's II law of electrolysis

$$\frac{\text{Weight of Au deposited}}{\text{Weight of Cu deposited}} = \frac{\text{Eq. wt. of Au}}{\text{Eq. wt. of Cu}}$$

$$\text{Eq. wt. of Au} = \frac{197}{3} = 65.66 \quad (\text{Au}^{3+} + 3e^- \rightarrow \text{Au})$$

$$\text{Eq. wt. of Cu} = \frac{63.5}{2} = 31.75 \quad (\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu})$$

On substituting these values, we get

$$\frac{9.85 \text{ g}}{x} = \frac{65.66}{31.75}$$

$$\therefore x = \frac{9.85 \times 31.75}{65.66} = 4.76 \text{ g [Amount of Cu deposited]}$$

$$\text{Now } Q = I \times t \quad \Rightarrow I = \frac{Q}{t}$$

1 mol i.e. 63.5 g Cu is deposited by 1F = 96500 c



For Cu deposition, 2F = 2 × 96500 c deposit = 63.5 g

$$63.5 \text{ g Cu will be deposited by } \frac{2 \times 96500}{63.5} \times 4.76 = 14.467 \text{ c}$$

$$\therefore I = \frac{14467}{5 \times 60 \times 60} = 0.8 \text{ ampere}$$

b) Redox Equation: $2\text{MnO}_4^- + 16\text{H}^+ + 5\text{Sn}^{2+} \rightarrow 2\text{Mn}^{2+} + 5\text{Sn}^{4+} + 8\text{H}_2\text{O}$

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \quad \text{Or} \quad E^\circ_{\text{cell}} = +1.36 \quad E^\circ_{\text{cell}} > 0 \text{ so Product Favoured}$$

PASSAGE-BASED INTEGRATED QUESTIONS

Passage-1

Metallic conductance involves movement of electrons where as electrolytic conductance involves movement of ions. Specific conductance increases with increase in concentration where as Λ_m (molar conductivity) decreases with increase in concentration. Electrochemical cell converts chemical energy of redox reaction into electricity.

Electrochemical series is arrangement of elements in increasing order of their reduction potential. Electrolytic cell converts electrical energy into chemical energy which is used in electrolysis. Amount of products formed are decided with the help of Faraday's laws of Electrolysis. Kohlrausch law helps to determine limiting molar conductivity of weak electrolyte, their degree of ionisation (α) and their dissociation constants. Corrosion is electrochemical phenomenon. Metal undergoing corrosion acts as anode, loses electrons to form ions which combine with substances present in atmosphere to form surface compounds.

(a) Out of 0.5 M, 0.01 M, 0.1 M and 1.0 M which solution of KCl will have highest value of specific conductance? Why?

Ans. 1.0 M KCl solution because it will have more number of ions per unit volume of solution.

(b) Write the product of electrolysis of aq. NaCl on

Ans. At cathode. $2\text{H}^+ + 2e^- \rightarrow \text{H}_2 (g)$

At anode $2\text{Cl}^- + e^- \rightarrow \text{Cl}_2 (g)$

(c) When does electrochemical cell behaves like electrolytic cell?

Ans. When $E_{\text{external}} > E^\circ_{\text{cell}}$

(d) For a electro chemical cell $\text{Mg}(s) + 2\text{Ag}^+(aq) \rightarrow 2\text{Ag}(s) + \text{Mg}^{2+}$. Give the cell representation and write Nernst equation.

Ans. $\text{Mg}(s) | \text{Mg}^{2+}(aq) || \text{Ag}^+(aq) | \text{Ag}(s)$

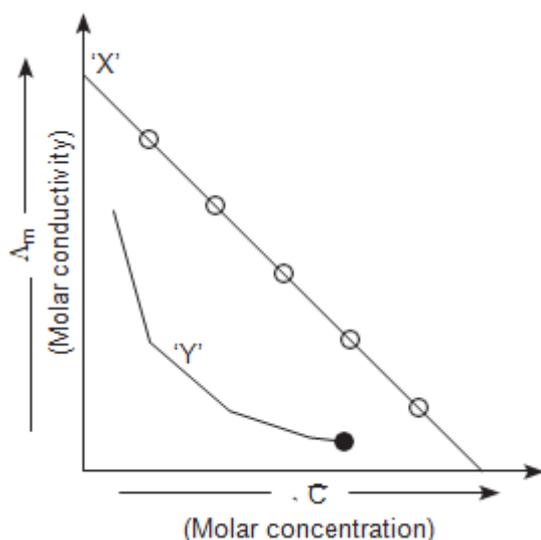
$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{2} \log \frac{[\text{Mg}^{2+}]}{[\text{Ag}^+]^2}$$

(e) Which will have higher conductance, silver wire at 30° or at 60°C?

Ans. Silver wire at 30°C. Metallic conductance decreases with increase in temperature.

Passage-2

Observe the graph shown in figure between Λ_m (molar conductivity) Vs \sqrt{C} (Molar concentration) and answer the questions based on graph.



(a) The curve 'Y' is for KCl or CH_3COOH ? **Ans.** It is for CH_3COOH .

(b) What is intercept on Λ_m axis for 'X' equal to?

Ans. It is equal α° (limiting molar conductivity).

(c) Give mathematical equation representing straight line.

Ans. $\Lambda_m = \Lambda_m^\circ - A\sqrt{C}$

(d) What is slope equal to? **Ans.** Slope = $-A$

(e) What happens to molar conductivity on dilution in case of weak electrolyte and why?

Ans. Λ_m for weak electrolyte increases sharply on dilution because both number of ions as well as mobility of ions increases.

Passage-3

Observe the following table in which conductivity and molar conductivity of NaCl at 298 K at different concentration for different electrolytes is given. Answer the questions based in the table that follows:

Conductivities and molar conductivities of NaCl at 298 K at different concentrations.

S. No.	Conc. (M)	$\kappa_m \text{ S cm}^{-1}$	$\Lambda_m \text{ S cm}^2 \text{ mol}^{-1}$	Λ_m°
1.	0.001	1.237×10^{-4}	$123.7 \text{ S cm}^2 \text{ mol}^{-1}$	NaCl $126.4 \text{ S cm}^2 \text{ mol}^{-1}$
2.	0.010	11.85×10^{-4}	$118.5 \text{ S cm}^2 \text{ mol}^{-1}$	HCl $426.1 \text{ S cm}^2 \text{ mol}^{-1}$
3.	0.020	23.15×10^{-4}	$115.8 \text{ S cm}^2 \text{ mol}^{-1}$	CH_3COONa $91 \text{ S cm}^2 \text{ mol}^{-1}$
4.	0.050	55.53×10^{-4}	$111.1 \text{ S cm}^2 \text{ mol}^{-1}$	NH_4Cl $129.8 \text{ S cm}^2 \text{ mol}^{-1}$
5.	0.100	106.74×10^{-4}	$106.7 \text{ S cm}^2 \text{ mol}^{-1}$	

(a) What happens to conductivity on dilution and why?

Ans. Conductivity decreases with decrease in concentration (dilution) because number of ions per unit volume decreases.

(b) Why is Λ_m° (limiting molar conductivity) for HCl more than NaCl?

Ans. because mobility of H^+ is more than Na^+ because H^+ are lighter than Na^+

(c) Calculate degree of dissociation (α) of NaCl of 0.001 M concentration using the table.

$$\text{Ans. } \alpha = \frac{\Lambda_m}{\Lambda_m^\circ} = \frac{123.7}{126.4} = 0.978 \Rightarrow \alpha = 97.8\%$$

(d) Calculate Λ_m° of CH_3COOH using the table.

$$\text{Ans. } \Lambda_m^\circ CH_3COOH = \Lambda^\circ CH_3COONa + \Lambda^\circ HCl - \Lambda^\circ NaCl$$

$$\Lambda_m^\circ CH_3COOH = 91.0 + 426.1 - 126.4 = 390.07S \text{ cm}^2 \text{ mol}^{-1}$$

(e) Calculate K_a of 0.01 M CH_3COOH solution if Λ_m° for CH_3COOH is $390.07S \text{ cm}^2 \text{ mol}^{-1}$ and $\Lambda_m = 39.07S \text{ cm}^{-1}$.

$$\text{Ans. } \alpha = \frac{\Lambda_m}{\Lambda_m^\circ} = \frac{39.07}{390.07} = 0.1$$

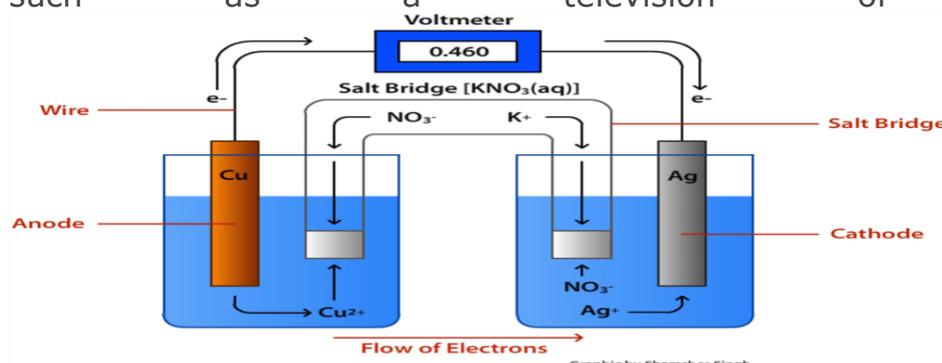
$$K_a = \frac{C\alpha}{1-\alpha} = \frac{0.01 \times (0.1)^2}{1-0.1}$$

$$K_a = \frac{10^{-4}}{0.9} = 1.11 \times 10^{-4}$$

Passage-4

The working of a galvanic cell is quite simple. It involves a chemical reaction that makes the electric energy available as the end result. During a redox reaction, a galvanic cell utilizes the energy transfer between electrons to convert chemical energy into electric energy.

Galvanic cell utilizes the ability to separate the flow of electrons in the process of oxidization and reduction, causing a half reaction and connecting each with a wire so that a path can be formed for the flow of electrons through such wire. This flow of electrons is essentially called a current. Such current can be made to flow through a wire to complete a circuit and obtain its output in any device such as a television or a watch.



(a) What is the electrochemical cell?

Ans:- change chemical energy in to electric energy

(b) When the salt bridge is removed from a cell, its voltage

Ans: will decrease to zero

(c) What is the direction of current flow in this galvanic cell

Ans: Ag electrode to Cu electrode

(d) How many coulombs of electricity flow in this galvanic cell?

Ans: 193000 C

(e) Write the formulation for the galvanic cell in which the reaction.

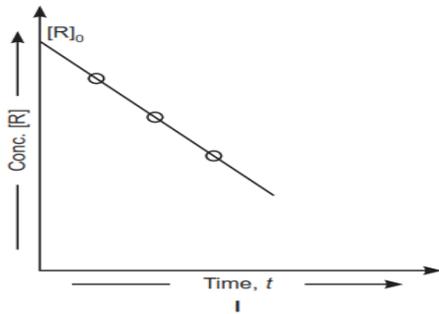
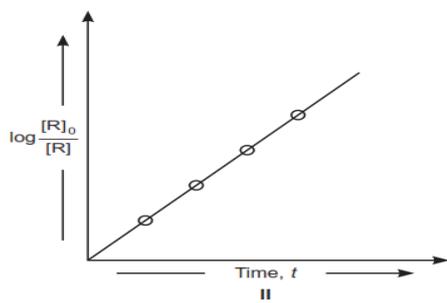
$\text{Cu (s)} + 2\text{Ag}^+(\text{aq}) \rightarrow \text{Cu}^{2+}(\text{aq}) + 2\text{Ag (s)}$ take place. Identify the cathode and anode reactions in it

Ans: (i) $\text{Cu (s)} \rightarrow \text{Cu}^{2+}(\text{aq}) + 2\text{e}^-$ (At anode)

(ii) $2\text{Ag}^+(\text{aq}) + 2\text{e}^- \rightarrow 2\text{Ag(s)}$ (At cathode)



CHAPTER-4 CHEMICAL KINETICS

SN	Question-5 MARKS																
1	<p>Observe the following graphs and answer the questions based on these graphs.</p> <div style="display: flex; justify-content: space-around; align-items: center;">   </div> <p>(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 minute, what will be $t_{99.9\%}$ for first order reaction? (e) What is $t_{1/2}$ of zero order reaction in terms of k'?</p>																
2	<p>Observe the table given showing volume of CO_2 obtained by reaction of CaCO_3 and dilute HCl after every minute. Answer the questions that follow: Table showing volume of CO_2 at one minute interval by reaction of CaCO_3 with dilute HCl.</p> <div style="display: flex;"> <div style="flex: 1;"> <p>(a) What happens to rate of reaction with time? (b) Why does CaCO_3 powder react faster than marble chips? (c) What happens to rate of reaction if concentrated HCl is used? (d) In manufacture of NH_3, $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3 + \text{heat}$ what is effect of pressure on rate of reaction? (e) Why does rate of reaction becomes almost double for energy 10° rise in temperature?</p> </div> <table border="1" style="margin-left: 20px; border-collapse: collapse; text-align: center;"> <thead> <tr style="background-color: #FFC0CB;"> <th>Time/mmm</th> <th>Volume of CO_2/cm^3</th> </tr> </thead> <tbody> <tr><td>0</td><td>0</td></tr> <tr><td>1</td><td>24 cm^3</td></tr> <tr><td>2</td><td>34 cm^3</td></tr> <tr><td>3</td><td>38 cm^3</td></tr> <tr><td>4</td><td>40 cm^3</td></tr> <tr><td>5</td><td>40 cm^3</td></tr> <tr><td>6</td><td>40 cm^3</td></tr> </tbody> </table> </div>	Time/mmm	Volume of CO_2/cm^3	0	0	1	24 cm^3	2	34 cm^3	3	38 cm^3	4	40 cm^3	5	40 cm^3	6	40 cm^3
Time/mmm	Volume of CO_2/cm^3																
0	0																
1	24 cm^3																
2	34 cm^3																
3	38 cm^3																
4	40 cm^3																
5	40 cm^3																
6	40 cm^3																
	Question-2 MARKS																
3	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?																
4	<p>(a) For a reaction, $\text{A} + \text{B} \rightarrow \text{Product}$, the rate law is given by, $\text{Rate} = k [\text{A}]^1 [\text{B}]^2$. What is the order of reaction? (b) Write the unit of rate constant 'k' for the first order reaction.</p>																
5	Define half-life of a reaction. Write the expression of half-life for (i) zero order reaction and (ii) first order reaction																
6	Define the following terms: (i) Pseudo first order reaction (ii) Half life period of reaction ($t_{1/2}$)																
7	(a) For a reaction $\text{A} + \text{B} \rightarrow \text{P}$, the rate law is given by $r = k [\text{A}]^{1/2} [\text{A}]^2$ What is the																

	order of this reaction? (b) A first order reaction is found to have a rate constant $k = 5.5 \times 10^{-14} \text{ s}^{-1}$. Find the half life of the reaction.															
8	The rate constant for a first order reaction is 60 s^{-1} . How much time will it take to reduce the initial concentration of the reactant to 1/10 th of its initial value?															
9	i) If half life period of first order reaction is x and 3/4 th life period of same reaction is 'y', how are x and 'y' related to each other? (ii) In some cases it is found that a large number of colliding molecules have energy more than threshold energy but yet the reaction is slow. Why?															
10	The rate of a reaction becomes four times when the temperature changes from 293 K to 313 K. Calculate the energy of activation (E_a) of the reaction assuming that it does not change with temperature. [$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$, $\log 4 = 0.6021$]															
11	A reaction is of second order with respect to a reactant. How is its rate affected if the concentration of the reactant is (i) doubled (ii) reduced to half															
12	Distinguish between 'rate expression' and rate constant' of a reaction.															
13	<p>For the given reaction $A + B \rightarrow \text{Product}$</p> <p>(a) Write the rate equation</p> <p>(b) Calculate the rate constant</p> <p><u>Following data are given</u></p> <table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th>Initial conc. (m/L)</th> <th>Initial conc. (m/L)</th> <th>Initial rate [$\text{mL}^{-1} \text{ s}^{-1}$]</th> </tr> <tr> <th>$[A]_0$</th> <th>$[B]_0$</th> <th></th> </tr> </thead> <tbody> <tr> <td>0.1</td> <td>0.1</td> <td>0.05</td> </tr> <tr> <td>0.2</td> <td>0.1</td> <td>0.1</td> </tr> <tr> <td>0.1</td> <td>0.2</td> <td>0.05</td> </tr> </tbody> </table>	Initial conc. (m/L)	Initial conc. (m/L)	Initial rate [$\text{mL}^{-1} \text{ s}^{-1}$]	$[A]_0$	$[B]_0$		0.1	0.1	0.05	0.2	0.1	0.1	0.1	0.2	0.05
Initial conc. (m/L)	Initial conc. (m/L)	Initial rate [$\text{mL}^{-1} \text{ s}^{-1}$]														
$[A]_0$	$[B]_0$															
0.1	0.1	0.05														
0.2	0.1	0.1														
0.1	0.2	0.05														
14	<p>Rate of reaction, $A + B \rightarrow \text{Product}$ is given below as a function of different initial concentration of A and B</p> <table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th>$[A] \text{ mol/L}$</th> <th>$[B] \text{ (mol/L)}$</th> <th>Initial rate ($\text{mol L}^{-1} \text{ min}^{-1}$)</th> </tr> </thead> <tbody> <tr> <td>0.01</td> <td>0.01</td> <td>0.005</td> </tr> <tr> <td>0.02</td> <td>0.01</td> <td>0.010</td> </tr> <tr> <td>0.01</td> <td>0.02</td> <td>0.005</td> </tr> </tbody> </table> <p>(a) Determine the order of the reaction with respect of A and B.</p> <p>(b) What is the half-life of A in the reaction</p>	$[A] \text{ mol/L}$	$[B] \text{ (mol/L)}$	Initial rate ($\text{mol L}^{-1} \text{ min}^{-1}$)	0.01	0.01	0.005	0.02	0.01	0.010	0.01	0.02	0.005			
$[A] \text{ mol/L}$	$[B] \text{ (mol/L)}$	Initial rate ($\text{mol L}^{-1} \text{ min}^{-1}$)														
0.01	0.01	0.005														
0.02	0.01	0.010														
0.01	0.02	0.005														
15	One of the hazards of nuclear explosion is the generation of Sr^{90} and its subsequent incorporation in bones. This nuclide has a half life of 28.1 year. Suppose one microgram was absorbed by a new born-child, How much Sr^{90} will remain in his bones after 20 year															
16	At 380°C , the half-life period for the first order decomposition of H_2O_2 is 360 min. The energy of activation of the reaction is 200 kJ mol^{-1} . Calculate the time required for 75% decomposition at 450°C															
	Question-3 MARKS															
17	Rate constant is equal to the rate of reaction when molar conc, of reactants is unity. Its unit depends upon order of reaction. A reactant has a half-life of 10 minutes. (i) Calculate the rate constant for the first order reaction. (ii) What fraction of the reactant will be left after an hour of the reaction has occurred?															
18	A first order reaction takes 10 minutes for 25% decomposition. Calculate $t_{1/2}$ for the reaction. (Given: $\log 2 = 0.3010$, $\log 3 = 0.4771$, $\log 4 = 0.6021$).															

19	<p>The following data were obtained during the first order thermal decomposition of SO_2Cl_2 at a constant volume: Calculate the rate constant. (Given: $\log 4 = 0.6021$, $\log 2 = 0.3010$)</p> <table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th>Experiment</th> <th>Time/s^{-1}</th> <th>Total pressure/atm</th> </tr> </thead> <tbody> <tr> <td>1</td> <td>0</td> <td>0.4</td> </tr> <tr> <td>2</td> <td>100</td> <td>0.7</td> </tr> </tbody> </table>	Experiment	Time/ s^{-1}	Total pressure/atm	1	0	0.4	2	100	0.7
Experiment	Time/ s^{-1}	Total pressure/atm								
1	0	0.4								
2	100	0.7								
20	A first order gas phase reaction: $\text{A}_2\text{B}_2(\text{g}) \rightarrow 2\text{A}(\text{g}) + 2\text{B}(\text{g})$ at the temperature 400°C has the rate constant $k = 2.0 \times 10^{-4} \text{ sec}^{-1}$. What percentage of A_2B_2 is decomposed on heating for 900 seconds? (Antilog $0.0781 = 1.197$)									
21	A first order reaction is 20% complete in 10 min. Calculate (i) the specific rate constant of the reaction, and (ii) Time taken for the reaction to go to 75% completion.									
22	Radioactive de cay is a first or der process. Radioactive carbon in wood sample de cays with a half-life of 5770 year. What is the rate constant (in year^{-1}) for the de cay? What fraction would remain after 11540 year?									
23	In Arrhenius equation for a certain reaction, the value of A and E_a (activation energy) are $4 \times 10^{13} \text{ s}^{-1}$ and 98.6 kJ mol^{-1} respectively. If the reaction is of first or der, at what temperature will its half-life period be 10 min?									
24	The rate constant for an isomerisation re action, $\text{A} \rightarrow \text{B}$ is $4.5 \times 10^{-3} \text{ min}^{-1}$. If the initial concentration of A is 1M. Calculate the rate of the reaction after 1 h.									
25	A first order reaction is 20% complete in 10 min. Calculate (i) the specific rate constant of the reaction (ii) the time taken for the reaction to go to 75% completion,									
	Question-5 MARKS									
26	(a) What do you mean by pseudo first order reaction? Explain with example (b) For a reaction: $\text{H}_2 + \text{Cl}_2 (\text{h}\nu) \rightarrow 2\text{HCl}$ Rate = k (i) Write the order and molecularity of this reaction. (ii) Write the unit of k.									
27	The rate of first or der reaction is $0.04 \text{ mol L}^{-1} \text{ s}^{-1}$ at 10 min and $0.03 \text{ mol L}^{-1} \text{ s}^{-1}$ at 20 min after initiation. Find the half-life of the reaction.									
28	<p>For the hydrolysis of methyl acetate in aqueous solution, the following result were obtained.</p> <table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th>t/s</th> <th>0</th> <th>30</th> <th>60</th> </tr> </thead> <tbody> <tr> <td>$[\text{CH}_3\text{COOCH}_3]/\text{mol L}^{-1}$</td> <td>0.60</td> <td>0.30</td> <td>0.15</td> </tr> </tbody> </table> <p>(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 interval 30 to 60 seconds. (Given: $\log 2 = 0.301$, $\log 3 = 0.4771$, $\log 4 = 0.6021$)</p>	t/s	0	30	60	$[\text{CH}_3\text{COOCH}_3]/\text{mol L}^{-1}$	0.60	0.30	0.15	
t/s	0	30	60							
$[\text{CH}_3\text{COOCH}_3]/\text{mol L}^{-1}$	0.60	0.30	0.15							
29	(a) For a reaction $\text{A} + \text{B} \rightarrow \text{P}$, the rate is given by $\text{Rate} = k[\text{A}]^2 [\text{B}]$ (i) How is the rate of reaction affected if the concentration of A is doubled? (ii) 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: $\log 2 = 0.301$, $\log 3 = 0.4771$, $\log 4 = 0.6021$)									

SN	ANSWERS
<u>1</u>	(a) Zero order reaction. (b) $k / 2.303$ where 'k' is rate constant. (c) $t_{1/2}$ is directly proportional to initial concentration. (d) $t_{99.9\%} = 10 t_{1/2} = 10 \times 40 = 400$ minutes (e) $t_{1/2} = [R]_0 / 2k$ for zero order reaction.
<u>2</u>	(a) The rate of reaction first decreases with time then becomes constant. (b) CaCO_3 powder has more surface area than marble chips therefore, more rate of reaction. (c) The rate of reaction will increase because rate of reaction increases with the increase in concentration. (d) The rate of reaction increases with increase in pressure. (e) It is because number of molecules undergoing effective collisions become almost double, hence rate of reaction almost doubled.
<u>3</u>	It is because the concentration of reactants goes on decreasing with time
<u>4</u>	The sum of powers to which concentration terms are raised in rate law or rate equation.
<u>5</u>	The extra energy which must be supplied to the reactants so that they can undergo effective collision to form products.
<u>6</u>	It is equal to the rate of reaction when molar concentration of reactant are taken as unity
<u>7</u>	(i) s^{-1} is the unit of first order rate constant. (ii) $\text{L mol}^{-1} \text{s}^{-1}$ is the unit of second order rate constant.
<u>8</u>	The change in the concentration of any one of the reactants or products per unit time is called rate of a reaction
<u>9</u>	$\frac{-d[\text{N}_2]}{dt} = \frac{-1}{3} \frac{d[\text{H}_2]}{dt} = + \frac{1}{2} \frac{d[\text{NH}_3]}{dt}$
<u>10</u>	S^{-1} is the unit for rate constant of first order reaction.
<u>11</u>	$\text{Mol L}^{-1} \text{S}^{-1}$
<u>12</u>	The $t_{1/2}$ of a first order reaction is independent of initial concentration of reactants.
<u>13</u>	$\frac{(\text{Rate})_1}{(\text{Rate})_2} = \frac{0.05}{0.10} = \frac{1}{2} = \left(\frac{1}{2}\right)^a \Rightarrow a = 1; \text{ order w.r.t } A.$ Order w.r.t B = 0 (a) $\text{Rate} = k [A]$ (b) $k = \frac{\text{Rate}}{[A]} = \frac{0.05}{0.10} = 0.5 \text{ s}^{-1}$

<p><u>14</u></p>	<p>Looking at the rate data of experiment number 1 and 2 indicates that rate is doubled on doubling concentration of A while concentration of B is constant. Therefore, order with respect to A is 1. Similarly, comparing data of experiment number 1 and 3, doubling concentration of B, while concentration of A is constant, has no effect on rate.</p> <p>Therefore, order with respect to B is zero.</p> $\Rightarrow \text{Rate} = k [A]$ $\Rightarrow k = \frac{0.005}{0.010} = 0.5 \text{ min}^{-1} = \frac{0.693}{t_{1/2}}$ $\Rightarrow t_{1/2} = \frac{0.693}{0.5} = 1.386 \text{ min}$
<p><u>15</u></p>	$k_t = \ln \frac{w_0}{w}$ $\Rightarrow \frac{\ln 2}{28.1} \times 20 = \ln \frac{10^{-6} \text{ g}}{w} \Rightarrow w = 6.1 \times 10^{-7} \text{ g}$
<p><u>16</u></p>	<p>For 1st order reaction :</p> $k \propto \frac{1}{t_{1/2}}$ $\Rightarrow \ln \left\{ \frac{k (450^\circ\text{C})}{k (380^\circ\text{C})} \right\} = \ln \left\{ \frac{t_{1/2} (380^\circ\text{C})}{t_{1/2} (450^\circ\text{C})} \right\} = \frac{E_a}{R} \left(\frac{450 - 380}{727 \times 653} \right)$ $\Rightarrow \ln \left\{ \frac{360}{t_{1/2} (450^\circ\text{C})} \right\} = \frac{200 \times 10^3}{8.314} \times \frac{70}{727 \times 653} = 3.54$ $\Rightarrow t_{1/2} (450^\circ\text{C}) = 10.37 \text{ min}$ $\Rightarrow \text{Time for 75\% reaction at } 450^\circ\text{C}$ $= 2 \times t_{1/2} = 2 \times 10.37 = 20.74 \text{ min}$
<p><u>17</u></p>	<p>(i) $t_{1/2} = 10 \text{ min} = 10 \times 60 = 600 \text{ s}$</p> $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{600 \text{ s}} = 1.155 \times 10^{-3} \text{ s}^{-1}$ <p>(ii) $k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$</p> <p>Given: $t = 1 \text{ h} = 1 \times 60 \times 60 = 3600 \text{ s}$</p> $\therefore 1.155 \times 10^{-3} = \frac{2.303}{3600} \log \frac{[R]_0}{[R]}$ $\Rightarrow \log \frac{[R]_0}{[R]} = \frac{1.155 \times 10^{-3} \times 3600}{2.303} = 1.8054$ $\Rightarrow \frac{[R]_0}{[R]} = 1.8054 \text{ (Antilog)} = 63.89$ $\Rightarrow \frac{[R]}{[R]_0} = \frac{1}{63.89} = 0.016$ <p>Therefore, fraction of reactant left = 0.016</p>
<p><u>18</u></p>	<p>The rate constant k for a first-order reaction is given by</p> $k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$ <p>where</p> <p>$[R]_0$ = Initial concentration of reactant</p> <p>$[R]$ = Final concentration of reactant</p> <p>$t = 10 \text{ min},$</p> $k = \frac{2.303}{10} \log \frac{100}{100 - 25} = \frac{2.303}{10} \log \frac{4}{3}$ $\Rightarrow k = \frac{2.303}{10} (\log 4 - \log 3) = \frac{2.303}{10} (0.6021 - 0.4771)$ $\Rightarrow k = 2.88 \times 10^{-2} \text{ min}^{-1}$ <p>For a first order reaction, half-life and rate constant are related as</p> $t_{1/2} = \frac{0.693}{k}$ $\Rightarrow t_{1/2} = \frac{0.693}{2.88 \times 10^{-2}} = 24.06 \text{ min}$ <p>Hence, the $t_{1/2}$ for the reaction is 24.06 minutes.</p>

<p><u>19</u></p>	<div style="border: 1px solid black; padding: 5px; display: inline-block; margin-bottom: 10px;"> $\text{SO}_2\text{Cl}_2(\text{g}) \longrightarrow \text{SO}_2(\text{g}) + \text{Cl}_2(\text{g})$ <table style="margin-left: auto; margin-right: auto;"> <tr> <td style="padding: 0 10px;">p_i</td> <td style="padding: 0 10px;">0</td> <td style="padding: 0 10px;">0</td> </tr> <tr> <td style="padding: 0 10px;">$p_i - x$</td> <td style="padding: 0 10px;">x</td> <td style="padding: 0 10px;">x</td> </tr> </table> $p_t = p_i - x + x + x = p_i + x$ <div style="border: 1px solid black; display: inline-block; padding: 2px;"> $x = p_t - p_i$ </div> <p style="margin-top: 5px;">where p_i = initial pressure $p_t - x$ = final pressure p_t = total pressure</p> </div> $k = \frac{2.303}{t} \log \frac{[R]_0}{[R]} = \frac{2.303}{100} \log \frac{0.4}{2 \times 0.4 - 0.7}$ $= \frac{2.303}{t} \log \frac{p_i}{p_i - x} \Rightarrow k = \frac{2.303}{100} \log \frac{0.4}{0.8 - 0.7} = \frac{2.303}{100} \log 4$ $= \frac{2.303}{t} \log \frac{p_i}{p_i - p_t + p_i} \Rightarrow k = \frac{2.303 \times 0.6021}{100} = \frac{1.386}{100 \text{ s}}$ $= \frac{2.303}{t} \log \frac{p_i}{2p_i - p_t} \Rightarrow k = 1.386 \times 10^{-2} \text{ s}^{-1}$	p_i	0	0	$p_i - x$	x	x
p_i	0	0					
$p_i - x$	x	x					
<p><u>20</u></p>	$\therefore k = \frac{2.303}{t} \log \frac{a}{a-x} \quad \log \frac{100}{x} = 0.781 \quad \Rightarrow \log \frac{a}{a-x} = 0.0781$ <p>Given : $k = 2.0 \times 10^{-4} \text{ sec}^{-1}$, $t = 900 \text{ sec}$ $\Rightarrow \frac{a}{a-x} = \text{antilog}(0.0781) = 1.197$</p> <p>Substituting these values, we get $\Rightarrow a = 1.197 a - 1.197 x$</p> $2.0 \times 10^{-4} = \frac{2.303}{900} \log \frac{a}{a-x} \quad \Rightarrow 0.197 a = 1.197 x$ $\Rightarrow \log \frac{a}{a-x} = \frac{2.0 \times 10^{-4} \times 900}{2.303} \quad \therefore \frac{x}{a} = \frac{0.197}{1.197} = 0.1645$ $\therefore \% \text{ decomposed} = 0.1645 \times 100 = \mathbf{16.45\%}$						
<p><u>21</u></p>	<p>For a first order reaction,</p> $kt = \ln \frac{[A]_0}{[A]}$ <p>where $[A]_0$ = Initial concentration of reactant $[A]$ = Concentration of reactant remaining unreacted at time t.</p> <p>(i) $\Rightarrow k = \frac{1}{t} \ln \frac{[A]_0}{[A]} = \frac{1}{10} \ln \frac{100}{100 - 20} = \frac{1}{10} \ln \frac{5}{4}$</p> $= \frac{2.303 (\log 5 - 2 \log 2)}{10} \text{ min}^{-1} = 0.023 \text{ min}^{-1}$ <p>(ii) $t = \frac{1}{k} \ln \frac{100}{25} = \frac{2 \ln 2}{k} = \frac{2 \times 0.693}{0.023} = 60 \text{ min}$</p>						
<p><u>22</u></p>	$k = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{5770} \text{ yr}^{-1} = 1.2 \times 10^{-4} \text{ yr}^{-1}$ <p>Also $kt = \ln \frac{1}{f} = \frac{\ln 2}{5770} \times 11540 = \ln 4 \Rightarrow f = \frac{1}{4} = 0.25$</p>						
<p><u>23</u></p>	<p>Arrhenius equation is :</p> $\log k = \log A - \frac{E_a}{2.303 RT}$ <p>when $t_{1/2} = 10 \text{ min}$, $k = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{10 \times 60} = 1.115 \times 10^{-3} \text{ s}^{-1}$</p> $\Rightarrow \frac{E_a}{2.303 RT} = \log A - \log k$ $= \log \frac{A}{k} = \log \frac{4 \times 10^{13}}{1.115 \times 10^{-3}} = 16.54$ $\Rightarrow T = \frac{E_a}{2.303 R \times 16.54} = \frac{98.6 \times 1000}{2.303 \times 16.54 \times 8.314}$ $= 311.34 \text{ K}$						

24	$kt = \ln \frac{[A]_0}{[A]}$ $\Rightarrow 4.5 \times 10^{-3} \times 60 = \ln \frac{1}{[A]} \Rightarrow [A] = 0.76 \text{ M}$ $\Rightarrow \text{Rate} = k[A] = 4.5 \times 10^{-3} \times 0.76$ $= 3.42 \times 10^{-3} \text{ mol L}^{-1} \text{ min}^{-1}$
25	<p>For a first order reaction,</p> $kt = \ln \frac{[A]_0}{[A]}$ <p>where $[A]_0$ = Initial concentration of reactant $[A]$ = Concentration of reactant remaining unreacted at time t.</p> <p>(i) $\Rightarrow k = \frac{1}{t} \ln \frac{[A]_0}{[A]} = \frac{1}{10} \ln \frac{100}{100 - 20} = \frac{1}{10} \ln \frac{5}{4}$</p> $= \frac{2.303 (\log 5 - 2 \log 2)}{10} \text{ min}^{-1} = 0.023 \text{ min}^{-1}$ <p>(ii) $t = \frac{1}{k} \ln \frac{100}{25} = \frac{2 \ln 2}{k} = \frac{2 \times 0.693}{0.023} = 60 \text{ min}$</p>
26	<p>(a) Those reactions which are not truly of the first order but under certain conditions become first order reactions are called pseudo first order reaction. eg Hydrolysis of Ester</p> <p>(i) This reaction is zero order reaction and molecularity is two. (ii) Unit of $k = \text{mol L}^{-1} \text{ s}^{-1}$</p>
27	<p>(i) $k = \frac{2.303}{t} \log \frac{[R]_0}{[R]} = \frac{2.303}{30} \log \frac{0.60}{0.30} = \frac{2.303}{30} \times 0.301 = 2.31 \times 10^{-2} \text{ s}^{-1}$</p> <p>Also, $k = \frac{2.303}{60} \log \frac{0.60}{0.15} = \frac{2.303}{60} \times 0.6021 = 2.31 \times 10^{-2} \text{ s}^{-1}$</p> <p>Since '$k$' is constant, it shows that it follows pseudo first order reaction.</p> <p>(ii) Average rate = $-\frac{(C_2 - C_1)}{\Delta t} = \frac{-(0.15 - 0.30)}{60 - 30} = 5 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$.</p>
28	$R = k[A]$ $\Rightarrow R_1 = k[A]_1 \text{ and } R_2 = k[A]_2$ $\Rightarrow \frac{R_1}{R_2} = \frac{4}{3} = \frac{[A]_1}{[A]_2}$ <div style="border-left: 1px solid red; padding-left: 10px; margin-left: 20px;"> <p>Also $k(t_2 - t_1) = \ln \frac{[A]_1}{[A]_2} = \ln \frac{4}{3}$</p> $\Rightarrow \frac{\ln 2}{t_{1/2}} \times 10 = \ln \frac{4}{3}$ $\Rightarrow t_{1/2} = \frac{10 \log 3}{\log 4 - \log 3} = \frac{3}{0.6 - 0.48} = 25 \text{ min}$ </div>

29

(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.

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

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

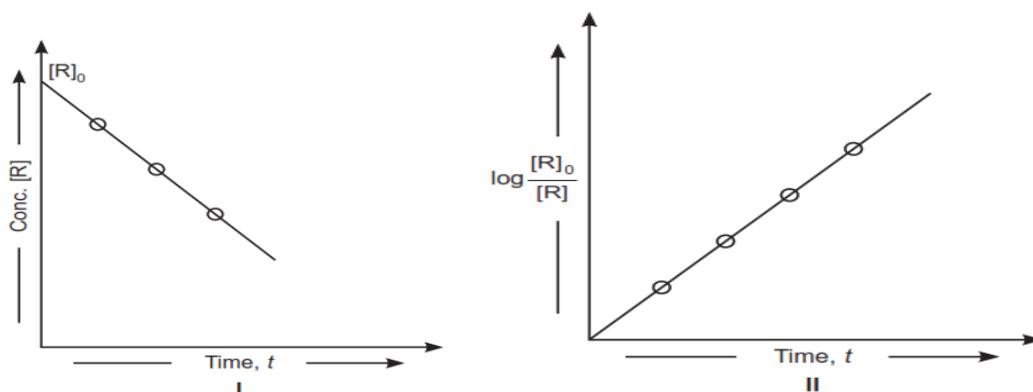
$$\Rightarrow t_{3/4} = \frac{2.303}{0.03} \log 4 = \frac{2.303 \times 0.6021}{0.03}$$

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

PASSAGE-BASED

Passage-1

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



(a) What is order of reaction shown in graph I?

Ans :- Zero order reaction.

(b) What is slope in graph II?

Ans: $k/2.303$ where 'k' is rate constant.

(c) How does $t_{1/2}$ varies with initial concentration in zero order reaction.

Ans: $t_{1/2}$ is directly proportional to initial concentration.

(d) If $t_{1/2}$ of first order reaction is 40 minute, what will be $t_{99.9\%}$ for first order reaction?

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

(e) What is $t_{1/2}$ of zero order reaction in terms of 'k'?

Ans: $t_{1/2} = [R]_0/2k$ for zero order reaction.

Passage-2

Observe the table given showing volume of CO_2 obtained by reaction of CaCO_3 and dilute HCl after every minute. Answer the questions that follow: Table showing volume of CO_2 at one minute interval by reaction of CaCO_3 with dilute HCl.

Time/mmm	Volume of CO ₂ /cm ³
0	0
1	24 cm ³
2	34 cm ³
3	38 cm ³
4	40 cm ³
5	40 cm ³
6	40 cm ³

(a) What happens to rate of reaction with time?

Ans:- The rate of reaction first decreases with time then becomes constant.

(b) Why does CaCO₃ powder react faster than marble chips?

Ans: CaCO₃ powder has more surface area than marble chips therefore, more rate of reaction.

(c) What happens to rate of reaction if concentrated HCl is used?

Ans: The rate of reaction will increase because rate of reaction increases with the increase in concentration.

(d) In manufacture of NH₃, N₂(g) + 3H₂(g) → 2NH₃ + heat what is effect of pressure on rate of reaction?

Ans: The rate of reaction increases with increase in pressure.

(e) Why does rate of reaction becomes almost double for energy 10° rise in temperature?

Ans: It is because number of molecules undergoing effective collisions become almost double, hence rate of reaction almost doubled.

Passage-3

The rate of a chemical reaction is expressed either in terms of decrease in the concentration of reactant per unit time or increase in the concentration of a product per unit time . rate of reaction depends upon the nature of reactants, concentration of reactants , temperature, presence of catalyst, surface area of reactants and presence of light. Rate of reaction is directly related to the concentration of reactant. Rate law states that the rate of reaction depends upon the concentration of terms on which the rate of reaction actually depends, as observed experimentally. The sum of powers of the concentration of the reactants in the rate law expression is called order of reaction while the number of reacting species taking part in an elementary reaction which must collide simultaneously in order to bring about a chemical reaction is called molecularity of the reaction.

(a) If the rate of a reaction is expressed by, rate = K [A]² [B], the order of reaction will be

Ans: 3

(b) The unit of rate constant for the reaction which has rate =K[H₂] [NO]²

Ans: mol⁻² L² s⁻¹

(c) For a reaction $x + y \rightarrow z$, rate $\propto [X]$. What is (i) molecularity and (ii) order of reaction?

Ans: (i) 2, (ii) 1

(d) The number of molecules of the reactants taking part in a single step of the reaction is indicative of-

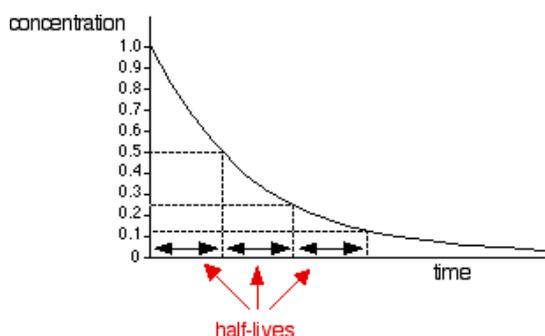
Ans:- molecularity of a reaction

Passage-4

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 in a finite time, but the reaction will never cease as the concentration of reactant will be zero only at infinite time.



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

(a) 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 reactant?

Ans : 230.3 s

(b) The rate constant for a first order reaction is $7.0 \times 10^{-4} \text{ s}^{-1}$. If initial concentration of reactant is 0.080 M, what is the half-life of reaction?

Ans :- 990 s

(c) 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. The half life of the reaction is

Ans: 24.086 min

(d) The plot of $t_{1/2}$ vs initial concentration $[A]_0$ for a first order reaction is given by



UNIT-5 SURFACE CHEMISTRY

The branch of the Chemistry which deals with the study of surface phenomena is called surface Chemistry.

Phenomenon which occurs at surfaces- Rusting of iron, Crystallization, dissolution, Adsorption on solids or on liquids etc.

1. Adsorption: - The accumulation of molecules species at the surface rather in the bulk of a solid or liquid is termed adsorption.

2. Desorption: - Removal of adsorbate from the surface of adsorbent is known as Desorption.

3. Sorption: - When adsorption and absorption both takes place simultaneously.

4. Type of adsorption: - On the basis of interaction between adsorption and absorption, adsorbate are of two types:

(i) **Physical adsorption/physisorption:** - van der Waals' forces / not specific /reversible /easily liquefiable gases adsorbed readily./ Enthalpy of adsorption is low/ Low temperature is favourable / Multimolecular layers.

(ii) **Chemical adsorption/chemisorption:** - chemical bond /highly specific / irreversible/Enthalpy of adsorption high / High temperature is favourable / /unimolecular layer.

5. Adsorption is always exothermic :-

- During adsorption, There is always a decrease in residual forces of the surface, this decrease in surface energy which appears as heat hence Adsorption is an exothermic process.
- Adsorption is accompanied by decrease in enthalpy, hence ΔH of adsorption is always negative (ΔH is -ve).
- ❖ There is decrease in entropy, ΔS is -ve. For a process to be spontaneous, ΔG must be negative, so ΔH should have sufficiently high -ve value.

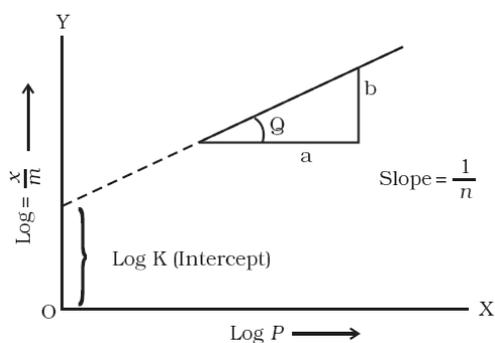
6. Adsorption and Absorption :- In adsorption, the substance is concentrated only at the surface while in absorption, the substance is uniformly distributed throughout the bulk of the solid.

7. Adsorption isotherm:-The variation in the amount of gas adsorbed by the adsorbent with pressure at constant temperature can be expressed by means of a curve termed as adsorption isotherm.

8. Application of adsorption:-.

- (a) Removal of colouring matter from solution using animal charcoal.
- (b) Chromatographic analysis is based on adsorption.

9. Freundlich adsorption isotherm:- It is a graph which shows relationship between the quantity of gas adsorbed by unit mass of solid adsorbent and pressure at a particular temperature.



$$X / m = k.P^{1/n} \quad (n > 1) \log$$

$$x/m = \log k + 1/n \log P$$

where, x = amount of gas adsorbed on mass 'm' of adsorbent.

10. Factors affecting adsorption:-

- (i) **Surface area:** - Adsorption increases with increases of surface area of adsorbent.
- (ii) **Nature of adsorbate:-** Easily liquefiable gases are readily adsorbed.
- (iii) **Temperature:-** Low temperature is favorable for physical adsorption and High temperature for chemisorption.
- (iv) **Pressure:** - Pressure increases, adsorption increases.

11. Colloid-a colloid is a heterogeneous system in which one substance is dispersed (dispersed phase) in another substance called dispersion medium and size of dispersed phase is from 1nm- 1000 nm.

[Here dispersed phase as solute and dispersion medium as solvent]

12. TYPES OF COLLOIDS

(I) **On the basis of nature of interaction between dispersed phase and dispersion medium.** (a) **Lyophilic colloid** :- Liquid(solvent)-loving/ can be reconstituted/ reversible/easily prepared/stable/ eg- gum, starch etc

(b) **Lyophobic colloid**- Liquid-hating/ not be reconstituted/ irreversible/ prepared by special methods/ precipitated on addition of electrolytes/heating/shaking/ not stable./ eg -metal sols , sulphide sols.

(II) **On the basis of types of particles of the dispersed phase**

(a) **Multimolecular** Large number of atoms or molecules of a substance aggregate eg- gold sol , sulphur sol.

(b) **Macromolecular colloids** -macromolecules are suitable solvent from solution in which size of the particles are in range of colloidal range.eg starch sol

(c) **Associated colloids (micelles)**-some substances in low concentration behaves as normal strong electrolyte but at higher concentration exhibit colloidal behavior due to formation of aggregates. The aggregated particles are called micelles and also known as associated colloids.

13. Kraft temperature- Temp. above which formation of micelles takes places.

14. Critical micelle concentration (cmc) - concentration above which micelle formation takes place is known as cmc.

15. Cleansing action of soaps :- Soap molecules form micelle around the oil droplet in such a way that hydrophobic part of the stearate ions is in the oil droplet and hydrophilic part projects out of the grease droplet like the bristles . Since the polar groups can interact with water, the oil droplet surrounded by stearate ions is now pulled in water and removed from the dirty surface.

16. PREPERATION OF COLLOIDS

(a) **Bredig's arc method**- For preparation of metallic sol. It involves dispersion as well as condensation.

(c) **Peptization**- Process of converting a precipitate into colloidal sol. By shaking it with dispersion medium in the presence of a of electrolyte (peptizing agent).

17. PURIFICATION OF COLLOIDAL SOLUTION :-

(a) **Dialysis**-it is a process of removing a dissolved substance from a colloidal solution by membrane.

(b) **Electro dialysis**-when dialysis is carried out with an electric field applied around the membrane.

(c) **Ultra filtration**- Use of special filters which are permeable to all ionic substances except colloidal particles.

18. PROPERTIES OF COLLOIDAL SOLUTION:-

(1) **Brownian movement**-zig-zag motion of colloidal particles

(2) **Tyndall effect**-scattering of light by colloidal particles by which path of beam becomes clearly visible. This effect is known as tyndall effect.

Conditions for Tyndall effect

- **Diameter of particles is not much smaller than wavelength of the light used;**

- Refractive indices of the phase and medium differ greatly in magnitude

19. **Charge on colloidal particles** – Colloidal particles which carry on electric charge and nature of charge is same on all particles.

+ve charged sols :- Hydrated metallic oxides,/methylene blue sol. /Haemoglobin (blood)

- ve charged sols :- Metals,/ sulphides/ eosin, congo red / starch, gum, gelatin, clay,charcoal.

Origin of charge on colloidal particles :- Preferential adsorption of ions . The sol particles acquire positive or negative charge by preferential adsorption of +ve or -ve ions. When two or more ions are present in the dispersion medium, preferential adsorption of the ion common to the colloidal particle usually takes place. AgI/I^-

20. **Zeta potential** :- **Potential difference between the fixed layer and the diffused layer** 1.**Electrophoresis** - **Movement of Colloidal particles towards opposite electrode in presence of external electric field.**

2. **Coagulation** – The process of setting of colloidal particles is called coagulation of the sol.

21.**Hardy Schulze Law** – Coagulating value of a coagulating ion is directly proportional to the charge on the ion.

For coagulation of a negative sol, : $\text{Al}^{3+} > \text{Ba}^{2+} > \text{Na}^+$

For coagulation of a negative sol : $[\text{Fe}(\text{CN})_6]^{4-} > \text{PO}_4^{3-} > \text{SO}_4^{2-} > \text{Cl}^-$

Coagulation value :- The minimum amount of an electrolyte in millimoles required to coagulate 1 litre colloidal solution is called coagulating value or Flocculation value.

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

Electrical precipitation of smoke(Cottrellppter) :- The smoke, before it comes out from the chimney, is led through a chamber containing plates having a charge opposite to that carried by smoke particles. The particles on coming in contact with these plates lose their charge and get precipitated.

Leather tanning: Tanning is the process of treating the skins of animals to obtain the leather. Skin of animals is also a colloidal system in which the colloidal particles are positively charged. the charged particles of skin are coagulated using negatively charged material like tannin and compounds of Al and Cr.

SHORT ANSWER TYPE – 1 (2 MARKS EACH)

- Q. 1. Define the terms : (a) Helmholtz electrical double layer (b) Zeta potential
- Q. 2. Mention the two necessary conditions for the observation of Tyndall effect.
- Q. 3.(a) Why does a gas mixed with another gas not form a colloidal system ?
(b)Why are adsorbate particles attracted and retained on the surface of adsorbent ?
- Q. 4. Explain the terms sorption and desorption.
- Q 5. (a)"Adsorbents in finely divided form are more effective." Why ?
(b) Why gas masks are used by miners in coal mines while working ?
- Q6.(a) Name two compounds used as adsorbent for controlling humidity.
(b) Generally high temperature is favourable for chemisorption.' Why ?
- Q7. (a)What is the composition of colloidion solution ?
(b) Why do colloidal particles show Brownian movement ?
- Q8. (a)"Chemisorption is highly specific." Illustrate with an example.
(b) State the sign of entropy change involved when the molecules of a substance get adsorbed on a solid surface.
- Q9. Define the term peptization and mention its cause.
- Q.10.(a).What do 'x' and 'm' represent in the expression for Freundlich adsorption isotherm $x/m = kp^{1/n}$
(b)What is the main drawback of the freundlich adsorption isotherm?

SHORT ANSWER TYPE –II (3 MARKS EACH)

- Q.1. What do you understand by activation of adsorbent? How is it achieved?
- Q.2. (a)Why is adsorption always exothermic?
(b) What is saturation pressure in Freundlich's isotherm ?

Q.3 What are lyophilic and lyophobic sols? Give one example of each type.

Q.4.(a) Why are hydrophobic sols easily coagulated?

(b) When river water meets the sea water.

Q. 5.(a) Explain the terms : (i) CMC, (ii) Kraft temperature (T_k).

(b) State the purpose of impregnating the filter paper with colloidal solution.

Q. 6. Distinguish between multimolecular, macromolecular and associated colloids with the help of one example of each.

Q. 7. Write short notes on the following :

(a) Tyndall Effect (b) Brownian Movement (c) Hardy Schulze Rule

Q.8. Explain what is observed when-

i) An electrolyte, NaCl is added to hydrate ferric oxide sol.

ii) Electric current is passed through a colloidal sol.

iii) When a beam of light is passed through a colloidal sol.

Q.9. (a) Name the fixed layer and the diffused layer

(1) when AgNO_3 is added to KI

(2) When KI is added to AgNO_3

(b) What happens when dialysis is prolonged ?

Q.10. "Action of soap is due to emulsification and micelle formation". Comment.

LONG ANSWER TYPE QUESTIONS (5 marks each)

1. What is the difference between physisorption and chemisorption?

2. Explain the following with diagrams:

(a) Dialysis (b) Electro-dialysis (c) Electrophoresis.

3. (a) Why is ferric chloride preferred over potassium chloride in case of a cut leading to bleeding?

(b) Cottrell's smoke precipitator is fitted at the mouth of the chimney used in factories.

(c) What is the main cause of charge on a colloidal solution?

(d) How does an increase in temperature affect both physical as well as chemical adsorption ? (e). Why the sun looks red at the time of setting? Explain on the basis of colloidal properties.

SHORT ANSWER TYPE-I (2 MARKS EACH)

1. **Ans** :- (a) The combination of the two layers of opposite charges around the colloidal particles.

E.g., $\text{AgI}/\text{I}^- : \text{K}^+$

(b) The potential difference between the fixed layer and diffused layer of opposite charges is called zeta potential.

2. **Ans** :- (a) The size of dispersed phase particles is not much smaller than the wavelength of light used.

(b) The refractive indices of the dispersed phase and the dispersion medium

differ greatly in magnitude.

3. **Ans** :- (a) Gaseous mixture is homogeneous.

(b) The unbalanced forces of the adsorbent are responsible for attracting adsorbate particles at adsorbent surface.

4. **Ans** :- Sorption is used to describe the process when adsorption and absorption take place simultaneously.

Desorption : Removal of adsorbate from the surface of adsorbent.

5. **Ans** (a) Due to their more surface area in finely divided form.

(b) To absorb poisonous gases

6. **Ans.(a)** Silica gel, Alumina gel **(b)** To provide energy of activation.

7. **Ans**:- (a) 4% solution of nitrocellulose in a mixture of alcohol and ether.

(b) Due to unbalanced bombardment of the dispersed phase particles by the molecules of the dispersion medium.

8. **Ans** : (a) As it involves chemical bonding between adsorbent and adsorbate

(b) **Entropy decreases (-ve)**

9. **Ans** : - It is the process of converting a ppt into a colloidal sol by shaking it with small amount of electrolyte with dispersion medium.

Cause:- Ppts adsorb one of the ions of the electrolyte on its surface.

10. **Ans**:- (a) 'm' is the mass of the adsorbent and 'x' is the number of moles of the adsorbate when the dynamic equilibrium has been achieved between the free gas and the adsorbed gas

(b) The main drawback of the Freundlich's adsorption isotherm is that it does not confirm the experimental results at high pressure i.e. it fails at high pressure of the gas.

SHORT ANSWER TYPE -II (3 MARKS EACH)

1. **Ans** -By activating an adsorbent, we tend to increase the adsorbing power of the adsorbent. Some ways to activate an adsorbent are:

(i) By increasing the surface area of the adsorbent. This can be done by breaking it into smaller pieces or powdering it.

(ii) Some specific treatments can also lead to the activation of the adsorbent. For example, wood charcoal is activated by heating it between 650 K and 1330 K in vacuum or air. It expels all the gases absorbed or adsorbed and thus, creates a space for adsorption of gases.

2. **Ans** :- (a) Adsorption is always exothermic. This statement can be explained in two ways.

(i) Adsorption leads to a decrease in the residual forces on the surface of the adsorbent.

This causes a decrease in the surface energy of the adsorbent. Therefore, adsorption is always exothermic.

(ii) ΔH of adsorption is always negative. When a gas is adsorbed on a solid surface, its movement is restricted leading to decrease in the entropy of the gas i.e., ΔS is negative. Now for a process to be spontaneous, ΔG should be negative.

$$\Delta G = \Delta H - T\Delta S$$

Since ΔS is negative, ΔH has to be negative to make ΔG negative. Hence, adsorption is always exothermic.

(b) High pressure

3. Ans

Lyophobic sols	Lyophilic sols
solvent hating colloids	solvent loving colloids
In these colloids the particles of dispersed phase have no affinity for the dispersion medium	In these colloids, the particles of dispersed phase have great affinity for the dispersion medium
They are not stable	They are stable.
They cannot be prepared by mixing substances directly. They are prepared only by special methods	They can be prepared by mixing substances directly
They need stabilizing agents for their preservation.	They do not need stabilizing agents for their preservation.
They are irreversible sols.	They are reversible sols.
colloidal solutions of gold, silver, Fe(OH) ₃ , As ₂ S ₃ , etc. or metallic sols.	Eg:- gums, gelatin, starch, albumin in water.

4. Ans :-the stability of hydrophilic sols depends on two things- **the presence of a charge** and the **solvation of colloidal** particles. On the other hand, the stability of hydrophobic sols is only because of the presence of a charge. Therefore, the latter are much less stable than the former. If the charge of hydrophobic sols is removed (by addition of electrolytes), then the particles present in them come closer and form aggregates, leading to precipitation.

(b) Delta formation takes place due to coagulation of river water.

5. Ans :- (a) (i) CMC : Concentration above which micelle formation took place.
(ii) Kraft Temperature : It is the temperature above the micelle formation took place.

(b) To reduce pore size of filter paper, so that colloidal particles cannot pass through.

6. Ans: (i) Multimolecular colloids formed by aggregation of small atoms or molecules. Example, gold sol, sulphur sol.

(ii) Macromolecular colloids formed by dispersing macromolecules having colloidal size in proper dispersion medium. Example, protein, starch colloid.

(iii) Associated colloids are formed by aggregation of particles at higher concentration to colloidal range. Example, micelles.

7. Ans. (a) **Tyndall Effect** : Scattering of light by colloidal particles by which part of beam becomes clearly visible. This effect is known as tyndall effect.

(b) **Brownian Movement** : Zig-zag motion of colloidal particles.

(c) **Hardy Schulze Rule** : Coagulating value of a coagulating ion is directly proportional to the charge on the ion.

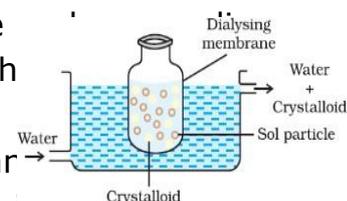
e.g: $\text{Na}^{+1} < \text{Ca}^{2+} < \text{Al}^{3+}$ for negatively charged sol.

$\text{Cl}^{-} < \text{CO}_3^{2-} < \text{PO}_4^{3-} < [\text{Fe}(\text{CN})_6]^{4-}$ for positive sol.

8. Ans -(i) The positively charged colloidal particles of Fe(OH)₃ get coagulated by the negatively charged Cl⁻ ions provided by NaCl.

Specificity	2. It is not specific in nature	2. It is highly specific in nature.
Reversibility	3. It is reversible in nature	3. It is irreversible.
Nature of gas	4. It depends on the nature of gas. More easily liquefiable gases are adsorbed readily.	4. It also depends on the nature of gas. Gases which can react with the adsorbent show chemisorption.
Enthalpy of Adsorption	5. Enthalpy of adsorption is low (20-40 kJ mol ⁻¹) in this case.	5. Enthalpy of adsorption is high (80-240 kJ mol ⁻¹) in this case
Temperature	6. Low temperature is favourable for adsorption. It decreases with increase of temperature.	6. High temperature is favourable for adsorption. It increases with the increase of temperature.
Activation Energy	7. No appreciable activation energy is needed.	7. High activation energy is sometimes needed.
Surface Area.	8. It depends on the surface area. It increases with an increase of surface area	8. It also depends on the surface area. It too increases with an increase of surface area.

2. Ans: i) Dialysis: It is a process of purification of sols containing electrolyte by keeping the sol in a bag made of parchment or cellophane the bag in pure water. Small molecules or ions can pass through but the sol is retained.



(ii) **Electro-dialysis:** The process of dialysis is quite slow. It can be speeded up by applying an electric field if the dissolved substance in the solution is only an electrolyte. The process is then named electro-dialysis. A colloidal solution is placed in a bag of suitable membrane which is taken outside. Electrodes are fitted in the compartment as shown in the diagram. The ions present in the colloidal solution migrate out to the opposite electrodes.

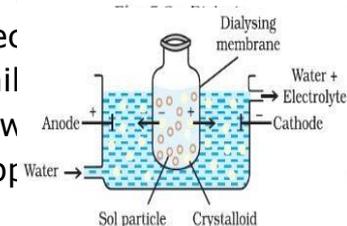


Fig. 5.10: Electro-dialysis

(b) Electrophoresis: The existence of charge on colloidal particles is confirmed by electrophoresis experiment. When an electric potential is applied across two platinum electrodes dipping in a colloidal solution, the particles move towards one or the other electrode. The movement of colloidal particles towards a positive electrode in an electric field is called electrophoresis. Positively charged particles move towards the cathode while negatively charged particles move towards the anode.

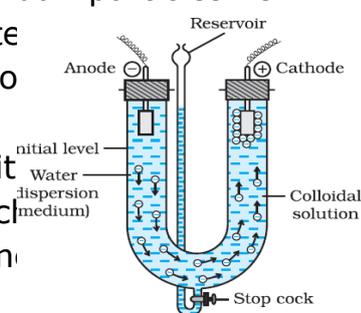


Fig. 5.13: Electrophoresis

3. Ans: (a) Blood is a colloidal solution of an albuminoid substance. The styptic action of alum and ferric chloride solution is due to coagulation of blood forming a clot which stops further bleeding.

(b) Smoke is a colloidal solution of solid particles such as carbon, arsenic

compounds, dust, etc., in air. This smoke is led through a chamber containing plates having a charge opposite to that carried by smoke particles. The particles on coming in contact with these plates lose their charge and get precipitated. The particles thus settle down on the floor of the chamber.

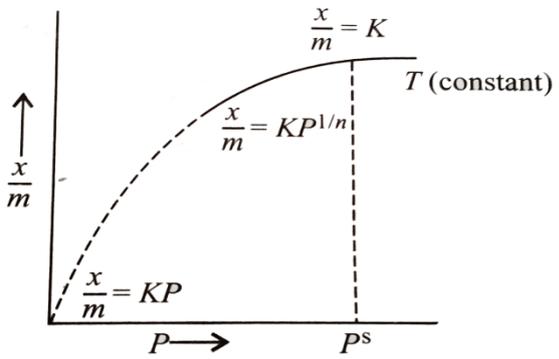
(C) The charge on the colloidal particles is due to adsorption of common ions of the electrolyte on the surface of the colloidal particles, e.g: Fe^{3+} from FeCl_3 on the surface of $\text{Fe}(\text{OH})_3$ particles.

(d) With increase of temperature, physical adsorption decreases while chemisorption first increases and then decreases.

(e) At the time of setting, the sun is at the horizon. The light emitted by the sun has to travel a longer distance through the atmosphere. As a result, blue part of the light is scattered away by the dust particles in the atmosphere. Hence, the red part is visible.

S.No	CASE BASED QUESTIONS
1.	<p>The degree of interaction by which the adsorbate molecules are accumulated onto the adsorbents defines the nature and type of adsorption. Furthermore, the mechanism can either be classified as physisorption (physical adsorption) or chemisorption (chemical adsorption). Physisorption is the adsorption in which the molecular interactions between the adsorbate molecules and the adsorbent are primarily governed by van der Waals forces whereas chemisorption is the adsorption that takes place if there are chemical bonds between adsorbate molecules and the adsorbent.</p> <p>Physisorption is non-specific in nature and is generally regarded as a weak, reversible process governed by competitive adsorption and desorption which takes place at different rates at the heterogeneous surface. Adsorption selectivity refers to the preferential adsorption ability of adsorbents for some substances because of their particular composition and the structure of the adsorbents. For example, activated carbon is composed of covalently linked carbon atoms, and can preferentially adsorb high-molecular-weight organic molecules due to its large aperture.</p> <p>Whereas due to specificity, the nature of chemisorption can greatly differ, depending on the chemical identity and the surface structural properties. The bond between the adsorbate and adsorbent in chemisorption is either ionic or covalent. An important example of chemisorption is in heterogeneous catalysis which involves molecules reacting with each other via the formation of chemisorbed intermediates. After the chemisorbed species combine (by forming bonds with each other) the product desorbs from the surface.</p>

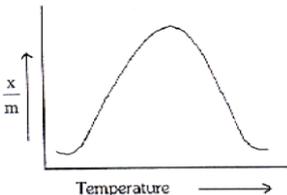
(A)	At the same temperature and pressure, arrange in increasing order of adsorption the following gases on the same mass of charcoal: H ₂ , SO ₂ , CH ₄ and NH ₃ .
(B)	Which of the two adsorptions give rise to monolayer adsorption? Why?
(C)	Write one similarity between physisorption and chemisorption.
(D)	Why is adsorption always exothermic? OR Adsorption of a gas on surface of solid is generally accompanied by a decrease in entropy, still it is a spontaneous process. Explain.
2.	<p>Coagulation is the destabilization of Colloids by neutralizing the electric charge of the dispersed phase particles, which results in aggregation of the colloidal particles. Aggregation is a formation of groups of particles bonded to each other by van der Waals or other intermolecular forces. Aggregation usually refers to solid particles. In a stable colloid system the dispersed particles are electrically charged. Two charged particles repel each other preventing collision and aggregation. When the charges are neutralized the particles may collide and bond to each other.</p> <p>A coagulation process may be subdivided in two stages: electric neutralization of the dispersed phase and aggregation of the destabilized particles. The following methods are used for the destabilization of the colloidal particles by neutralization:</p> <p>Addition of an electrolyte to the colloid. The colloidal particles are neutralized by the oppositely charged electrolyte ions. The destabilization of a lyophobic colloid occurs at the electrolyte concentrations exceeding the value of the critical coagulation concentration. The critical coagulation concentration is strongly dependent on the valence of the electrolyte ions. The higher the valence the lower the critical concentration of the electrolyte.</p> <p>Addition of another colloid, particles of which are charged oppositely to the particles of the first colloid. The oppositely charged particles of the colloids attract each other and neutralize the electric charge.</p> <p>Using electrodes connected to a DC power supply. The electric circuit provides the charges for neutralizing the colloidal particles. The term coagulation is often interchangeably used with the term flocculation. However the coagulation and flocculation processes are similar but not the same. Flocculation is the aggregation of a colloid by polymer molecules (flocculent) bridging between the colloidal particles and forming large fragile network structures</p>

	(flocs), which may be easily removed by sedimentation/flotation and filtering.
(A)	“Using electrodes connected to a DC power supply. The electric circuit provides the charges for neutralizing the colloidal particles.” What is the name of technique following this principle?
(B)	Which of the following is most effective in coagulating positively charged methylene blue sol? - Na_3PO_4 or $\text{K}_4[\text{Fe}(\text{CN})_6]$ or Na_2SO_4
(C)	Define “Coagulating value”.
(D)	Can boiling lead to coagulation of a sol? Explain. OR When a small amount of lyophilic colloid is added to lyophobic colloid it may coagulate the latter. However, the addition of large amount of lyophilic colloid increases the stability of the lyophobic colloid. Explain
3.	<p>The 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.</p>  <p>The Freundlich adsorption isotherm is mathematically expressed as</p> $\frac{x}{m} = KP^{\frac{1}{n}}$ <p>K and n are constants for a given adsorbate and adsorbent at a given temperature. At high pressure $1/n = 0$, hence extent of adsorption becomes independent of pressure.</p> <p>Homogeneous surfaces have a constant ΔH of adsorption. On the other hand, heterogeneous adsorption has a variable ΔH of adsorption depending on the percent of sites occupied.</p> <p>Experimentally it was determined that extent of gas adsorption varies directly with pressure, and then it directly varies with pressure raised to the power $1/n$ until saturation pressure P_s is</p>

	reached. Beyond that point, the rate of adsorption saturates even after applying higher pressure. Thus, the Freundlich adsorption isotherm fails at higher pressure.
(A)	What is the value of '1/n' for Freundlich adsorption equation?
(B)	What will happen to the curve, if the temperature of the adsorption system increases by 20 K?
(C)	Draw plot of x/m Vs T representing adsorption isobar for chemisorption.
(D)	In which pressure range, Freundlich adsorption isotherm fails? Why? OR The plot of log x/m against log P is a straight line inclined at an angle of 45°. When the pressure is 0.5 atm and K is 10, what will be the amount of solute adsorbed per gram of adsorbent?

ANSWER KEY

S. No.	ANSWER
1A	$H_2 < CH_4 < NH_3 < SO_2$
1B	Chemisorption. In chemisorption the adsorbate is held on the surface of adsorbent by chemical bonds. Once all the bonds on the surface of adsorbent are used for chemical bonding, no further adsorption is possible. Hence chemisorption is monolayered
1C	Both physisorption and chemisorption increase with increase in pressure. Both increase with increase in surface area. (Any one)
1D	Adsorption is accompanied by decrease of randomness. For the process to be spontaneous, ΔG must be negative. Hence, according to equation $\Delta G = \Delta H - T\Delta S$, ΔG can be negative only if ΔH is negative. OR We know $\Delta G = \Delta H - T\Delta S$ for adsorption. ΔH and ΔS are negative and $\Delta H > T\Delta S$. Thus from this equation ΔG is negative. Therefore, for adsorption ΔH , ΔG and ΔS all are negative.
2A	Electrophoresis
2B	$K_4[Fe(CN)_6]$
2C	The minimum concentration of an electrolyte in millimoles per litre required to cause precipitation of a sol in two hours is called coagulating value.
2D	Yes, boiling can cause coagulation. When a sol is boiled, the adsorbed layer is disturbed due to increased collisions with the

	<p>molecules of dispersion medium. This reduces the charge on the particles and ultimately leads to settling down in the form of a precipitate.</p> <p>OR</p> <p>When a small amount of lyophilic colloid is added to lyophobic colloids it may coagulate the latter due to neutralisation of the charge on the lyophobic colloidal particles.</p> <p>However, the addition of large amount of hydrophilic colloid increases the stability of the hydrophobic colloidal system. This is due to adsorption of lyophilic sol on the surface of lyophobic sol. The layer of the protective colloid prevents direct collision between the lyophobic colloidal particles and thus prevents coagulation.</p>
3A	Any value between 0 and 1.
3B	The slope of the curve will decrease so it will move downwards.
3C	
3D	<p>Freundlich adsorption isotherm fails at higher pressure range. Because at a particular high pressure, saturation pressure P_s is reached. Beyond that point, the adsorption saturates even after applying higher pressure.</p> <p>OR</p> <p>According to Freundlich adsorption equation, $x/m = kP^{1/n}$ or $\log(x/m) = \log k + 1/n \log P$ Plot of $\log x/m$ vs. $\log P$ is a straight line with slope = $1/n$ and intercept = $\log k$. Thus, $1/n = \tan \theta = \tan 45^\circ = 1$ or $n = 1$ At $p = 0.5$ atm and $k = 10$, $x/m = 10(0.5) = 5$ When $m = 1$g, x (i.e., amount adsorbed per gram) = 5 g</p>



The d-and f-Block Elements

- Elements in which the last electron enters any one of the five *d*-orbitals of their respective penultimate shell are known as *transition elements* or *d-block elements*.
- Their general electronic configuration is $(n - 1)d^{1-10}ns^{0-2}$.

Melting and boiling points	High due to strong metallic bonding
Enthalpies of atomization	High due to strong interatomic interactions
Ionisation enthalpies	Generally increases from left to right in a series
Oxidation states	Variable due to participation of <i>ns</i> and $(n - 1)d$ electrons
Atomic radii	Decrease from left to right but become constant when pairing of electrons takes place
Complex formation	Form complexes due to high nuclear charge and small size and availability of empty <i>d</i> -orbitals to accept lone pair of electrons donated by ligands.
Coloured compounds	Form coloured compounds due to <i>d-d</i> transitions
Magnetic properties	Transition metal ions and their compounds are paramagnetic due to presence of unpaired electrons in the $(n - 1)d$ -orbitals and it is calculated by using the formula, magnetic moment $\mu = \sqrt{n(n+2)}\text{BM}$ where, <i>n</i> is the no. of unpaired electrons.
Catalytic behaviour	Due to variable oxidation states and ability to form complexes
Interstitial compounds	Due to empty spaces in their lattices, small atoms can be easily accommodated
Alloy formation	Due to similar atomic sizes

Inner Transition Elements(f-Block Elements)

Lanthanoids :	Last electron enters one of the <i>4f</i> -orbitals. Cerium (At. no. 58) to Lutetium(At.no.71).
Actinoids :	Last electron enters one of the <i>5f</i> -orbitals. Thorium (At. no. 90) to Lawrencium(At. no.103).
Lanthanoid contraction	In lanthanoid series, with increasing atomic number, there is progressive decrease in atomic/ionic radii (M^{3+} ions) from La^{3+} to Lu^{3+} .

Question No 1 to 10 are 2 Mark questions:

1. Why E° values for Mn, Ni and Zn are more negative than expected?
2. Why first ionisation enthalpy of Cr is lower than that of Zn ?
3. Transition elements show high melting points. Why?
4. Out of Cu_2Cl_2 and CuCl_2 , which is more stable and why?
5. Although fluorine is more electronegative than oxygen, but the ability of oxygen to stabilise higher oxidation states exceeds that of fluorine. Why?
6. Although Cr^{3+} and Co^{2+} ions have same number of unpaired electrons but the magnetic moment of Cr^{3+} is 3.87 B.M. and that of Co^{2+} is 4.87 B.M. Why?
7. Ionisation enthalpies of Ce, Pr and Nd are higher than Th, Pa and U. Why?
8. Although Zr belongs to 4d and Hf belongs to 5d transition series but it is quite difficult to separate them. Why?
9. A solution of KMnO_4 on reduction yields either a colourless solution or a brown precipitate or a green solution depending on pH of the solution. What different stages of the reduction do these represent and how are they carried out?
10. The halides of transition elements become more covalent with increasing oxidation state of the metal. Why?

THREE MARK QUESTIONS:

11. Explain briefly how +2 state becomes more and more stable in the first half of the first row transition elements with increasing atomic number?
12. What may be the stable oxidation state of the transition element with the following d electron configurations in the ground state of their atoms : $3d^5$ and $3d^8$?
13. What is lanthanoid contraction? What are the consequences of lanthanoid contraction?
14. Explain giving reasons:
 - (i) The enthalpies of atomisation of the transition metals are high.
 - (ii) The transition metals generally form coloured compounds.
 - (iii) Transition metals and their many compounds act as good catalyst.
15. Predict which of the following will be coloured in aqueous solution? Ti^{3+} , V^{3+} , Cu^+ , Sc^{3+} , Mn^{2+} , Fe^{3+} . Give reasons for each.
16. How would you account for the following:
 - (i) Of the d^4 species, Cr^{2+} is strongly reducing while manganese(III) is strongly oxidising.
 - (ii) Cobalt(II) is stable in aqueous solution but in the presence of complexing reagents it is easily oxidised.

17. Use Hund's rule to derive the electronic configuration of Ce^{3+} ion, and calculate its magnetic moment on the basis of 'spin-only' formula

18. What can be inferred from the magnetic moment values of the following complex species ?

Compound	Magnetic Moment (BM)
(i) $\text{K}_4[\text{Mn}(\text{CN})_6]$	2.2
(ii) $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$	5.3

19. What are inner transition elements? Decide which of the following atomic numbers are the atomic numbers of the inner transition elements : 29, 59, 74, 95, 102, 104.

20. Calculate the number of unpaired electrons in the following gaseous ions: Mn^{3+} , Cr^{3+} , V^{3+} and Ti^{3+} . Which one of these is the most stable in aqueous solution?

FIVE MARK QUESTIONS:

21. Compare the chemistry of the actinoids with that of lanthanoids with reference to: (i) electronic configuration (ii) oxidation states

22. On the basis of Lanthanoid contraction, explain the following :

- (i) Nature of bonding in La_2O_3 and Lu_2O_3 .
- (ii) Trends in the stability of oxo salts of lanthanoids from La to Lu.
- (iii) Stability of the complexes of lanthanoids.
- (iv) Radii of 4d and 5d block elements.
- (v) Trends in acidic character of lanthanoid oxides.

23.(a) Answer the following questions :

- (i) Which element of the first transition series has highest second ionisation enthalpy?
- (ii) Which element of the first transition series has highest third ionisation enthalpy?
- (iii) Which element of the first transition series has lowest enthalpy of atomisation?

(b) Identify the metal and justify your answer.

- (i) Carbonyl $\text{M}(\text{CO})_5$
- (ii) MO_3F

24. 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.

25. (a) Transition metals can act as catalysts because these can change their oxidation state. How does $\text{Fe}(\text{III})$ catalyse the reaction between iodide and persulphate ions?

(b) Mention any three processes where transition metals act as catalysts.

ANSWERS

1. Negative E° values for Mn^{2+} and Zn^{2+} are related to stabilities of half filled and fully filled configuration respectively. But for Ni^{2+} , E° value is related to the highest negative enthalpy of hydration.

2. Ionisation enthalpy of Cr is lower due to stability of d^5 and the value for Zn is higher because its electron comes out from 4s orbital.

3. The high melting points of transition metals are attributed to the involvement of greater number of electrons in the interatomic metallic bonding from (n-1) d-orbitals in addition to ns electrons

4. $CuCl_2$ is more stable than Cu_2Cl_2 . The stability of Cu^{2+} (aq.) rather than Cu^+ (aq.) is due to the much more negative $\Delta_{hyd}H$ of Cu^{2+} (aq.) than Cu^+ (aq.).

5. It is due to the ability of oxygen to form multiple bonds to metals.

6. Due to symmetrical electronic configuration there is no orbital contribution in Cr^{3+} ion. However appreciable orbital contribution takes place in Co^{2+} ion.

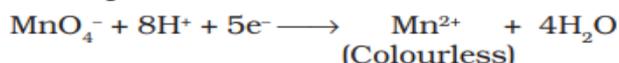
7. It is because in the beginning, when 5f orbitals begin to be occupied, they will penetrate less into the inner core of electrons. The 5f electrons will therefore, be more effectively shielded from the nuclear charge than 4f electrons of the corresponding lanthanoids.

8. Due to lanthanoid contraction, they have almost same size (Zr, 160 pm) and (Hf, 159 pm).

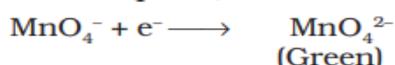
9.

Oxidising behaviour of $KMnO_4$ depends on pH of the solution.

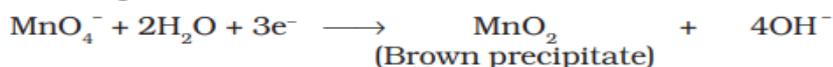
In acidic medium (pH < 7)



In alkaline medium (pH > 7)



In neutral medium (pH = 7)



10. As the oxidation state increases, size of the ion of transition element decreases. As per Fajan's rule, as the size of metal ion decreases, covalent character of the bond formed increases.

11. It can be easily observed that except Sc, all other metals display +2 oxidation state. Also, on moving from Sc to Mn, the atomic number increases from 21 to 25. This means the number of electrons in the 3d-orbital also increases from 1 to 5. +2 oxidation state is attained by the loss of the two 4s electrons by these metals. Since the number of d electrons in (+2) state also increases from Ti(+2) to Mn(+2), the stability of +2 state increases (as d-orbital is becoming more and more half-filled). Mn (+2) has d5 electrons (that is half-filled d shell, which is highly stable).

$3d^5$ (Chromium)	+3, +4, +6
$3d^5$ (Manganese)	+2, +4, +6, +7
$3d^8$ (Cobalt)	+2, +3

12.

13. The 4f electrons have poor shielding effect. Therefore, the effective nuclear charge experienced by the outer electrons increases. Consequently, the attraction of the nucleus for the outermost electrons increases. This results in a steady decrease in the size of lanthanoids with the increase in the atomic number.

Consequences of lanthanoid contraction

(i) There is similarity in the properties of second and third transition series.

(ii) It is due to lanthanide contraction that there is variation in the basic strength of lanthanide hydroxides. (Basic strength decreases from $\text{La}(\text{OH})_3$ to $\text{Lu}(\text{OH})_3$.)

14. (i) Transition elements have high effective nuclear charge and a large number of valence electrons. Therefore, they form very strong metallic bonds. As a result, the enthalpy of atomization of transition metals is high.

(ii). This is because of the absorption of radiation from visible light region to promote an electron from one of the d -orbitals to another. In the presence of ligands, the d -orbitals split up into two sets of orbitals having different energies.

(iii) The catalytic activity of the transition elements can be explained by two basic facts.

(a) Owing to their ability to show variable oxidation states

(b) Transition metals also provide a suitable surface for the reactions to occur

15. on the basis of electronic configuration that only Sc^{3+} has an empty d -orbital. All other ions, except Sc^{3+} , will be coloured in aqueous solution because of $d-d$ transitions.

16. (i) Cr^{2+} is strongly reducing in nature. It has a d^4 configuration. While acting as a reducing agent, it gets oxidized to Cr^{3+} (electronic configuration, d^3). This d^3 configuration can be written as t_{2g}^3 configuration, which is a more stable configuration. In the case of Mn^{3+} (d^4), it acts as an oxidizing agent and gets reduced to Mn^{2+} (d^5). This has an exactly half-filled d -orbital and is highly stable.

(ii) $\text{Co}(\text{II})$ is stable in aqueous solutions. However, in the presence of strong field complexing reagents, it is oxidized to $\text{Co}(\text{III})$. Although the 3rd ionization energy for Co is high, but the higher amount of crystal field stabilization energy (CFSE) released in the presence of strong field ligands overcomes this ionization energy.

17. n = number of unpaired electrons In Ce, $n = 2$

2.828 BM

18. (i) $K_4[Mn(CN)_6]$

For in transition metals, the magnetic moment is calculated from the spin-only formula. Therefore,

$$\sqrt{n(n+2)} = 2.2$$

We can see from the above calculation that the given value is closest to $n=1$. Also, in this complex, Mn is in the +2 oxidation state. This means that Mn has 5 electrons in the d -orbital.

Hence, we can say that CN^- is a strong field ligand that causes the pairing of electrons.

(ii) $[Fe(H_2O)_6]^{2+}$

$$\sqrt{n(n+2)} = 5.3$$

We can see from the above calculation that the given value is closest to $n=4$. Also, in this complex, Fe is in the +2 oxidation state. This means that Fe has 6 electrons in the d -orbital.

Hence, we can say that H_2O is a weak field ligand and does not cause the pairing of electrons.

19. Inner transition metals are those elements in which the last electron enters the f -orbital. The elements in which the $4f$ and the $5f$ orbitals are progressively filled are called f -block elements. Among the given atomic numbers, the atomic numbers of the inner transition elements are 59, 95, and 102.

20. Cr^{3+} is the most stable in aqueous solutions owing to a t_{2g}^3 configuration.

21. Electronic configuration:

The general electronic configuration for lanthanoids is $[Xe]^{54} 4f^{0-14}$ actinoids is $[Rn]^{86} 5f^{1-14} 6d^{0-1} 7s^2$. Unlike $4f$ orbitals, $5f$ orbitals are participate in bonding to a greater extent. $5d^{0-1} 6s^2$ and that for not deeply buried and

Oxidation states:

This is because of extra stability of fully-filled and half-filled orbitals. Actinoids exhibit a greater range of oxidation states. This is because the $5f$, $6d$, and $7s$ levels are of comparable energies. Again, (+3) is the principal oxidation state for actinoids. Actinoids such as lanthanoids have more compounds in +3 state than in +4 state.

22. (i) As the size decreases covalent character increases. Therefore La_2O_3 is more ionic and Lu_2O_3 is more covalent.

(ii) As the size decreases from La to Lu, stability of oxosalts also decreases.

(iii) Stability of complexes increases as the size of lanthanoids decreases.

(iv) Radii of $4d$ and $5d$ block elements will be almost same.

(v) Acidic character of oxides increases from La to Lu.

23. (a) (i) Cu, because the electronic configuration of Cu is $3d^{10}4s^1$. So second electron needs to be removed from completely filled d -orbital.

(ii) Zn (iii) Zn [No unpaired electron for metallic bonding]

(b) (i) $\text{Fe}(\text{CO})_5$ [EAN rule]

(ii) MnO_3F [Mn shows +7 oxidation state; *d*-electrons are not involved in bonding.]

24. Interstitial compounds. Characteristic properties :

(i) High melting points, higher than those of pure metals.

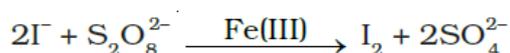
(ii) Very hard.

(iii) Retain metallic conductivity.

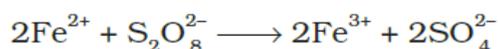
(iv) Chemically inert.

25.

(a) Reaction between iodide and persulphate ions is :



Role of Fe (III) ions :



(b) (i) Vanadium (V) oxide in contact process for oxidation of SO_2 to SO_3 .

(ii) Finely divided iron in Haber's process in conversion of N_2 and H_2 to NH_3 .

(iii) MnO_2 in preparation of oxygen from KClO_3 .

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

The f-block elements are those in which the differentiating electron enters the (n - 2)f orbital. There are two series of f-block elements corresponding to filling of 4f and 5f-orbitals. The series of 4f-orbitals is called lanthanides. Lanthanides show different oxidation states depending upon stability of f^0 , f^7 and f^{14} configurations, though the most common oxidation states is +3. There is a regular decrease in size of lanthanides ions with increase in atomic number which is known as lanthanide contraction.

(a) The atomic numbers of three lanthanide elements X, Y and Z are 65, 68 and 70 respectively, t What is their Ln^{3+} electronic configuration is

Ans. $4f^9, 4f^{11}, 4f^{13}$

(b) Name a member of the lanthanoid series which is well known to exhibit +4 oxidation state.

Ans. Cerium

(c) What is the reason of lanthanoid contraction?

Ans. The Lanthanide Contraction is caused by **a poor shielding effect of the 4f electrons.**

(d) Why Zr & Hf exist together?

Ans. Due to lanthanoid contraction, their sizes are similar.

2. Read the passage given below and answer the following questions:

The transition elements have incompletely filled *d*-subshells in their ground state or in any of their oxidation states. The transition elements occupy position in between *s*- and *p*-blocks in groups 3-12 of the Periodic table. Starting from fourth period, transition elements consists of four complete series : Sc to Zn, Y to Cd and La, Hf to Hg and Ac, Rf to Cn. In general, the electronic configuration of outer orbitals of these elements is $(n - 1) d^{1-10} ns^{1-2}$. The electronic configurations of outer orbitals of Zn, Cd, Hg and Cn are represented by the general formula $(n - 1)d^{10} n^2$. All the transition elements have typical metallic properties such as high tensile strength, ductility, malleability. Except mercury, which is liquid at room temperature, other transition elements have typical metallic structures. The transition metals and their compounds also exhibit catalytic property and paramagnetic behaviour. Transition metal also forms alloys. An alloy is a blend of metals prepared by mixing the components. Alloys may be homogeneous solid solutions in which the atoms of one metal are distributed randomly among the atoms of the other.

(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.

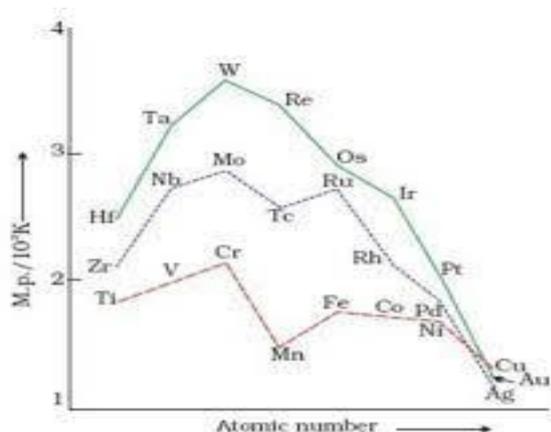
OR

(d) Why is Cu^{2+} ion coloured while Zn^{2+} ion is colorless?

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

3. Read the passage given below and answer the following questions:

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.

OR

(d) 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.

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

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

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	
Atomic number	21	22	23	24	25	26	27	28	29	30	
Electronic configuration											
M	$3d^1 4s^2$	$3d^2 4s^2$	$3d^3 4s^2$	$3d^5 4s^1$	$3d^5 4s^2$	$3d^6 4s^2$	$3d^7 4s^2$	$3d^8 4s^2$	$3d^{10} 4s^1$	$3d^{10} 4s^2$	
M ⁺	$3d^1 4s^1$	$3d^2 4s^1$	$3d^3 4s^1$	$3d^5$	$3d^5 4s^1$	$3d^6 4s^1$	$3d^7 4s^1$	$3d^8 4s^1$	$3d^{10}$	$3d^{10} 4s^1$	
M ²⁺	$3d^1$	$3d^2$	$3d^3$	$3d^4$	$3d^5$	$3d^6$	$3d^7$	$3d^8$	$3d^9$	$3d^{10}$	
M ³⁺	[Ar]	$3d^1$	$3d^2$	$3d^3$	$3d^4$	$3d^5$	$3d^6$	$3d^7$	-	-	
Enthalpy of atomisation, $\Delta_a H^\circ / \text{kJ mol}^{-1}$	326	473	515	397	281	416	425	430	339	126	
Ionisation enthalpy/ $\Delta_i H^\circ / \text{kJ mol}^{-1}$											
$\Delta_1 H^\circ$	I	631	656	650	653	717	762	758	736	745	906
$\Delta_2 H^\circ$	II	1235	1309	1414	1592	1509	1561	1644	1752	1958	1734
$\Delta_3 H^\circ$	III	2393	2657	2833	2990	3260	2962	3243	3402	3556	3829
Metallic/ionic radii/pm											
M	164	147	135	129	137	126	125	125	128	137	
M ²⁺	-	-	79	82	82	77	74	70	73	75	
M ³⁺	73	67	64	62	65	65	61	60	-	-	

(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 3rd ionization enthalpy of Mn high?

Ans. It is because after losing 2 electrons, it becomes 3d⁵ which is more stable.

(c) Why is Cr³⁺ more stable than Cr²⁺?

Ans. It is because Cr³⁺(t_{2g}³) half-filled orbitals are more stable than Cr²⁺(3d⁴).

(d) Why is E° Mn²⁺ /Mn = -1.18V?

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

OR

(d) Why is E° Cu²⁺/Cu = +0.34V?

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

Coordination compounds

Gist of chapter

Coordination compounds

The compounds in which a metal atom/ion is surrounded by a definite number of ligands by coordinate bonds.

They do not ionize into simple ions in aq. solution.

Ex: $K_4[Fe(CN)_6]$

Double salts

When two salts in their stoichiometric ratio crystallize together from their saturated solution.

They get ionized into all constituting ions. Ex: potash alum, Mohr salt

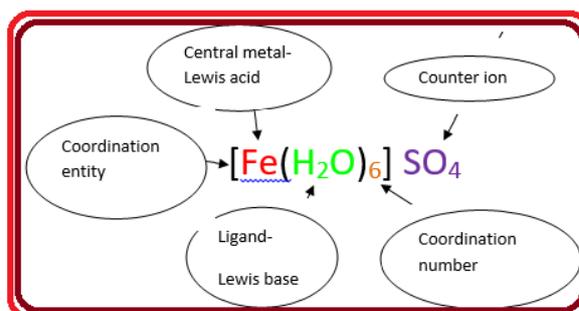
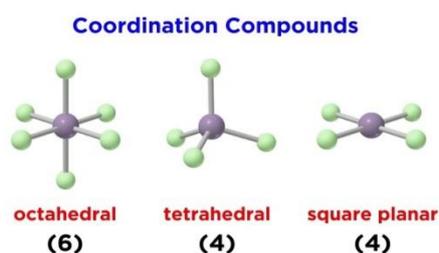
Coordination entity

Particle involving metal atom/ion with definite no of ligands. $[Fe(CN)_6]^{4-}$

Coordination polyhedra

The geometry of the complex entity is called Coordination polyhedral.

$[Cu(NH_3)_4]^{2+}$ -----square planar



Ligand

Species that provide a pair of electrons to the central metal atom/ion by coordinate bond. They act as Lewis bases in complexes NH_3 , H_2O , en

Types of ligands

Monodentate ligands: Only one donor atom, surround metal by one coordinate bond. Ex: NH_3 , H_2O , CN^{-1}

Bidentate ligands: Two donor atoms, surround metal by two coordinate bonds. Ex: SO_4^{2-} , en, $C_2O_4^{2-}$

Polydentate ligands: More than two donor atoms, surround metal by one coordinate bond. Ex: $EDTA^{4-}$

Ambident ligands: Two donor atoms but attached with only one at a time: CN^{-1} and NC^{-1}

Coordination number

Number of monodentate or equivalent ligands surrounding the metal in a complex. $[Fe(CN)_6]^{4-}$ coordination number is 6

Homoleptic and heteroleptic complexes

When all ligands surrounding metal are same-----homoleptic complex
 $[Fe(H_2O)_6]SO_4$ ----- all six ligands are same water molecules

When all ligands surrounding metal are not same-----heteroleptic complex.
 $[Fe(H_2O)_3(NH_3)_3]SO_4$ ----- Two different type of ligands

Nomenclature of Coordination Compounds

Cation is written first followed by anion.

While writing name of coordination sphere ligands are named first followed by central metal atom.

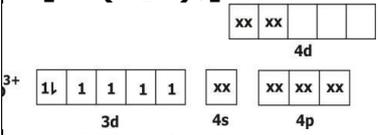
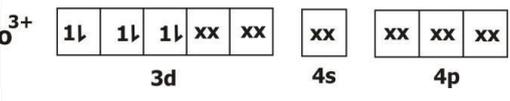
To indicate number of ligands prefix di, tri, tetra, penta, hexa, hepta etc are used. If ligands itself involve such prefixes in its name then prefix bis, tris, tetrakis, and so on are used to indicate number of ligands.

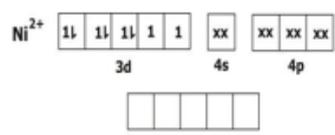
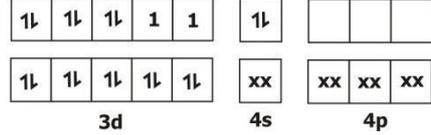
While writing name of central metal atom: -

(i) If coordination sphere is cation name of metal atoms written as such: Fe – Iron, Au – Gold, Cu – Copper, Cr – Chromium, Ag – Silver.

(ii) If, coordination sphere is anion suffix 'ate' is used to write name of central metal atom. Such as: Fe – Ferrate, Hg – Mercurate, Cu – Cuperate, Ag – Argentate, Au – Aurate, Pd – Peladate, Cr - Chromate

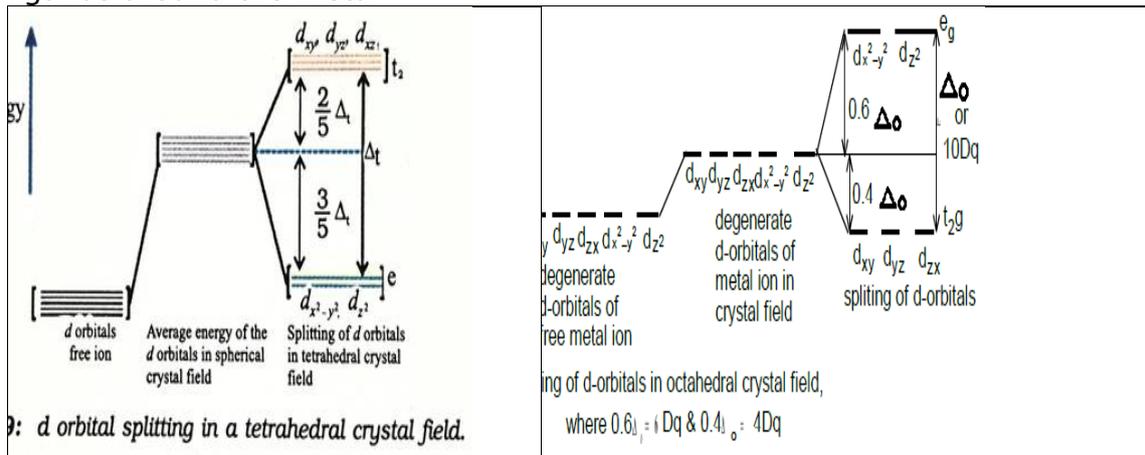
After writing name of central metal atom its oxidation number is indicated in perantheses'()'.

Valance bond theory of coordination compound	
Write electronic configuration of metal atom/ion	
Observation	Prediction
C.N. of metal	If 4 --- dsp^2/sp^3 hybridization If 6--- d^2sp^3/sp^3d^2 hybridization
Inner d- orbital is /are vacant	dsp^2 ----C.N.=4 d^2sp^3--- C.N=6
Inner- d orbital is/are not vacant but can be vacated by pairing of electrons	C.N=4 dsp^2 -ligand is CN^{-1} or CO (Strong ligand) sp^3 - weak ligand C.N=6 d^2sp^3 -ligand is CN^{-1} or CO (Strong ligand) sp^3d^2 weak ligand
Inner d- orbitals are not vacant and can't be vacated by pairing of e-	C.N=4 sp^3 -weak ligand (SFL / WFL) C.N=6 sp^3d^2 - weak ligand (SFL /WFL)
dsp^2 -hybridization sp^3 -hybridization d^2sp^3/sp^3d^2 -hybridization	Sq. planar Tetrahedral Octahedral
Presence of unpaired e- Unpaired electron absent Magnetic moment	paramagnetic Diamagnetic $\mu_{spin\ only} = \sqrt{n(n+2)}$
<p>[Co(H₂O)₆]³⁺</p>  <p>$3d$ $4s$ $4p$</p> <p>Sp^3d^2 hybridization Paramagnetic in nature Outer sphere complex Octahedral complex spin complex</p> <p>[Ni Cl₄]²⁻</p>	<p>[Co(NH₃)₆]³⁺</p>  <p>$3d$ $4s$ $4p$</p> <p>d^2sp^3 hybridization Inner sphere complex Diamagnetic in nature Low spin complex Octahedral complex</p> <p>[Ni(CO)₄]</p>

Ni^{2+}  $3d$ $4s$ $4p$ Sp^3 hybridization Paramagnetic in nature Tetrahedral complex	 $3d$ $4s$ $4p$ Sp^3 hybridization Low spin Diamagnetic in nature Tetrahedral complex
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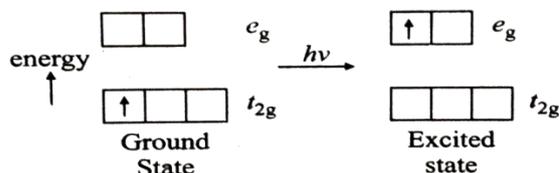
CRYSTAL FIELD theory of coordination compound

The d- orbitals of metal split into two sets of orbitals due to electronic interaction between ligands and metal depending upon the crystal field produced by the ligands around the metal.



COLOUR OF THE COMPLEXES

The d-d transition of electrons in visible region causes colouration in the complexes.



Application of coordination compound

a) Biological System:

- Chlorophyll – complex of Mg
- Hemoglobin – complex of Fe
- Vitamin B-12 – complex of Co

B) Metallurgy:

- Extraction of Au, Ag, by cyanide
- Refining of Ni by Mond's process
- Refining of Zr by Van Arkel process.

C) Quantitative Analysis:

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

d) Black & White Photography:

In black and white photography the film is fixed by washing with hypo solution which dissolves the undecomposed AgBr

- As medicines:** Cisplatin -Cancer Treatment EDTA [Used to remove heavy metal poison]

2-Marks Questions

Q1. $[\text{NiCl}_4]^{2-}$ is paramagnetic while $[\text{Ni}(\text{CO})_4]$ is diamagnetic though both are tetrahedral. Why?

Ans. In $[\text{Ni}(\text{CO})_4]$, Ni is in zero oxidation state whereas in $[\text{NiCl}_4]^{2-}$ it is in +2 oxidation state. In the presence of strong ligand, CO, the unpaired d-electrons of Ni pair up but Cl^- being weak ligand is unable to pair up the unpaired electrons.

Q2. A solution of $[\text{Ni}(\text{H}_2\text{O})_6]^{3+}$ is green but a solution of $[\text{Ni}(\text{CN})_4]^{2-}$ is colourless. Explain.

Ans. H_2O being a weak ligand is unable to pair the unpaired electrons in Ni^{2+} . So d-d transition is possible in the complex $[\text{Ni}(\text{H}_2\text{O})_6]^{3+}$. Hence it is coloured. But CN^- being a strong ligand paired the unpaired electrons in Ni^{2+} . So d-d transition is not possible in the complex $[\text{Ni}(\text{CN})_4]^{2-}$. Hence it is colourless.

Q3. When a co-ordination compound $\text{CoCl}_3 \cdot 4\text{NH}_3$ is mixed with AgNO_3 , 1 mole of AgCl is precipitated per mole of the compound. Write

a) structural formula of the complex. b) IUPAC name of the complex.

Ans. (a) $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ (b) Tetraamminedichloridocobalt(III) chloride.

Q4. For the complex $[\text{Fe}(\text{CN})_6]^{4-}$, write the hybridization, magnetic character and spin type of the complex.

Ans. Hybridization: d^2sp^3 , magnetic character: Diamagnetic, spin: Low spin complex

Q5. Distinguish between Double salt and Coordination compound.

Double Salt	Coordination Compound
1. They completely dissociate into simple ions when dissolved in water.	1. They do not dissociate into simple ions when dissolved in water
2. They give the tests for the constituent ions.	2. They does not give tests for the constituent ions.
3. Ex. $\text{FeSO}_4 \cdot (\text{NH}_4)_2 \text{SO}_4 \cdot 6\text{H}_2\text{O}$ (Mohr's salt)	3. Ex. $\text{K}_4[\text{Fe}(\text{CN})_6]$

Q6. Explain Homoleptic and Heteroleptic complexes with example.

Ans. The complex in which metal atom is bound to only one type of ligand is called homoleptic complex. Ex. $[\text{Ni}(\text{CO})_4]$

The complex in which metal atom is bound to more than one type of ligand is called heteroleptic complex.

Ex. $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$

Q7. The hexaaquamanganese(II) ion contains five unpaired electrons while the hexacyanomanganes(II) ion contain one unpaired electron. Explain

Ans: In hexaaquamanganese(II) ion the ligand H_2O is a weak field ligand and so can not cause pairing of electrons in 3d orbital while in hexacyanomanganes(II) ion the ligand CN^- is a strong field ligand so it causes the pairing of electron in the 3d orbital

Q8 The Spin magnetic moment of $[\text{MnBr}_4]^{2-}$ is 5.9 BM .Predict the geometry of the complex ion?

Ans: Since coordination number of Mn^{2+} ion is 4 it will either sp^3 with tetrahedral shape or dsp^2 with square planar shape but it is tetrahedral as d orbital will occupy by the presence of 5 unpaired electrons.

Q 9. What do you meant by chelate ligands & ambidentate ligands ?

Ans: When di or polydentate ligands uses its two or more donor atoms to bind a single metal ion is called chelate ligand. eg ethylene diamine.

Ambidentate ligands: ligands which can ligate through two different donor sites. eg NO

3-MARKS-QUESTIONS

Q1. Write IUPAC names of the following coordination compounds:

a) $[\text{Fe}(\text{CN})_6]^{4-}$ b) $\text{K}_2 [\text{PdCl}_4]$ c) $[\text{Co}(\text{NH}_3)_4\text{Cl}(\text{NO}_2)]\text{Cl}$

Ans. a) Hexacyanoferrate(II) ion b) Potassium tetrachloridopalladate(II)
c) Tetraamminechloridonitro-N-cobalt(III) chloride

Q2. Write the formulas for the following co-ordination compounds:

- a) Tetraammineaquachloridocobalt(III) chloride
- b) Potassium tetrahydrozincate(II)
- c) Potassium trioxalatoaluminate(III)

Ans. a) $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]\text{Cl}_2$ b) $\text{K}_2 [\text{Zn}(\text{OH})_4]$ c) $\text{K}_3 [\text{Al}(\text{C}_2\text{O}_4)_3]$

Q3. Write IUPAC names of the following coordination compounds:

a) $[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{NO}_2)]$ b) $\text{K}_3 [\text{Cr}(\text{C}_2\text{O}_4)_3]$ c) $[\text{CoCl}_2(\text{en})_2]\text{Cl}$

- a) Diamminechloridonitrito-N-Platinum(II)
- a) Potassium trioxalatochromate(III)
- b) Dichloridobis(ethane-1,2-diammine)cobalt(III) chloride

Q4. Write the name, structure and the magnetic behavior of the following complex: $[\text{Ni}(\text{CO})_4]$

Ans. Tetracarbonylnickel(0), tetrahedral, diamagnetic

Q5. Write the name, structure and the magnetic behavior of the following complex: $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$

Ans. Tetraamminedichloridocobalt(III) chloride, octahedral, diamagnetic

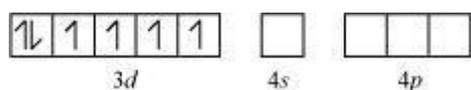
5 _MARKS QUESTIONS :

Q1. Discuss the nature of bonding in the following coordination entities on the basis of valence bond theory: (i) $[\text{Fe}(\text{CN})_6]^{4-}$ (ii) $[\text{FeF}_6]^{3-}$ (iii) $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$ (iv) $[\text{CoF}_6]^{3-}$

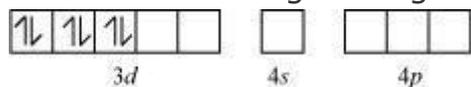
(i) $[\text{Fe}(\text{CN})_6]^{4-}$

In the above coordination complex, iron exists in the +II oxidation state. Fe^{2+} :
Electronic configuration is $3d^6$

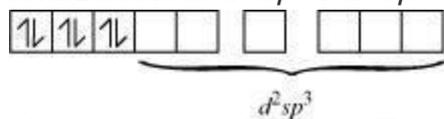
Orbitals of Fe^{2+} ion:



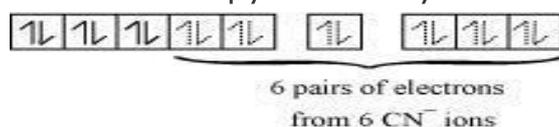
As CN^- is a strong field ligand, it causes the pairing of the unpaired 3d electrons.



Since there are six ligands around the central metal ion, the most feasible hybridization is d^2sp^3 . d^2sp^3 hybridized orbitals of Fe^{2+} are:



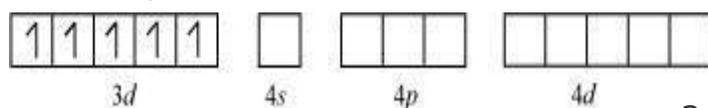
6 electron pairs from CN^- ions occupy the six hybrid d^2sp^3 orbitals. Then,



hence, the geometry of the complex is octahedral and the complex is diamagnetic (as there are no unpaired electrons).

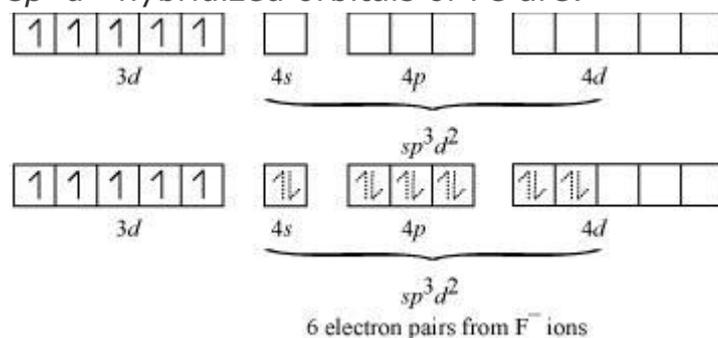
(ii) $[\text{FeF}_6]^{3-}$

In this complex, the oxidation state of Fe is +3. Orbitals of Fe^{+3} ion:



There are 6 F^- ions. Thus, it will undergo d^2sp^3 or sp^3d^2 hybridization. As F^- is a weak field ligand, it does not cause the pairing of the electrons in the 3d orbital. Hence, the most feasible hybridization is sp^3d^2 .

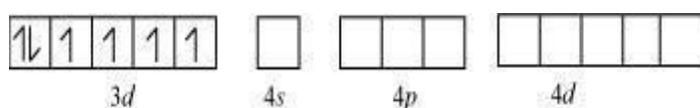
sp^3d^2 hybridized orbitals of Fe are:



Hence, the geometry of the complex is found to be octahedral.

(iii) $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$

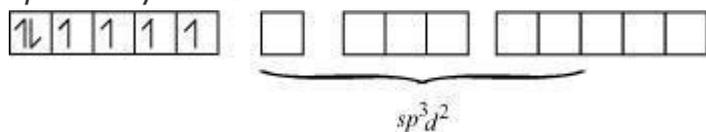
Cobalt exists in the +3 oxidation state in the given complex. Orbitals of Co^{3+} ion:



Oxalate is a weak field ligand. Therefore, it cannot cause the pairing of the 3d orbital electrons. As there are 6 ligands, hybridization has to be either sp^3d^2 or

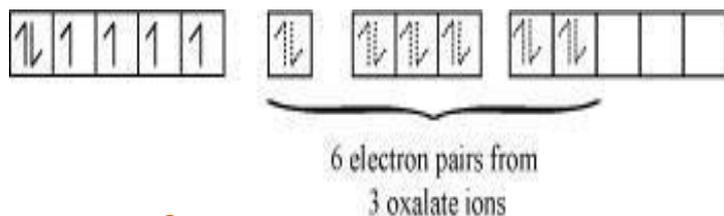
d^2sp^3 hybridization.

sp^3d^2 hybridization of Co^{3+} :



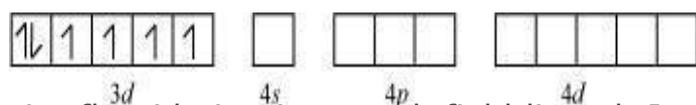
The 6 electron pairs from the 3 oxalate ions (oxalate anion is a bidentate ligand) occupy these sp^3d^2 orbitals.

Hence, the geometry of the complex is found to be octahedral.



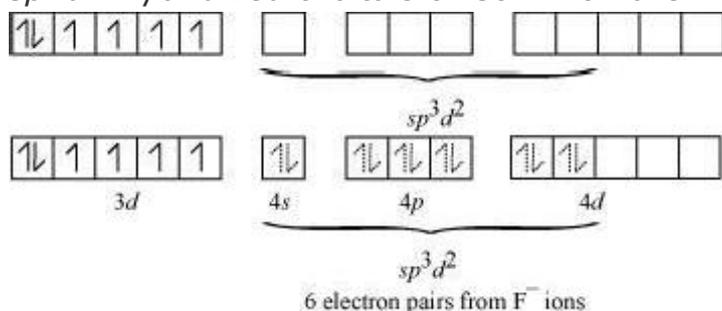
(iv) $[CoF_6]^{3-}$

Cobalt exists in the +3 oxidation state. Orbitals of Co^{3+} ion:



Again, fluoride ion is a weak field ligand. It cannot cause the pairing of the $3d$ electrons. As a result, the Co^{3+} ion will undergo sp^3d^2 hybridization.

sp^3d^2 hybridized orbitals of Co^{3+} ion are:



Hence, the geometry of the complex is octahedral and paramagnetic.

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 ion which are ionisable 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 B₁₂ is complex of cobalt. Hemoglobin, oxygen carrier is complex of Fe²⁺ and chlorophyll essential for photosynthesis is complex of Mg²⁺.

(a) What is the oxidation state and coordination number of Ni in [Ni(CO)₄]?

Ans. Zero and four

(b) One mole of CrCl₃. 6H₂O reacts with excess of AgNO₃ to yield 2 mole of AgCl. Write formula of complex. Write IUPAC name also.

Ans. [Cr(H₂O)₅Cl]Cl₂.H₂O, Penta aqua chloride chromium (III) chloride

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

Ans. EDTA⁴⁻ (ethylene diamine tetra acetate)

(d) What is hybridization of [CoF₆]³⁻? [Co = 27].

Give its shape and magnetic properties.

Ans. sp³d², octahedral, paramagnetic. It is outer orbital complex.

(e) Out [Fe(CO)₅], [Fe(C₂O₄)₃]³⁻, [Fe(H₂O)₆]³⁺, [Fe(CN)₆]³⁻ which is most stable

Ans. [Fe(CO)₅] is most stable because CO is strongest ligand.

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

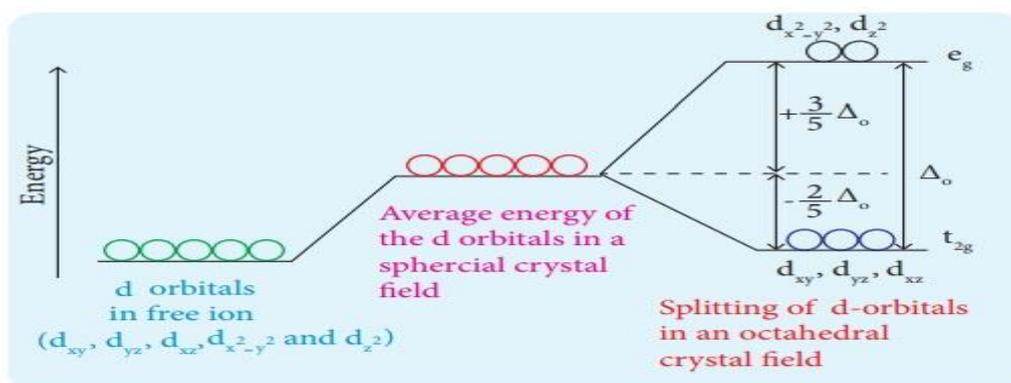


Figure: 5.10 - Crystal field splitting in octahedral field

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 Δ_0

(b) Why dx^2-y^2 , dz^2 have higher energy than dxy , dyz , dzx orbitals in octahedral crystal field?

Ans: The orbitals dx^2y^2 , dz^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 dxy , dyz , dzx lying in between the axis away from the approach of ligand.

(c) What is relationship between (CFSE) Δ_0 and strength of ligand?

Ans. Greater the (CFSE) Δ_0 , more will be strength of ligand.

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

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

OR

(d) What is spectrochemical series?

Ans. The series in which ligands are arranged in increasing order of magnitude of crystal field splitting energy (Δ_0) is called spectrochemical series.

3. Read the passage given below and answer the following questions:

Werner, a Swiss chemist in 1892 prepared and characterised a large number of coordination compounds and studied their physical and chemical behaviour. He proposed that, in coordination compounds, metals possess two types of valencies, viz. primary; valencies, which are normally ionisable and secondary valencies which are non-ionisable. In a series of compounds of cobalt (III) chloride with ammonia, it was found that some of the chloride ions could be precipitated as AgCl on adding excess of AgNO₃ solution in cold, but some remained in solution. The number of ions furnished by a complex in a solution can be determined by precipitation reactions. The measurement of molar conductance of solutions of coordination compounds helps to estimate the number of ions furnished by the compound in solution.

(i) Why the complex $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$ does not give precipitate with silver nitrate solution

Ans. The given complex is non-ionisable.

(ii) The complex $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ will give precipitate corresponding to how many mol of AgCl with AgNO₃ solution.

Ans. It ionises as $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+ + \text{Cl}^-$, so it will give ppt. of 1 mol of AgCl..

(iii) **What is the secondary valency in** $[\text{CrCl}_2(\text{CH}_2\text{O})_4]\text{Cl} \cdot 2\text{H}_2\text{O}$.

Ans. 6

(iv) $\text{CoCl}_3 \cdot 3\text{NH}_3$ is not conducting while $\text{CoCl}_3 \cdot 5\text{NH}_3$ is conducting. Why?

Ans.: The complex of $\text{CoCl}_3 \cdot 3\text{NH}_3$ is $[\text{CoCl}_3(\text{3NH}_3)_3]$ while that of $\text{CoCl}_3 \cdot 5\text{NH}_3$ is $[\text{CoCl}_3(\text{3NH}_3)_5]\text{Cl}_2$.

4. Read the passage given below and answer the following questions:

For understanding the structure and bonding in transition metal complexes, the magnetic properties are very helpful. Low spin complexes are generally diamagnetic because of pairing of electrons, whereas high spin complexes are usually paramagnetic because of presence of unpaired electrons. Larger the number of unpaired electrons, stronger will be the paramagnetism. However

magnetic behaviour of a complex can be confirmed from magnetic moment measurement.

Magnetic moment $\mu = n(n+2) \dots \dots \dots \sqrt{B.M.}$ $\mu = n(n+2) B.M.$ where n = number of unpaired electrons. Greater the number of unpaired electrons, more will be the magnetic moment.

(i) Both $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ have same magnetic moment. Why?

Ans.: Number of unpaired electrons in Cr^{2+} and Fe^{2+} are same.

(ii) $[\text{Fe}(\text{H}_2\text{O})_6]\text{SO}_4$ is paramagnetic. Why?

Ans. The Fe in $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]\text{SO}_4$ has three unpaired electrons.

(iii): $[\text{Co}(\text{en})_3]^{3+}$ is diamagnetic. '

Ans. It is an inner orbital complex. (en is a strong field ligand, therefore, pairing of electrons will take place.

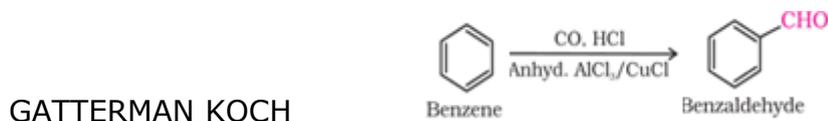
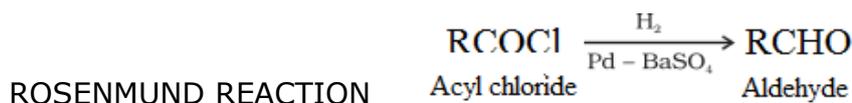
(iv) $[\text{Ni}(\text{CN})_4]^{2-}$ is diamagnetic complex.

Reason: It involves sp^2 hybridisation and there is no unpaired electron.

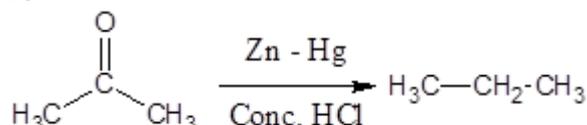


ALDEHYDES KETONES AND CARBOXYLIC ACIDS

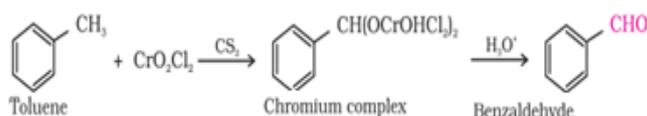
NAMED REACTION



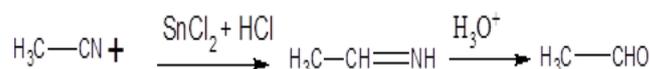
CLEMMENSON'S REACTION



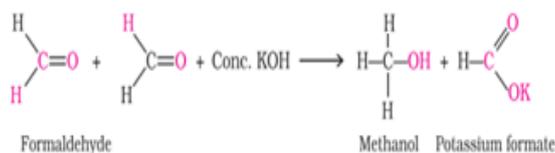
ETARD REACTION



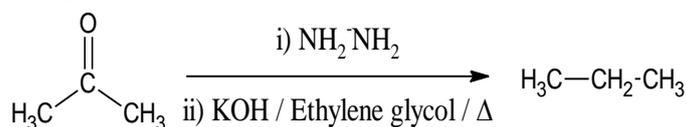
STEPHAN'S REACTION



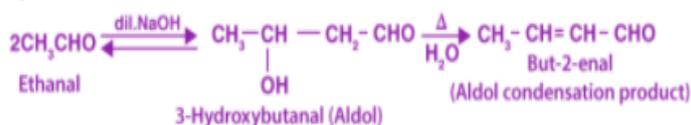
CANNIZZARO REACTION



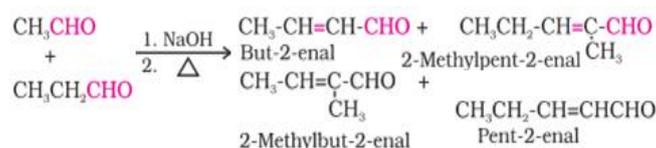
WOLF KISHNER REACTION



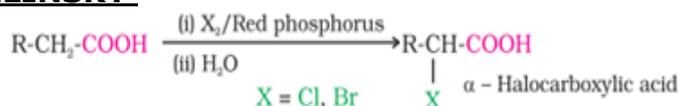
ALDOL CONDENSATION'



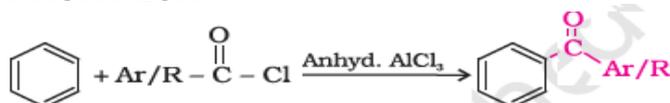
CROSS ALDOL



HELL VOLHARD ZELINSKY



FRIEDAL AND CRAFT ACYATION



DISTINGUISH BY SINGLE CHEMICAL TEST

Examples	Reagents	Test performed by
(i) Propanal and Propanone (ii) Acetophenone and Benzophenone (iii) Phenol and Benzoic acid (iv) Benzoic acid and Ethyl benzoate (v) Pentan-2-one and Pentan-3-one (vi) Benzaldehyde and Acetophenone (vii) Ethanal and Propanal (viii) Benzoic acid and Ethyl benzoate	(i) Tollens reagents (ii) Iodoform test (iii) FeCl ₃ Test (iv) NaHCO ₃ Test (v) Iodoform test (vi) Iodoform test (vii) Iodoform test (viii) NaHCO ₃ test	(i) Propanal (ii) Acetophenone (iii) Phenol (iv) Benzoic acid (v) Pentan-2-one (vi) Acetophenone (vii) Ethanal (viii) Benzoic acid

Important Reasoning Question

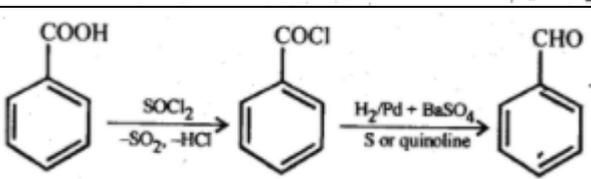
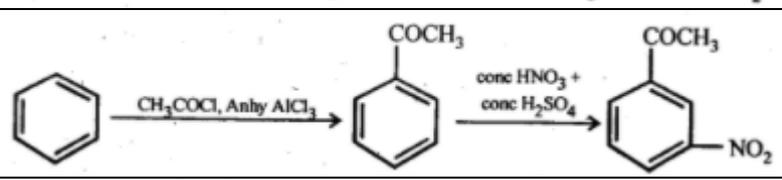
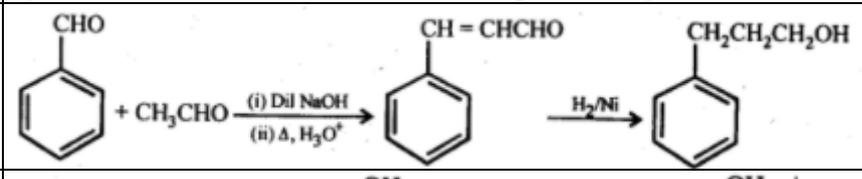
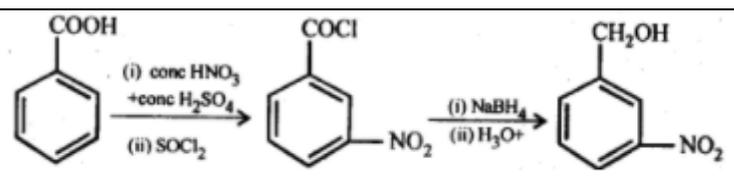
Question	Answer
Cyclohexanone forms cyanohydrin in good yield but 2,2,6-trimethylcyclohexanone does not.	Due to steric hinderance and decrease in the electrophilicity of Carbonyl carbon by +I alkyl group
There are two -NH ₂ groups in semicarbazide. However, only one is involved in the formation of semicarbazones.	Due to resonance Lone pair of -NH ₂ group decrease the electrophilicity of carbonyl carbon.
During the preparation of esters from a carboxylic acid and an alcohol in presence of an acid catalyst, the water or the ester should be removed as soon as it is formed.	due to reversible reaction
Carboxylic acids are stronger acids than phenols.	than Phenoxide ion due to Carboxylate ion is more stable dispersion of -ve Charge on higher electronegative element
Aromatic carboxylic acids do not undergo Friedel - Crafts reaction	COOH group is m- directing-
Ethanal is more reactive towards nucleophilic addition reactions than propanone.	Due greater +I effect and steric hinderance in propanone
Ethanoic acid is a stronger acid than ethanol.	carboxylate ion are more stable than alkoxide ion
Monochloroethanoic acid has a higher pK _a value than dichloroethanoic acid	Due to greater -I effect of two Cl atom in dichloroethanoic acid than Monochloroacetic acid
The aldehydes & ketones undergo a no. of addition reactions	Due to polarity of carbonyl group Carbon become more electrophilic
Ethanoic acid is weaker acid than benzoic acid	due to -I effect of Sp ² hybridized carbon atom of phenyl group
Although phenoxide ion has more number of resonating structures than carboxylate ion, carboxylic acid is a stronger acid than phenol. Why?	Carboxylate ion is more stable than Phenoxide ion due to delocalisation of -ve Charge on higher electronegative - element

CONVERSIONS (SINGLE STEP)

Question	REAGENTS
(i) Hexan-1-ol to hexanal	(i) C ₅ H ₅ NH + CrO ₃ Cl-(PCC)
(ii) Cyclohexanol to cyclohexanone	(ii) Anhydrous CrO ₃
(iii) <i>p</i> -Fluorotoluene to <i>p</i> -fluorobenzaldehyde	(iii) CrO ₃ in presence of acetic anhydride/1. CrO ₂ Cl ₂ 2. HOH
(iv) Ethanenitrile to ethanal	(iv) (Diisobutyl) aluminium hydride (DIBAL-H)
(v) Allyl alcohol to propenal	(v) PCC
(vi) But-2-ene to ethanal	

(vii) Butan-1-ol to butanoic acid (viii) Cyclohexene to hexane-1,6-dioic acid (ix) Butanal to butanoic acid.	(vi) O ₃ /H ₂ O-Zn dust (vii) CrO ₃ - H ₂ SO ₄ (viii) KMnO ₄ - H ₂ SO ₄ (ix) Tollens reagents
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CONVERSIONS

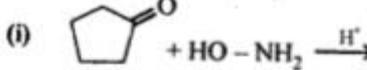
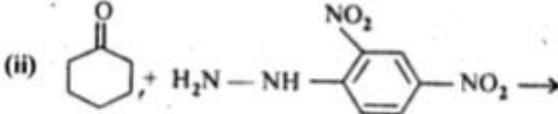
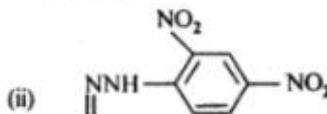
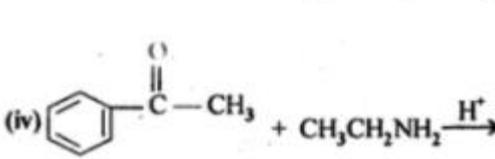
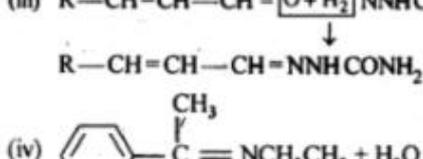
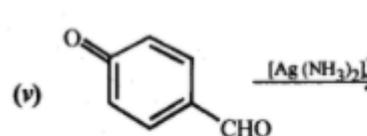
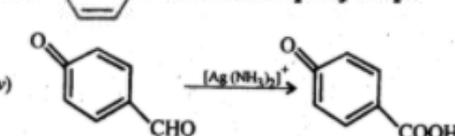
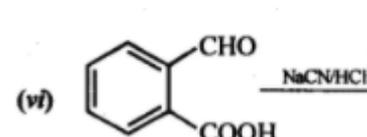
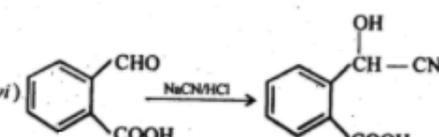
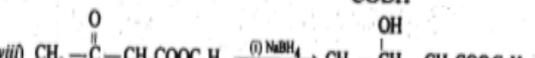
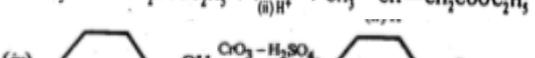
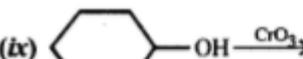
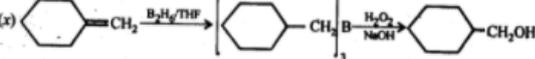
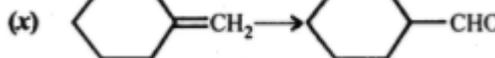
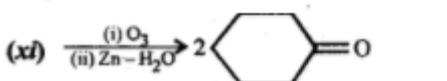
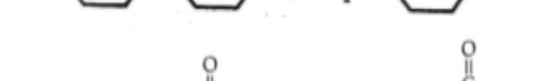
(i) Propanone to Propene	$\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3 \xrightarrow{\text{NaBH}_4} \text{CH}_3-\overset{\text{OH}}{\text{CH}}-\text{CH}_3 \xrightarrow[\text{-H}_2\text{O}]{\text{Conc. H}_2\text{SO}_4, 433-443\text{K}} \text{CH}_3-\text{CH}=\text{CH}_2$
(ii) Benzoic acid to Benzaldehyde	
(iii) Ethanol to 3-Hydroxybutanal	$\text{CH}_3\text{CH}_2\text{OH} \xrightarrow{\text{Cu}/573\text{K}} \text{CH}_3\text{CHO} \xrightarrow{\text{Dil NaOH}} \text{CH}_3-\overset{\text{OH}}{\text{CH}}-\text{CH}_2\text{CHO}$
(iv) Benzene to m-Nitroacetophenone	
(v) Benzaldehyde to Benzophenone	$\text{C}_6\text{H}_5\text{CHO} \xrightarrow[\text{(ii) CaCO}_3]{\text{(i) K}_2\text{C}_2\text{O}_7/\text{H}_2\text{SO}_4} (\text{C}_6\text{H}_5\text{COO})_2\text{Ca} \xrightarrow[\text{-CaCO}_3]{\text{Dry Distillation}} (\text{C}_6\text{H}_5)_2\text{CO}$
(vi) Bromobenzene to 1-Phenylethanol	$\text{C}_6\text{H}_5\text{Br} \xrightarrow{\text{Mg/dry ether}} \text{C}_6\text{H}_5\text{MgBr} \xrightarrow[\text{(ii) H}_3\text{O}^+]{\text{(i) CH}_3\text{CHO}} \text{C}_6\text{H}_5-\overset{\text{OH}}{\text{CH}}-\text{CH}_3$
(vii) Benzaldehyde to 3-Phenylpropan-1-ol	
(viii) Benzaldehyde to α-Hydroxy phenylacetic acid	$\text{C}_6\text{H}_5\text{CHO} \xrightarrow[\text{pH, 9-10}]{\text{HCN}} \text{C}_6\text{H}_5-\overset{\text{OH}}{\text{CH}}-\text{CN} \xrightarrow{\text{H}^+/\text{H}_2\text{O}} \text{C}_6\text{H}_5-\overset{\text{OH}}{\text{CH}}-\text{COOH}$
(ix) Benzoic acid to m-nitrobenzyl alcohol	

Arrangement order(Decreasing/Increasing)

In order of-	Questions	Answers
(i) In increasing order of boiling points:	CH ₃ CH ₂ CH ₂ CHO, CH ₃ CH ₂ CH ₂ CH ₂ OH, H ₅ C ₂ -O-C ₂ H ₅ , CH ₃ CH ₂ CH ₂ CH ₃	CH ₃ CH ₂ CH ₂ CH ₃ , H ₅ C ₂ -O-C ₂ H ₅ , CH ₃ CH ₂ CH ₂ CHO, CH ₃ CH ₂ C H ₂ CH ₂ OH
(ii) decreasing order reactivity towards HCN	Acetaldehyde, Acetone, Di- <i>tert</i> -butyl ketone, Methyl <i>tert</i> -butyl ketone	Acetaldehyde, Acetone, Di- <i>tert</i> -butyl ketone, Methyl <i>tert</i> -butyl ketone
(iii) In increasing order of acid strength	CH ₃ CH ₂ CH(Br)COOH, CH ₃ CH(Br)CH ₂ COOH, (CH ₃) ₂ CHCOOH, CH ₃ CH ₂ CH ₂ COOH	(CH ₃) ₂ CHCOOH, CH ₃ CH ₂ CH ₂ COOH,

(iv) In increasing order of acid strength	Benzoic acid, 4-Nitrobenzoic acid, 3,4 Dinitro benzoic acid, 4-Methoxybenzoic acid	CH ₃ CH(Br)CH ₂ COOH, CH ₃ CH ₂ CH(Br)COOH
(v) increasing order of their reactivity in nucleophilic addition reactions	Ethanal, Propanal, Propanone, Butanone.	4-Methoxybenzoic acid, Benzoic acid, 4-Nitrobenzoic acid, 3,4-Dinitrobenzoic acid,
(vi) increasing order of reactivity in nucleophilic addition reactions	Benzaldehyde, <i>p</i> -Tolualdehyde, <i>p</i> -Nitrobenzaldehyde, Acetophenone.	Butanone, Propanone, Propanal, Ethanal
(vii) increasing order of their boiling points.	CH ₃ CHO, CH ₃ CH ₂ OH, CH ₃ OCH ₃ , CH ₃ CH ₂ CH ₃	Acetophenone, <i>p</i> -Tolualdehyde, Benzaldehyde, <i>p</i> -Nitrobenzaldehyde. CH ₃ CH ₂ CH ₃ < CH ₃ OCH ₃ < CH ₃ CHO < CH ₃ CH ₂ OH

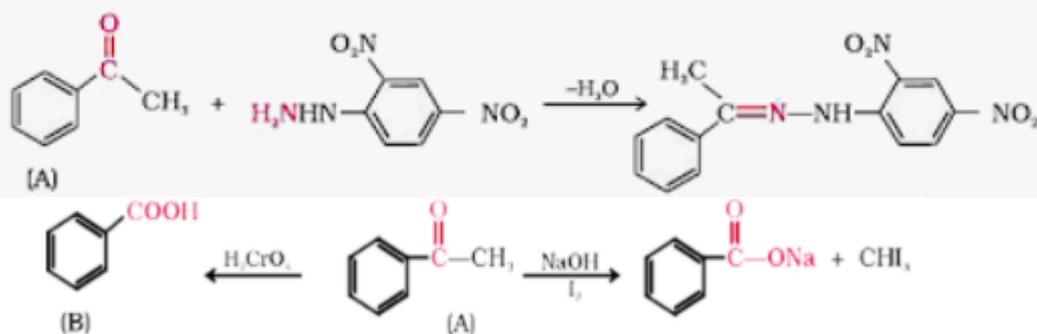
Predict the products of the following reactions:

Questions	Answers
(i) 	(i) 
(ii) 	(ii) 
(iii) $R-CH=CH-CHO + NH_2-C(=O)-NH-NH_2 \xrightarrow{H^+}$	(iii) $R-CH=CH-CH=O + H_2 \rightarrow R-CH=CH-CH=NNHCONH_2 + H_2O$
(iv) 	(iv) 
(v) 	(v) 
(vi) 	(vi) 
(vii) $C_6H_5CHO + CH_3CH_2CHO \xrightarrow{dil NaOH}$	(vii) 
(viii) $CH_3COCH_2COOC_2H_5 \xrightarrow{(i) NaBH_4, (ii) H^+}$	(viii) 
(ix) 	(ix) 
(x) 	(x) 
(xi) 	(xi) 
(xii) 	(xii) 

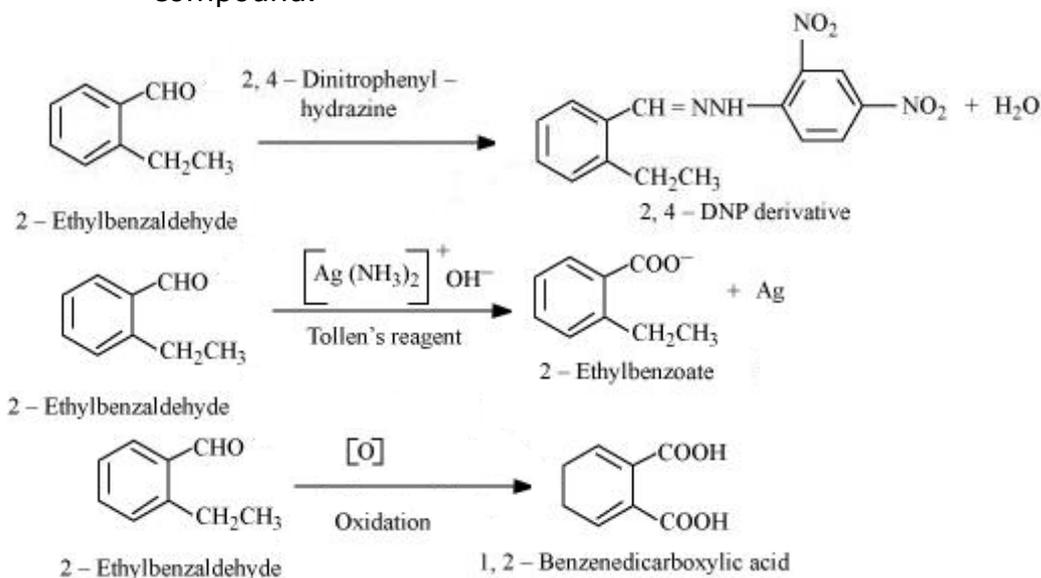
WORD PROBLEM

- (i) An organic compound (A) with molecular formula C_8H_8O forms an orange-red precipitate with 2,4-DNP reagent and gives yellow precipitate on heating with iodine in the presence of sodium hydroxide. It neither reduces Tollens' or Fehlings' reagent, nor does it decolourise bromine water or Baeyer's reagent. On drastic oxidation with chromic acid, it gives a carboxylic acid (B) having molecular formula $C_7H_6O_2$. Identify the compounds (A) and (B) and explain the reactions involved.

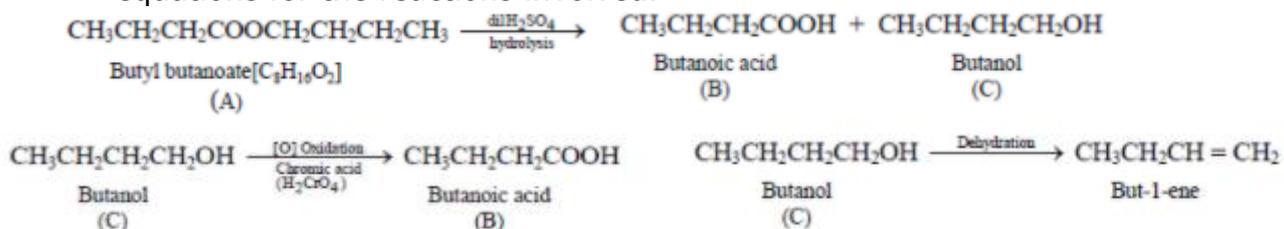
Answers :- (A) Acetophenone (B) Benzoic Acid



- (ii) An organic compound with the molecular formula $\text{C}_9\text{H}_{10}\text{O}$ forms 2,4-DNP derivative, reduces Tollen's reagent, and undergoes Cannizzaro reaction. On vigorous oxidation, it gives 1,2-benzenedicarboxylic acid. Identify the compound.



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

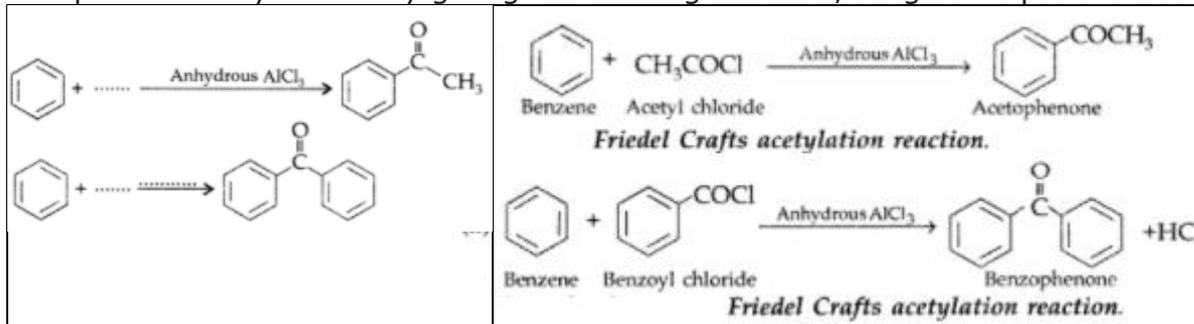


- (iv) An organic compound contains 69-77% carbon, 11-63 % hydrogen and rest oxygen. The molecular mass of the compound is 86. It does not reduce Tottens' reagent but forms an addition compound with sodium hydrogensulphite and give positive iodoform test. On vigorous oxidation, it gives ethanoic and propanoic acid. Write the possible structure of the compound.

$$\% \text{ of O}_2 = 100 - (\% \text{ of C} + \% \text{ of H}) = 100 - (69.77 + 11.63) = 100 - (81.40) = 19.6\%$$

Two Marks Questions

1. Complete each synthesis by giving the missing material, reagent or products :-



2. Give a chemical test to distinguish the following pairs:

(A) Phenol and benzoic acid (B) Benzaldehyde and acetophenone

Ans (A): Phenol gives the FeCl_3 test while benzoic acid does not.

Ans (B): Acetophenone gives iodoform test but benzaldehyde does not.

3. Account for the following:-

(A) Chloroacetic acid is a stronger acid than acetic acid

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

Ans (A): In $\text{Cl-CH}_2\text{COOH}$, the -I effect of Cl stabilizes the CH_2COO^- ion while in CH_3COOH the +I-effect of the methyl group destabilizes the CH_2COO^- ion so chloroacetic acid is a stronger acid than acetic acid.

Ans (B): In the resonating structures of carboxylic acids and carbonyls, the carbonyl carbon of a carboxylic acid is less electrophilic than that in carbonyls so carboxylic acids do not give reactions of the carbonyl group.

4. Arrange the following

(A): $\text{-C}_6\text{H}_5\text{COOH}$, FCH_2COOH , $\text{NO}_2\text{CH}_2\text{COOH}$ in the decreasing order of acidic character

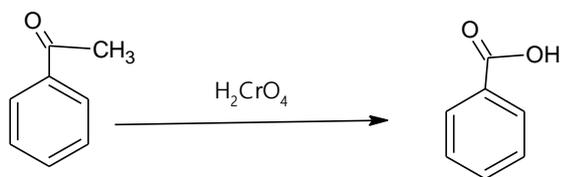
(B): Ethanal, Propanal, propanone and butanone in increasing order of nucleophilic addition reactions

Ans (A): $\text{NO}_2\text{CH}_2\text{COOH} > \text{FCH}_2\text{COOH} > \text{C}_6\text{H}_5\text{COOH}$

Ans (B): Butanone < propanone < Propanal < Ethanal

5. An organic compound A with molecular formula $\text{C}_8\text{H}_8\text{O}$ gives a positive DNP and iodoform test. It does not reduce Tollen's reagent and does not decolorise bromine water also. On oxidation with chromic acid it gives a carboxylic acid B with molecular formula $\text{C}_7\text{H}_6\text{O}_2$. Deduce the structures A and B.

Ans: Since A does not give Tollen's test but gives iodoform test and 2,4-DNP test so it should have CH_3 and CO group



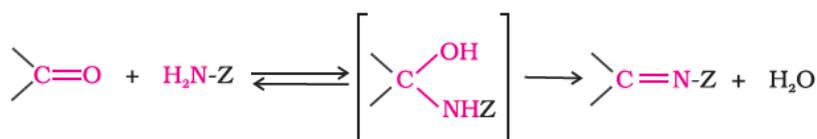
(A)

(B)

6. Explain nucleophilic addition reactions of aldehydes and ketones followed by elimination of a water molecule.

Addition of ammonia and its derivatives: Nucleophiles, such as ammonia and its derivatives H_2N-Z add to the carbonyl

Ans:- group of aldehydes and ketones. The reaction is reversible



and catalysed by acid. The equilibrium favours the product formation due to rapid dehydration of the intermediate to form $>C=N-Z$.

Z = Alkyl, aryl, OH, NH_2 , C_6H_5NH , $NHCONH_2$, etc.

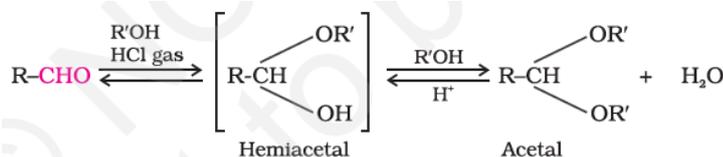
Three marks questions

1. Explain the following

(A) Formation of acetals

(B) Reactivity comparison of methanal and ethanal

(C) Effect of electron withdrawing group upon acidity of carboxylic acids



Ans:-

(B) The reactivity of carbonyl compounds is due to the polarity of carbonyl group, in ethanal methyl group decreases the polarity of carbonyl group by +I effect hence the reactivity of ethanal is less than that of methanal.

(C) The presence of EWG increases the stability of the carboxylate anion which is formed by donation of proton, hence the presence of EWG increases the strength of acid.

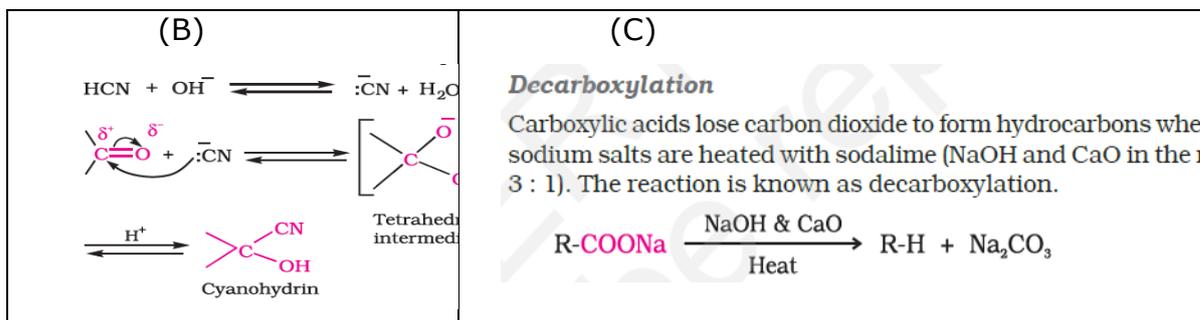
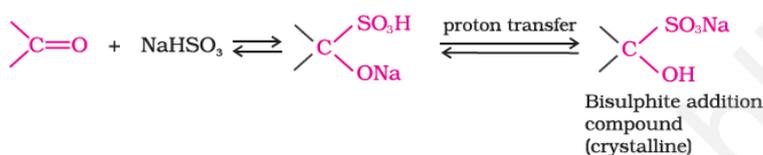
2. Explain the following

(A) Addition of $NaHSO_3$ to aldehydes and ketones.

(B) Addition of HCN to aldehydes and ketones.

(C) Decarboxylation of carboxylic acids.

Ans:-(A)



3. Explain the following:

(A) Formic acid is more acidic than acetic acid.

(B) Carboxylic acids are more acidic than phenols.

(C) Benzoic acid is more acidic than acetic acid.

Ans:-(A) In acetic acid +I effect of methyl group destabilises the carboxylate anion formed by donation of proton while in formic acid no any group is present which can destabilizes the carboxylate anion, hence formic acid is more strong than acetic acid.

(B) Carboxylate anion has two oxygen atoms in its resonating structures while in resonating structures of Phenol there is only one oxygen atom so negative charge in carboxylate anion is spread upon two O atoms so it is more stable than phenoxide anion in which the negative charge is situated upon only one O atom.

(C) In Benzoic acid the negative charge of carboxylate anion is in conjugation with benzene ring hence involved in resonance so carboxylate anion of benzoic acid is more stable than that of acetic acid, and +I effect of methyl group in acetic acid also makes it weaker acid.

FIVE MARKS QUESTION

How will you bring about the following conversions in not more than two steps?

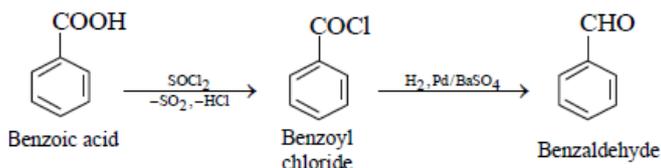
(i) Propanone to Propene	(ii) Benzoic acid to Benzaldehyde
(iii) Ethanol to 3-Hydroxybutanal	(iv) Benzene to <i>m</i> -Nitroacetophenone
(v) Benzaldehyde to Benzophenone	

I. Propanone to Propene:

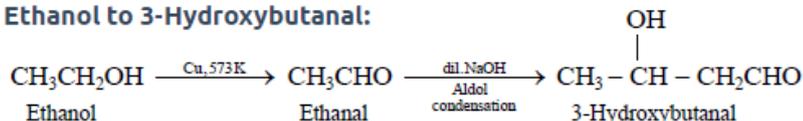
$$\text{CH}_3\text{COCH}_3 \xrightarrow[\text{reduction}]{\text{NaBH}_4, \text{CH}_3\text{OH}} \text{CH}_3 - \overset{\text{OH}}{\text{CH}} - \text{CH}_3 \xrightarrow[443\text{K}]{\text{Conc. H}_2\text{SO}_4} \text{CH}_3\text{CH} = \text{CH}_2$$

Propanone Propan-2-ol Propene

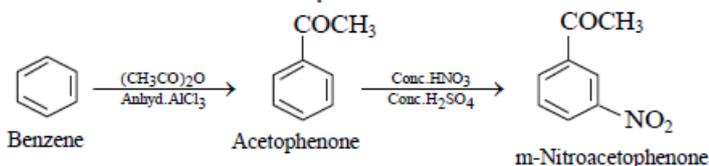
II. Benzoic acid to Benzaldehyde:



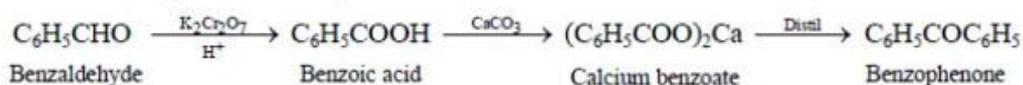
III. Ethanol to 3-Hydroxybutanal:



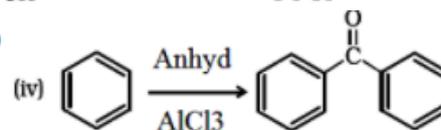
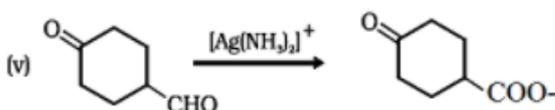
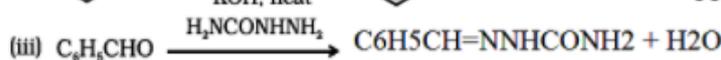
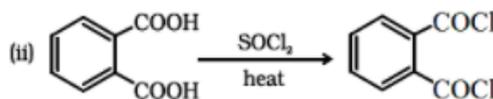
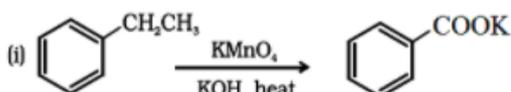
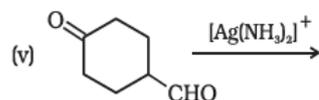
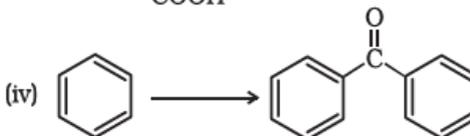
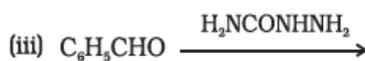
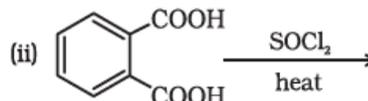
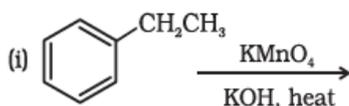
IV. Benzene to m-Nitroacetophenone:



V. Benzaldehyde to Benzophenone:

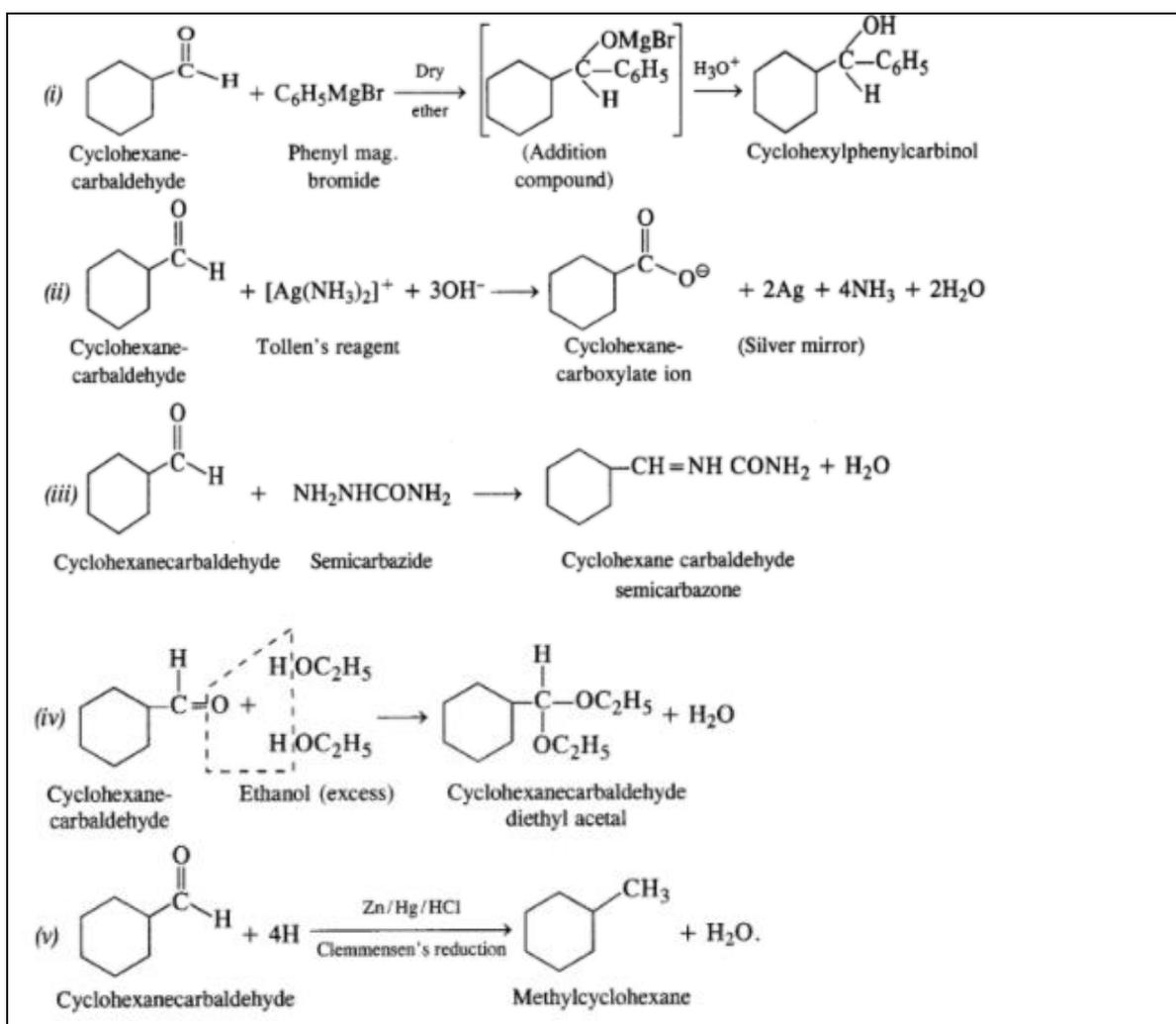


Complete each synthesis by giving missing starting material, reagent or products



Q3. Predict the product when cyclohexanecarbaldehyde reacts with following reagents :

- (i) $\text{C}_6\text{H}_5\text{MgBr}$ followed by H_3O^+ (ii) Tollen's reagent
 (iii) Semicarbazide in the weakly acidic medium
 (iv) Excess of ethanol in the presence of acid
 (v) Zinc amalgam and Cyclohexanecarbaldehyde Semicarbazide



ALDEHYDES , KETONES & CARBOXYLIC ACIDS

CASE BASED QUESTIONS

(a) The aldehydes and ketones undergo nucleophilic addition reactions. A nucleophile attacks the electrophilic carbon atom of the polar carbonyl group from a direction approximately perpendicular to the plane of sp² hybridised orbitals of carbonyl carbon. The hybridisation of carbon changes from sp² to sp³ in this process, and a tetrahedral alkoxide intermediate is produced. This intermediate captures a proton from the reaction medium to give the electrically neutral product. The net result is addition of Nu⁻ and H⁺ across the carbon oxygen double bond.

- Though carboxylic acid contains C=O group but it do not give nucleophilic addition reactions, why?
- How will you convert ethanal to lactic acid?
- Arrange the following compounds in their increasing order of reactivity towards nucleophilic addition reactions- C₆H₅CHO, HCHO, CH₃CHO, CH₃COCH₃
- Complete the following reactions-
 - CH₃CHO + C₂H₅OH \rightarrow
 - CH₃CHO + NaOH (Dil) \rightarrow

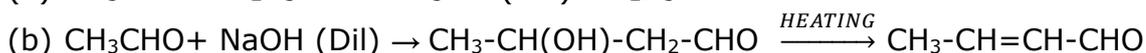
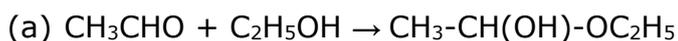
ANSWER-

1. Because electrophilicity on carbon atom of COOH group is not present due to resonance.



3. C₆H₅CHO < CH₃COCH₃ < CH₃CHO < HCHO

4.



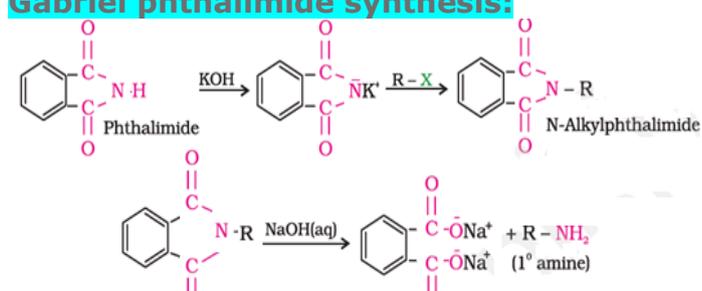
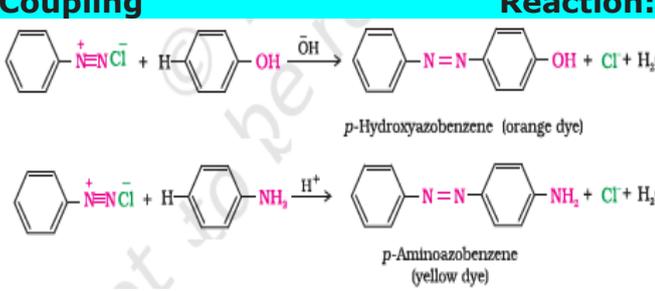
(b) Aliphatic carboxylic acids upto nine carbon atoms are colourless liquids at room temperature with unpleasant odours. The higher acids are wax like solids and are practically odourless due to their low volatility. Carboxylic acids are higher boiling liquids than aldehydes, ketones and even alcohols of comparable molecular masses. Carboxylic acids are weaker than mineral acids, but they are stronger acids than alcohols and many simple phenols (pKa is ~16 for ethanol and 10 for phenol). In fact, carboxylic acids are amongst the most acidic organic compounds you have studied so far.

- Ethanoic acid forms dimer in vapour state, justify.
- Why carboxylic acids have higher boiling points than that of aldehydes & ketones of comparable molecular masses, why?
- Though phenoxide ion has more number of resonating structures than carboxylate ion but phenol is weaker acid than carboxylic acids, why?
- Arrange the following compounds in their increasing order of pKa-
 - HCOOH , $\text{C}_6\text{H}_5\text{COOH}$, CH_3COOH
 - BrCH_2COOH , ClCH_2COOH , FCH_2COOH

ANSWER-

- Due to formation of intermolecular hydrogen bond.
- Due to formation of intermolecular hydrogen bond.
- In carboxylate ion charge separation is among same atoms i.e. oxygen atoms whereas in phenoxide ion it is among different atoms i.e. oxygen and carbon atoms hence carboxylate ion is more stable and carboxylic acids are stronger acids.
- $\text{C}_6\text{H}_5\text{COOH} > \text{CH}_3\text{COOH} > \text{HCOOH}$
 $\text{BrCH}_2\text{COOH} > \text{ClCH}_2\text{COOH} > \text{FCH}_2\text{COOH}$

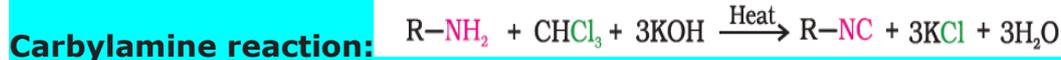
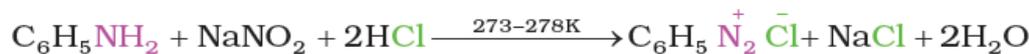
AMINES

<p>Hoffmann Ammonolysis reaction:</p> $\text{RNH}_2 \xrightarrow{\text{RX}} \text{R}_2\text{NH} \xrightarrow{\text{RX}} \text{R}_3\text{N} \xrightarrow{\text{RX}} \text{R}_4\text{N}^+\text{X}^-$ <p style="text-align: center;">(1°) (2°) (3°) Quaternary ammonium salt</p>	<p>Hoffmann bromamide degradation reaction</p> $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}_2 + \text{Br}_2 + 4\text{NaOH} \longrightarrow \text{R}-\text{NH}_2 + \text{Na}_2\text{CO}_3 + 2\text{NaBr} + 2\text{H}_2\text{O}$
<p>Gabriel phthalimide synthesis:</p>  <p>The diagram shows the Gabriel phthalimide synthesis. It starts with phthalimide (a benzene ring fused to a five-membered imide ring). Treatment with KOH yields potassium phthalimide. This intermediate then reacts with an alkyl halide (R-X) to form N-alkylphthalimide. Finally, treatment with aqueous NaOH (NaOH(aq)) results in the cleavage of the imide ring, yielding potassium phthalate (a benzene ring with two carboxylate groups, -COO⁻Na⁺) and a primary amine (R-NH₂).</p>	<p>Coupling Reaction:</p>  <p>The diagram illustrates two coupling reactions. In the first, benzene diazonium chloride (C₆H₅N₂⁺Cl⁻) reacts with p-hydroxyphenol (H-C₆H₄-OH) in the presence of hydroxide ions (OH⁻) to form p-hydroxyazobenzene (an orange dye) and chloride ions (Cl⁻) and water (H₂O). In the second reaction, benzene diazonium chloride reacts with p-aminophenylamine (H-C₆H₄-NH₂) in the presence of acid (H⁺) to form p-aminoazobenzene (a yellow dye) and chloride ions (Cl⁻) and water (H₂O).</p>

Sandmeyer reaction:	Gatterman reaction:
$\text{ArN}_2\text{X} \begin{cases} \xrightarrow{\text{Cu}_2\text{Cl}_2/\text{HCl}} \text{ArCl} + \text{N}_2 \\ \xrightarrow{\text{Cu}_2\text{Br}_2/\text{HBr}} \text{ArBr} + \text{N}_2 \\ \xrightarrow{\text{CuCN}/\text{KCN}} \text{ArCN} + \text{N}_2 \end{cases}$	$\text{ArN}_2\text{X} \begin{cases} \xrightarrow{\text{Cu}/\text{HCl}} \text{ArCl} + \text{N}_2 + \text{CuX} \\ \xrightarrow{\text{Cu}/\text{HBr}} \text{ArBr} + \text{N}_2 + \text{CuX} \end{cases}$

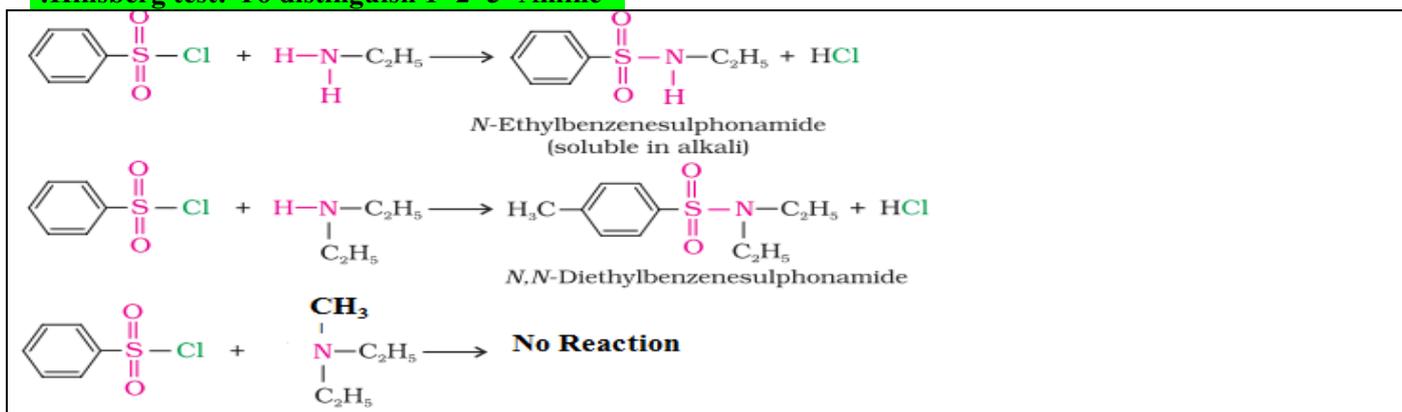
Diazotisation:

Prepared by M R Choudhary 8469113570



NAME REACTION

-Hinsberg test:-To distinguish 1^o 2^o 3^o Amine



DISTINGUISH BY SINGLE CHEMICAL TEST

Examples	Reagents	Test performed by
(i) Methylamine and dimethylamine	Carbyl amine test	Methylamine
(ii) Secondary and tertiary amines	Hinsberg reagent	Secondary amines
(iii) Ethylamine and aniline	Azo dye test	Aniline
(iv) Aniline and benzylamine	Azo dye test	Aniline
(v) Aniline and N-methylaniline.	Carbyl amine test	Aniline

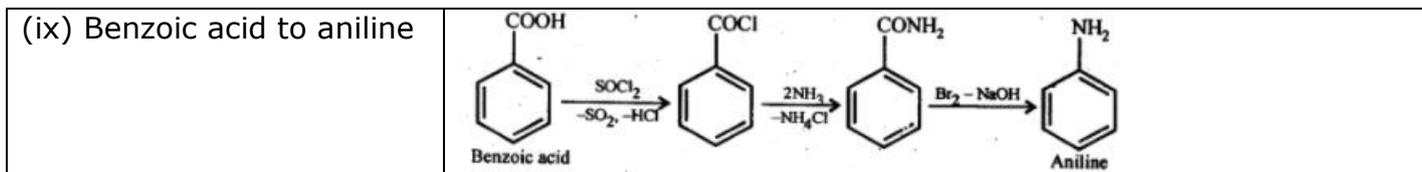
Important Reasoning Question

Question	Answer
Why pH of reaction should be carefully controlled while preparing ammonia derivatives of carbonyl compound?	amonia derivated get protenated in acidic medium so nucleophilic attack on CO group would not possible
pK _b of aniline is more than that of methylamine.	Due to delocalisation of lone pair of electron of N aton in aniline it is less basic and have higher value of PK _b
Ethylamine is soluble in water whereas aniline is not.	due to formation of H bonding by ethyl amine
Methylamine in water reacts with ferric chloride to precipitate hydrated ferric oxide.	$\text{RNH}_2 + \text{H}_2\text{O} \rightarrow \text{RNH}_3^+ + \text{OH}^-$ $-\text{FeCl}_3 + 3\text{OH}^- \rightarrow \text{Fe(OH)}_3 + 3\text{Cl}^-$
Although amino group is o- and p- directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of m-nitro aniline.	due to formaton of anilinium ion under stron acidic condition
Aniline does not undergo Friedel-Crafts reaction.	Due to formation of salt
Diazonium salts of aromatic amines are more stable than those of aliphatic amines.	Due to resonance

Gabriel phthalimide synthesis is preferred for synthesising primary amines.	due to only one replacable H in phthalamide
Why cannot aromatic primary amines be prepared by Gabriel phthalimide synthesis?	Aromatic 1° amines cannot be prepared by this method because aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide.
Why are amines less acidic than alcohols of comparable molecular masses?	Due to less electronegativity of N
Why do primary amines have higher boiling point than tertiary amines?	Due to Intermolecular H bonding
Why aliphatic amines stronger are bases than aromatic amines?	Due to delocalisation of lone pair of electron of N atom in aromatic amine

CONVERSIONS

Question	REAGENTS
(i) Benzene into aniline	<p>(i) <chem>c1ccccc1</chem> $\xrightarrow[333\text{ K}]{\text{Conc. HNO}_3, \text{Conc. H}_2\text{SO}_4}$ <chem>O=[N+]([O-])c1ccccc1</chem> $\xrightarrow[\text{(Reduction)}]{\text{Fe/HCl}}$ <chem>Nc1ccccc1</chem></p>
(ii) Benzene into N,N-dimethylaniline	<p>(ii) <chem>c1ccccc1</chem> $\xrightarrow[333\text{ K}]{\text{Conc. HNO}_3, \text{Conc. H}_2\text{SO}_4}$ <chem>O=[N+]([O-])c1ccccc1</chem> $\xrightarrow{\text{Reduction}}$ <chem>Nc1ccccc1</chem> $\xrightarrow[\Delta]{\text{2 moles CH}_3\text{I}, (-2\text{ HI})}$ <chem>CN(C)c1ccccc1</chem></p>
(iii) Cl-(CH ₂) ₄ -Cl into Hexane-1,6-diamine	<p>(iii) <chem>ClCCCCl</chem> $\xrightarrow[\Delta]{\text{2 KCN (alc.)}}$ <chem>N#CCCC#N</chem> $\xrightarrow[2. \text{H}_3\text{O}^+]{1. \text{LAH}}$ <chem>NCCCCCCN</chem></p>
(iv) 3-Methylaniline into 3-nitrotoluene	<p>(iv) <chem>Cc1cccc(N)c1</chem> $\xrightarrow[273-278\text{ K}]{\text{NaNO}_2/\text{HBF}_4}$ <chem>[N+]#Nc1cccc(C)c1.[B-](F)(F)(F)F</chem> $\xrightarrow[\Delta]{\text{NaNO}_2/\text{Cu}}$ <chem>Cc1cccc([N+](=O)[O-])c1</chem></p>
(v) Aniline into 1,3,5-Tribromo benzene	<p>(v) <chem>Nc1ccccc1</chem> $\xrightarrow[\text{or H}_3\text{PO}_2/\text{Cu}^+]{\text{CH}_3\text{CH}_2\text{OH}/\Delta}$ <chem>BrC1=CC(=CC=C1)Br</chem></p>
(v) Ethanoic acid into methanamine	<p>(v) <chem>CC(=O)O</chem> $\xrightarrow[-\text{SO}_2, -\text{HCl}]{\text{SOCl}_2}$ <chem>CC(=O)Cl</chem> $\xrightarrow[\text{NH}_4\text{Cl}]{\text{NH}_3(\text{excess})}$ <chem>CC(=O)N</chem> $\xrightarrow{\text{Br}_2/\text{NaOH}}$ <chem>CN</chem></p>
(vi) Ethanamine into methanamine	<p>(vi) <chem>CCN</chem> $\xrightarrow[-\text{N}_2, -\text{H}_2\text{O}]{\text{HONO}}$ <chem>CCO</chem> $\xrightarrow{\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4}$ <chem>CC=O</chem> $\xrightarrow{\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4}$ <chem>CC(=O)O</chem> $\xrightarrow{\text{NH}_3}$ <chem>CC(=O)N</chem> $\xrightarrow{\text{Br}_2/\text{NaOH}}$ <chem>CN</chem></p>
(vii) Nitromethane into dimethylamine	<p>(vii) <chem>CN=[O+]</chem> $\xrightarrow{\text{Sn/HCl}}$ <chem>CN</chem> $\xrightarrow[\Delta]{\text{CHCl}_3, \text{KOH}}$ <chem>CN=C</chem> $\xrightarrow{\text{LiAlH}_4}$ <chem>CN(C)C</chem></p>
(viii) Nitrobenzene to benzoic acid	<p>(viii) <chem>O=[N+]([O-])c1ccccc1</chem> $\xrightarrow{\text{Fe/HCl}}$ <chem>Nc1ccccc1</chem> $\xrightarrow[273-278\text{ K}]{\text{NaNO}_2 + \text{HCl}}$ <chem>[N+]#Nc1ccccc1.[Cl-]</chem> $\xrightarrow{\text{CuCN/KCN}}$ <chem>N#Cc1ccccc1</chem> $\xrightarrow{\text{H}_3\text{O}^+}$ <chem>OC(=O)c1ccccc1</chem></p>



Arrangement order(Decreasing/Increasing)

In order of-	Questions	Answers
(i) In decreasing order of the pK_b values:	$\text{C}_2\text{H}_5\text{NH}_2$, $\text{C}_6\text{H}_5\text{NHCH}_3$, $(\text{C}_2\text{H}_5)_2\text{NH}$ and $\text{C}_6\text{H}_5\text{NH}_2$	$\text{C}_2\text{H}_5\text{NH}_2$, $\text{C}_6\text{H}_5\text{NHCH}_3$, $(\text{C}_2\text{H}_5)_2\text{NH}$ and $\text{C}_6\text{H}_5\text{NH}_2$
(ii) In increasing order of basic strength:	$\text{C}_6\text{H}_5\text{NH}_2$, $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$, $(\text{C}_2\text{H}_5)_2\text{NH}$ and CH_3NH_2	$\text{C}_6\text{H}_5\text{NH}_2$, $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$, $(\text{C}_2\text{H}_5)_2\text{NH}$ and CH_3NH_2
(iii) In increasing order of basic strength:	Aniline, <i>p</i> -nitroaniline and <i>p</i> -toluidine	Aniline, <i>p</i> -nitroaniline and <i>p</i> -toluidine
(iv) In decreasing order of basic strength in gas phase:	$\text{C}_2\text{H}_5\text{NH}_2$, $(\text{C}_2\text{H}_5)_2\text{NH}$, $(\text{C}_2\text{H}_5)_3\text{N}$ and NH_3	$\text{C}_2\text{H}_5\text{NH}_2$, $(\text{C}_2\text{H}_5)_2\text{NH}$, $(\text{C}_2\text{H}_5)_3\text{N}$ and NH_3
(v) In increasing order of boiling point:	$\text{C}_2\text{H}_5\text{OH}$, $(\text{CH}_3)_2\text{NH}$, $\text{C}_2\text{H}_5\text{NH}_2$	$\text{C}_2\text{H}_5\text{OH}$, $(\text{CH}_3)_2\text{NH}$, $\text{C}_2\text{H}_5\text{NH}_2$
(vi) In increasing order of solubility in water:	$\text{C}_6\text{H}_5\text{NH}_2$, $(\text{C}_2\text{H}_5)_2\text{NH}$, $\text{C}_2\text{H}_5\text{NH}_2$.	$\text{C}_6\text{H}_5\text{NH}_2$, $(\text{C}_2\text{H}_5)_2\text{NH}$, $\text{C}_2\text{H}_5\text{NH}_2$.

WORD PROBLEM

A colourless substance 'A' ($\text{C}_6\text{H}_7\text{N}$) is sparingly soluble in water and gives a water soluble compound 'B' on treating with mineral acid. On reacting with CHCl_3 and alcoholic potash 'A' produces an obnoxious smell due to the formation of compound 'C'. Reaction of 'A' with benzenesulphonyl chloride gives compound 'D' which is soluble in alkali. With NaNO_2 and HCl , 'A' forms compound 'E' which reacts with phenol in alkaline medium to give an orange dye 'F'. Identify compounds 'A' to 'F'

(A) Aniline ($\text{C}_6\text{H}_7\text{N}$) (colourless liquid, sparingly soluble in water)	(B) Anilinium chloride (water soluble salt)	(C) Benzene isonitrile (obnoxious smell)
(D) <i>N</i> -Phenylbenzenesulphonamide (soluble in alkali)	(E) Benzene diazonium chloride	(F) <i>p</i> -Hydroxyazobenzene (orange dye)

Two Marks Questions

1	Write the short note on reductive amination reactions?
ANS	When aldehydes or ketones react with ammonia imines is formed. These imines give the primary amine by catalytic reduction. $\text{RCHO} + \text{NH}_3 \xrightarrow[\text{-H}_2\text{O}]{\text{Heat}} \text{RCH}=\text{NH} \xrightarrow{\text{H}_2 / \text{Ni}} \text{RCH}_2\text{NH}_2$
2	How will you form quaternary ammonium salt from haloalkane?
ANS	When haloalkanes heated with an ethanolic solution of ammonia in a sealed tube at 100°C . $\text{RX} + \text{NH}_3 \xrightarrow{-\text{HX}} \text{RNH}_2 \xrightarrow[\text{-HX}]{\text{RX}} \text{R}_2\text{NH} \xrightarrow[\text{-HX}]{\text{RX}} \text{R}_3\text{N} \xrightarrow{\text{RX}} \text{R}_4^+\text{NX}^-$ <p style="text-align: center;"> Haloalkane P. amine S. Amine T. Amine Quaternary Ammonium salt </p>
3	Why is aniline a weaker base than methylamine?
ANS	Aniline and methylamine both have nitrogen with lone pair of electron. In aniline the phenyl group is electron attracting. It tend to decrease the electron density on nitrogen atom and hence decreases electron releasing tendency of nitrogen. While

	in methylamine CH ₃ - group is electron repelling in nature. It tends to increase the electron density on the nitrogen atom and helps in electron releasing tendency of nitrogen. So, the aniline is a weaker base than methylamine.						
4	Arrange the following in increasing order of basic strength: - (i) Triethylamine, ethylamine and ammonia. (ii) p-nitroaniline, aniline and p-toluidine.						
ANS	(i) Ammonia < Triethylamine < Ethylamine (ii) Aniline < p-nitroaniline < p-toluidine.						
5	Can we prepare aniline by Gabriel-phthalimide reaction?						
ANS	We can not prepare aniline by Gabriel-phthalimide reaction because this preparation requires the reaction of pot. Phthalimide with chlorobenzene or bromobenzene. But aryl halides do not give nucleophilic substitution reaction at ordinary condition in laboratory.						
6	Arrange the following in increasing order of their basic strength C₂H₅NH₂, C₆H₅NH₂, NH₃, C₆H₅CH₂NH₂ and (C₂H₅)₂NH						
ANS	C ₆ H ₅ NH ₂ < NH ₃ < C ₆ H ₅ CH ₂ NH ₂ < C ₂ H ₅ NH ₂ < (C ₂ H ₅) ₂ NH						
7	Complete the following reactions: (i) CH₃NH₂ + C₆H₅COCl → + (ii) C₆H₅NH₂ + (CH₃CO)₂O → +						
ANS	(i) CH ₃ NH ₂ + C ₆ H ₅ COCl → CH ₃ NHCOC ₆ H ₅ + HCl (ii) C ₆ H ₅ NH ₂ + (CH ₃ CO) ₂ O → C ₆ H ₅ NH-COCH ₃ + CH ₃ COOH						
8	How will you distinguish between cyanides and isocyanides?						
ANS	<table border="1"> <thead> <tr> <th>Properties</th> <th>Cyanide</th> <th>Isocyanides</th> </tr> </thead> <tbody> <tr> <td>1. Solubility in water 2. Odour 3. Hydrolysis 4. Reduction</td> <td>1. Soluble in water 2. Pleasant smell 3. Give acid on hydrolysis with acid and alkalis 4. Give primary amine on complete reduction.</td> <td>1. Sparingly soluble in water. 2. Highly unpleasant smell 3. Give primary amines and formic acid on hydrolysis with dil. Acids. 4. Give secondary amines on complete reduction.</td> </tr> </tbody> </table>	Properties	Cyanide	Isocyanides	1. Solubility in water 2. Odour 3. Hydrolysis 4. Reduction	1. Soluble in water 2. Pleasant smell 3. Give acid on hydrolysis with acid and alkalis 4. Give primary amine on complete reduction.	1. Sparingly soluble in water. 2. Highly unpleasant smell 3. Give primary amines and formic acid on hydrolysis with dil. Acids. 4. Give secondary amines on complete reduction.
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9	Why is NO₂ group called an ambident group?						
ANS	Nitro group can attach itself through two different atoms, i.e., through O atom and N atom. Thus, nitro group is an ambident group						
	Three Marks Questions						
1	Predict the products of and balance the following reactions: (i) C₂H₅NO₂ $\xrightarrow{\text{Sn/HCl}}$ (ii) C₂H₅-O-N=O $\xrightarrow{\text{Sn/HCl}}$ + + (iii) $\xrightarrow[372\text{K}]{\text{HNO}_3 + \text{H}_2\text{SO}_4}$ $\xrightarrow{(\text{NH}_4)_2\text{S}}$						
ANS	(i) C ₂ H ₅ NO ₂ $\xrightarrow{\text{Sn/HCl}}$ C ₂ H ₅ NH ₂ + 2H ₂ O (ii) C ₂ H ₅ -O-N=O $\xrightarrow{\text{Sn/HCl}}$ C ₂ H ₅ OH + NH ₃ + H ₂ O (iii) C ₆ H ₅ NO ₂ $\xrightarrow[372\text{K}]{\text{HNO}_3 + \text{H}_2\text{SO}_4}$ m-C ₆ H ₄ (NO ₂) ₂ $\xrightarrow{(\text{NH}_4)_2\text{S}}$ H ₂ N.C ₆ H ₄ .NO ₂						
2	Account for the following :- (i) pK_b of aniline is more than that of methylamine.						

	<p>(ii) Ethylamine is soluble in water whereas aniline is not.</p> <p>(iii) Why has aniline a weak basic nature than aliphatic amines?</p>
ANS	<p>Ans: (i) aniline has an electron withdrawing phenyl group so it is the weaker base than ammonia. Methyl group in methylamine is electron donating group so it is stronger base than ammonia.</p> <p>(ii) ethyl group in ethylamine is comparatively a small group and causes no hindrance in formation of hydrogen bonding and hence it is soluble in water.</p> <p>(iii) Due to resonance in aniline</p>
3	<p>(i) Arrange the following in the order of basicity in aqueous solution $(\text{Me})_3\text{N}$, MeNH_2, $(\text{Me})_2\text{NH}$, NH_3</p> <p>(ii) Complete and name the following reactions: (a) $\text{RNH}_2 + \text{CHCl}_3 + 3\text{KOH} \rightarrow$ (b) $\text{RCONH}_2 + \text{Br}_2 + 4\text{NaOH} \rightarrow$</p>
ANS	<p>(i) Arrange the following in the order of basicity in aqueous solution $\text{NH}_3 < (\text{Me})_3\text{N} < \text{MeNH}_2 < (\text{Me})_2\text{NH}$,</p> <p>(ii)(a) $\text{R-NH}_2 + \text{CHCl}_3 + 3\text{KOH} \xrightarrow{\text{Heat}} \text{R-NC} + 3\text{KCl} + 3\text{H}_2\text{O}$</p> <p>(ii)(b) $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}_2 + \text{Br}_2 + 4\text{NaOH} \longrightarrow \text{R}-\text{NH}_2 + \text{Na}_2\text{CO}_3 + 2\text{NaBr} + 2\text{H}_2\text{O}$</p>
4	<p>An aromatic compound 'A' on treatment with aqueous ammonia and heating forms a compound 'B' which on heating with Br_2 and KOH forms a compound 'C' of molecular formula $\text{C}_6\text{H}_7\text{N}$. Write the structures and IUPAC names of the compounds A, B, C.</p>
ANS	<p>From the available information, we find that 'B' upon heating with Br_2 and KOH forms a compound 'C'. The compound 'B' is expected to be an acid amide. Since 'B' has been formed upon heating compound 'A' with aqueous ammonia, the compound 'A' is an aromatic acid.</p> <p>It is benzoic acid. The reactions involved are given as follows:</p> <div style="text-align: center;"> <p> $\text{C}_6\text{H}_5\text{COOH} \xrightarrow[\text{heat}]{\text{NH}_3(aq)} \text{C}_6\text{H}_5\text{CONH}_2 \xrightarrow[\text{heat}]{\text{Br}_2/\text{KOH}} \text{C}_6\text{H}_5\text{NH}_2$ </p> <p> Benzoic acid (A) Benzamide (B) Aniline (C) $(\text{C}_6\text{H}_7\text{N})$ </p> </div>
5	<p>Give the structures of A, B and C in the following reactions:</p> <p>(i) $\text{CH}_3\text{CH}_2\text{I} \xrightarrow{\text{NaCN}} \text{A} \xrightarrow[\text{Partial hydrolysis}]{\text{OH}^-} \text{B} \xrightarrow{\text{NaOH} + \text{Br}_2} \text{C}$</p>
ANS	<div style="text-align: center;"> <p> $\text{H}_3\text{C}-\text{CH}_2-\text{I} \xrightarrow{\text{NaCN}} \text{H}_3\text{C}-\text{CH}_2-\text{C}\equiv\text{N} \xrightarrow[\text{OH}^- \text{ hydrolysis}]{} \text{H}_3\text{C}-\text{CH}_2-\text{C}(=\text{O})-\text{NH}_2 \xrightarrow[\text{Br}_2]{\text{NaOH}} \text{H}_3\text{C}-\text{CH}_2-\text{NH}_2$ </p> </div>

FIVE MARKS QUESTIONS	
1	<p>Account for the following:</p> <p>(i) pK_b of aniline is more than that of methylamine.</p> <p>(ii) Ethylamine is soluble in water whereas aniline is not.</p> <p>(iii) Methylamine in water reacts with ferric chloride to precipitate hydrated ferric oxide.</p> <p>(iv) Although amino group is o- and p- directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of m-nitroaniline.</p> <p>(v) Aniline does not undergo Friedel-Crafts reaction.</p>
	<p>i) In aniline, the lone pair of electrons on N atom is in resonance with benzene ring. Hence, it cannot be easily donated to an acid. This decreases its basicity. In methyl amine, the +I effect of methyl group increases the electron density on N atom so that the lone pair of electrons on N atom can be easily donated to an acid. Hence, methylamine is more basic than aniline. Higher is the basicity, lower is the pK_b and vice versa.</p> <p>(ii) Ethylamine is soluble in water whereas aniline is not. With increase in the molecular weight, the solubility decreases. Aniline has higher molecular weight than ethylamine.</p> <p>(iii) Methylamine in water reacts with ferric chloride to precipitate hydrated ferric oxide. Due to the +I effect of $-CH_3$ group, methylamine is more basic than water. Therefore, in water, methylamine produces OH^- ions by accepting H^+ ions from water. OH^- ions react with ferric chloride to precipitate hydrated ferric oxide.</p> <p>(iv) In aniline NH_2 increases e density at o- and p- positions due to +R effect. But when it is nitrated by nitrating mixture, a substantial amount of m-nitro aniline is formed. But in acidic medium (Nitrating mixture - $HNO_3(c) + H_2SO_4(c)$). $NH_2 + H^+ \rightleftharpoons NH_3^+$ is e^- withdrawing group and so is m- directing. So gives larger amount of m- nitroaniline.</p> <p>(v) Aniline does not undergo Friedel craft's reactions because the reagent $AlCl_3$ (the Lewis acid which is used as a catalyst in friedel crafts reaction), being electron deficient acts as a Lewis base.</p>
2.	<p>Arrange the following:</p> <p>(i) In decreasing order of the pK_b values: $C_2H_5NH_2$, $C_6H_5NHCH_3$, $(C_2H_5)_2NH$ and $C_6H_5NH_2$</p> <p>(ii) In increasing order of basic strength: $C_6H_5NH_2$, $C_6H_5N(CH_3)_2$, $(C_2H_5)_2NH$ and CH_3NH_2</p> <p>(iii) In increasing order of boiling point: (a) Aniline, p-nitroaniline and p-toluidine (b) $C_6H_5NH_2$, $C_6H_5NHCH_3$, $C_6H_5CH_2NH_2$.</p> <p>(iv) In decreasing order of basic strength in gas phase: $C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$ and NH_3</p> <p>(v) In increasing order of boiling point: C_2H_5OH, $(CH_3)_2NH$, $C_2H_5NH_2$</p> <p>Answers</p> <p>$(C_2H_5)_2NH > C_2H_5NH_2 < C_6H_5NHCH_3 > C_6H_5NH_2$ → Increasing pK_b value</p> <p>$C_6H_5NH_2 < C_6H_5NHCH_3 < C_6H_5CH_2NH_2$ → Increasing basic strength</p> <p>p-nitroaniline $<$ aniline $<$ p-toluidine $C_6H_5NH_2 < C_6H_5NHCH_3 < C_6H_5CH_2NH_2$ → Increasing basic strength → Increasing basic strength</p> <p>$(C_2H_5)_3N > (C_2H_5)_2NH > C_2H_5NH_2 > NH_3$ → Decreasing basic strength</p>

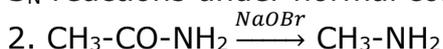
AMINES

CASE BASED QUESTIONS

(a) Amines constitute an important class of organic compounds derived by replacing one or more hydrogen atoms of ammonia molecule by alkyl/aryl group(s). In nature, they occur among proteins, vitamins, alkaloids and hormones. Synthetic examples include polymers, dye stuffs and drugs. Two biologically active compounds, namely adrenaline and ephedrine, both containing secondary amino group, are used to increase blood pressure. Novocain, a synthetic amino compound, is used as an anaesthetic in dentistry. Benadryl, a well known antihistaminic drug also contains tertiary amino group. Amine can be prepared by a numbers of ways.

1. Can aniline be prepared by Gabriel phthalimide synthesis, justify?
2. What happens when Acetamide treated with NaOBr?
3. An aromatic compound 'A' on treatment with aqueous ammonia and heating forms compound 'B' which on heating with Br₂ and KOH forms a compound 'C' of molecular formula C₆H₇N. Write the structures and IUPAC names of compounds A, B and C.

Answer- 1. No, aniline can not be prepared by Gabriel phthalimide synthesis because to prepare aniline by this method chlorobenzene is required which do not undergo S_N reactions under normal conditions.



3. A- C₆H₅COOH- Benzene carboxylic acid B- C₆H₅CONH₂- Benzamide
C- C₆H₅NH₂ – Aniline (Benzenamine)

(b) The reaction of amines with mineral acids to form ammonium salts shows that these are basic in nature. Amines have an unshared pair of electrons on nitrogen atom due to which they behave as Lewis base. Basic character of amines can be better understood in terms of their K_b and pK_b values.

1. Aniline is weaker base than ammonia, why?
2. Tertiary amines becomes less basic than secondary amines in solution, justify.
3. Aqueous solution of methyl amine gives brown ppt with neutral FeCl₃, why?
4. Arrange the following amines in their increasing order of basic nature in gas phase and in solution- (CH₃)₃N, (CH₃)₂NH, CH₃NH₂

Answer- 1. Because in aniline lone pair of electron is involved in resonance.

2. Due to steric hindrance of bulkier alkyl group of tertiary amine lone pair can not be donated easily.

3. Methyl amine reacts with water to give OH⁻ ion which reacts with Fe³⁺ ion to form brown ppt of Fe(OH)₃.

4. In gas phase- CH₃NH₂ < (CH₃)₂NH < (CH₃)₃N

In solution - CH₃NH₂ < (CH₃)₃N < (CH₃)₂NH

Kendriya Vidyalaya Sangathan, Ahmedabad Region
Sample question paper (2021-22)
Term II Class XII Chemistry Theory (043)

Max. Marks: 35

Time: 2 hrs

General instructions:

- There are 12 questions in this question paper.
- Section A - Q. No.1 to 3 are very short answer questions carrying 2 marks each.
- Section B - Q. No.4 to 11 are short answer questions carrying 3 marks each.
- Section C - Q. No.12 is case based question carrying 5 marks.
- All questions are compulsory.
- There is no overall choice. However, internal choices have been provided.
- Use of log tables and calculators is not allowed

SECTION A		
1	Give names of the reagents to bring about the following transformations: (a) Hexan-1-ol to hexanal (b) Cyclohexanol to cyclohexanone	2
2	(i) Write one function of salt bridge (ii) How much charge is required for changing 1 mol of Al^{3+} to Al?	2
3	Which acid of each pair shown here would you expect to be stronger? (a) CH_3COOH or CH_2FCOOH (b) CH_2FCOOH or $CH_2ClCOOH$	2
SECTION B		
4	Arrange the following in increasing order of property specified: (i) Aniline, ethanamine, 2-ethylethanamine (solubility in water) (ii) Ethanoic acid, ethanamine, ethanol (boiling point) (iii) Methanamine, N, N- dimethylmethanamine and N- methylmethanamine (basic strength in aqueous phase) OR (i) Give a chemical test to distinguish between N-methyl Ethan amine and N,N-dimethyl Ethan amine. (ii) Write the reaction for catalytic reduction of nitrobenzene followed by reaction of product so formed with bromine water. (iii) Out of butan-1-ol and butan-1-amine, which will be more soluble in water and why?	3
5	Answer the following questions: a. $[Ni(H_2O)_6]^{2+}$ (aq) is green in colour whereas $[Ni(H_2O)_4 en]^{2+}$ (aq) is blue in colour , give reason in support of your answer . b. Write the formula and hybridization of the following compound: tris(ethane-1,2-diamine) cobalt(III) sulphate OR In a coordination entity, the electronic configuration of the central metal ion is $t_{2g}^3 e_g^1$ a. Is the coordination compound a high spin or low spin complex? b. Draw the crystal field splitting diagram for the above complex.	1+2
6	Explain giving reasons: (i) Transition metals and many of their compounds show paramagnetic behaviour. (ii) The enthalpies of atomisation of the transition metals are high. (iii) The transition metals generally form coloured compounds.	3
7	An organic compound (A) with molecular formula C_8H_8O forms an orange-red precipitate with 2,4-DNP reagent and gives yellow precipitate on heating with iodine in the presence of sodium hydroxide. It neither reduces Tollens' or Fehling's reagent, nor does it decolourise bromine water or Baeyer's reagent. On drastic oxidation with chromic acid, it gives a	1+2

	carboxylic acid (B) having molecular formula $C_7H_6O_2$. Identify the compounds (A) and (B) and explain the reactions involved.	
8	(i) Define the terms – (a) Brownian movement (b) Electrophoresis? (ii) State Hardy- Schulze rule?	2+1
9	What happens when reactions: a. N-ethylethanamine reacts with benzenesulphonyl chloride. b. Benzylchloride is treated with ammonia followed by the reaction with Chloromethane. c. Aniline reacts with chloroform in the presence of alcoholic potassium hydroxide. OR (i) Write structure of following (i) Aminobut -2- ene (ii) A compound (X) having formula C_3H_7NO reacts with Br_2 in the presence of NaOH to give another compound (Y). Compound (Y) reacts with HNO_2 to form ethanol and N_2 gas . Identify (X) and (Y) . Write the reaction involved.	1x3 =3 1+2 =3
10	What is the cell potential for the cell at $25^\circ C$ $Cr / Cr^{3+} 0.1 M // Fe^{2+} (0.01M) / Fe E^0 cr^+/cr = -0.74V ; E^0 Fe^{2+}/Fe = - 0.44V.$	3
11	What is the lanthanoid contraction? What are its causes and consequences? OR What is the general valence configuration of f-block elements? [1] What is the composition of mischmetal? Give its one use. [2]	1+2
SECTION C		
12	Rate law: Rate law or rate equation is the expression which relates the rate of reaction with concentration of the reactants. The constant of proportionality 'k' is known as rate constant. The rate law states that the rate of reaction is directly proportional to the product of molar concentration of reactants and each concentration is raised to some power which may or may not be equal to stoichiometric coefficients of reacting species. Rate = $k[A]^m [B]^n$ – Rate constant: Rate constant is also called specific reaction rate. When concentration of both reactants are unity (one), then the rate of reaction is known as rate constant. It is denoted by 'k'. Order of reaction: Order is defined as the sum of powers of concentration of the reactants in the experimentally derived rate equation or rate law expression. Order of reaction is experimentally determined and is not written from the balanced chemical equation. Order of reaction can be whole number, zero or fractional. First order reaction: The rate of reaction is directly proportional to the first power of the concentration of reacting substance. i.e., Rate = $k[A]^1$. Rate constant of the first order reaction is $k = 2.303/t \log (a / a - x)$ - where 'a' is initial concentration and (a - x) is the concentration after time 't'. Unit of 'k' is s^{-1} or min^{-1} (i) For a reaction $A + B \rightarrow P$, the rate is given by Rate = $k[A] [B]^2$ (a) How is the rate of reaction affected if the concentration of B is doubled? (b) What is the overall order of reaction if A is present in large excess? (ii) A first order reaction takes 30 minutes for 50% completion. Calculate the time required for 90% completion of this reaction. ($\log 2 = 0.3010$)	1+1 +3 =5

Answer key		
Section A		
1	Names of the reagents to bring about the following transformations: a) Hexan-1-ol to hexanal-PCC b) Cyclohexanol to cyclohexanone- $K_2Cr_2O_7/H_2SO_4$	1x2 =2
2	ii) Any One function of salt bridge -To connect to half-cells, to maintain electroneutrality iii) Charge required for changing 1 mol of Al^{3+} to Al^{---} 3F i.e. $3 \times 96500C$.	2
3	Stronger acid in pair (a) CH_2FCOOH (b) CH_2COOH	1x2 =2
SECTION B		
4	<p>Arrange the following in increasing order of property specified:</p> <p>i) Aniline, 2-ethylethanamine ethanamine (solubility in water)</p> <p>ii) ethanamine, ethanol, Ethanoic acid (boiling point)</p> <p>iii) n N, N- dimethylmethanamine , Methanamine, N- methylmethanamine (basic strength in aqueous phase)</p> <p>OR</p> <p>iv) Chemical test to distinguish between N-methyl Ethan amine and N,N-dimethyl Ethan amine. - Hinsberg Test</p> <p>N,N-dimethyl Ethan amine will not react with benzenesulphonyl chloride & N-methyl Ethanamine will react to give a ppt. which is insoluble in alc.KOH.</p> <p>v) the reaction for catalytic reduction of nitrobenzene followed by reaction of product so formed with bromine water.</p> $C_6H_5NO_2 \xrightarrow{Sn/HCl} C_6H_5NH_2 \xrightarrow{Br_2/H_2O} 2,4,6\text{TRIBROMOANILINE}$ <p>vi) Out of butan-1-ol and butan-1-amine, Butan1-ol is more soluble in water because the H bond formed is more strong.</p>	1x3 =3
5	<p>Answer the following questions:</p> <p>a. $[Ni(H_2O)_6]^{2+}$ (aq) is green in colour whereas $[Ni(H_2O)_4(en)]^{2+}$(aq)is blue in colour</p> <p>The colour of coordination compound depends upon the type of ligand and dd transition taking place . H_2O is weak field ligand , which causes small splitting , leading to the d-d transition corresponding green colour , however due to the presence of (en) which is strong field ligand , the splitting is increased . Due to the change in t_{2g} -eg splitting the colouration of the compound changes from green to blue.</p> <p>(b)Formula of the compound is $[Co(H_2NCH_2CH_2NH_2)_3]_2(SO_4)_3$ The hybridisation of the compound is: d^2sp^3</p> <p>OR</p> <p>5. In a coordination entity, the electronic configuration of the central metal ion is $t_{2g}^3 e_g^1$</p> <p>a)As the fourth electron enters one of the e_g orbitals giving the configuration $t_{2g}^3 e_g^1$,which indicates $\Delta_o < P$ hence forms high spin complex.</p> <p>b) the crystal field splitting diagram for the above complex. Correct diagram.</p>	1+2
		1+1 +1

Kendriya Vidyalaya Sangathan, Ahmedabad Region
Sample question paper -2(2021-22)
Term II Class XII Chemistry Theory (043)

Max. Marks: 35

Time: 2 hrs

General instructions:

- There are 12 questions in this question paper.
- Section A - Q. No.1 to 3 are very short answer questions carrying 2 marks each.
- Section B - Q. No.4 to 11 are short answer questions carrying 3 marks each.
- Section C - Q. No.12 is case based question carrying 5 marks.
- All questions are compulsory.
- There is no overall choice. However, internal choices have been provided.
- Use of log tables and calculators is not allowed

SECTION A		
1	Draw the structure of the following - i) I,2-Ethanedioic acid ii) Pent-3-ene -2-one	1x2=2
2	The conversion of molecule X to Y follows second order kinetics. If concentration of X is increased to three times, how will it affect the rate of formation of Y?	2
3	Give Reasons :- i) Carboxylic acids do not give characteristic reactions of carbonyl group. ii) Formaldehyde does not undergo aldol condensation	1x2=2
SECTION B		
4	i) Why do amines behave as nucleophiles? ii) What is the role of pyridine in the acylation reaction of amines? iii) What is the role of HNO ₃ in the nitrating mixture used for nitration of benzene OR Account for the following: (i) Aniline gets coloured on standing in air for a long time. (ii) MeNH ₂ is stronger base than MeOH. (iii) The presence of a base is needed in the ammonolysis of alkyl halides.	1x3=3
5	Write the formulas for the following coordination compounds: (i) tetraammineaqua cobalt(III) chloride (ii) potassium tetracyanonickelate(II) (iii) tris (ethane-1, 2-diamine) chromium(III) chloride OR Write IUPAC names of the following coordination compounds: (i) [(Co(NH ₃) ₆ Cl ₃)] (ii) [Co(NH ₃) ₅ Cl]Cl ₂ (iii) K ₃ [Fe(CN) ₆]	1+2
6	The elements of 3d transition series are given as: Sc Ti V Cr Mn Fe Co Ni Cu Zn Answer the following: (a) Which element has the highest m.p. and why? (b) Which element is a strong oxidising agent in +3 oxidation state and why?	

	c) Which element is soft and why?	
7	<p>a) Arrange the following compounds in increasing order of their reactivity in nucleophilic addition reactions.</p> <p>(i) Ethanal, Propanal, Propanone, Butanone</p> <p>(ii) Benzaldehyde, p-Tolualdehyde, p-Nitrobenzaldehyde, Acetophenone</p> <p>b) Arrange the following compounds in increasing order of their boiling points. CH_3CHO, $\text{CH}_3\text{CH}_2\text{OH}$, CH_3OCH_3, $\text{CH}_3\text{CH}_2\text{CH}_3$</p>	2+1
8	Write three differences between physisorption and chemisorption.	3
9	<p>Write short notes on the following:</p> <p>(i) Carbylamine reaction</p> <p>(ii) Diazotisation</p> <p>(iii) Hofmann's bromamide reaction</p> <p>OR</p> <p>(i) Coupling reaction</p> <p>(ii) Ammonolysis</p> <p>(iii) Acetylation</p>	1x3=3
10	The half-life for radioactive decay of C-14 is 5730 years. An archaeological artifact containing wood had only 80% of the C-14 found in a living tree. Estimate the age of the sample.	3
11	<p>Give reasons: (a) Among transition metals, the highest oxidation state is exhibited in oxoanions of a metal.</p> <p>(b) Ce^{4+} is used as an oxidising agent in volumetric analysis.</p> <p>(c) Zn^{2+} salts are white while Cu^{2+} salts are blue.</p> <p>OR</p> <p>Account for the following: (i) Mn_2O_7 is acidic whereas MnO is basic. (ii) Though copper has completely filled d-orbital (d^{10}) yet it is considered as a transition metal.</p> <p>(iii) Eu^{2+} is a strong reducing agent.</p>	1+2
	SECTION C	
12	<p>Redox reactions play an important role in chemistry. Whenever a redox reaction takes place directly in a single beaker, chemical energy in the form of heat is produced. By suitable means, it is possible to bring about the redox reactions indirectly so as to convert the chemical energy into electrical energy. A device used to convert the chemical energy produced in a redox reaction into electrical energy is called an electrochemical cell. If a redox reaction is allowed to take place in such a way that oxidation half reaction takes place in one beaker and the reduction half reaction in another beaker, the electrons given out by the former will be taken by the latter and the current will flow. The two portions of the cell are called half cells. The values of standard redox potential (E°) of two half cell reactions decides in which way the reaction will proceed. A redox reaction is feasible when the substance having higher reduction potential gets reduced and the one having lower reduction potential gets oxidised. For example, In Daniel cell, zinc goes into solution and copper gets deposited.</p> <p>a.</p> <p>i) Formulate the galvanic cell in which the following reaction takes place: $\text{Zn}(s) + 2\text{Ag}^+(aq) \rightarrow \text{Zn}^{2+}(aq) + 2\text{Ag}(s)$</p> <p>ii). Is it safe to stir AgNO_3 solution with a copper spoon? Why or why not? Given: $E^\circ \text{Ag}^+/\text{Ag} = 0.80$ volt and $E^\circ \text{Cu}^{2+}/\text{Cu} = 0.34$ volt.</p> <p>b.</p> <p>i) Two half cell reactions of an electrochemical cell are given below: $\text{MnO}_4^- (aq) + 8\text{H}^+ (aq) + 5e^- \rightarrow \text{Mn}^{2+}(aq) + 4\text{H}_2\text{O}(l)$,</p>	1x5=5

	$E^\circ = +1.51 \text{ V Sn}^{2+}(\text{aq}) \text{ Sn}^{4+}(\text{aq}) + 2e^-$, $E^\circ = +0.15 \text{ V}$ Construct the redox reaction from the two half cell reactions and predict if this reaction favours formation of reactants or products shown in the equation. ii). State the factors that influence the value of cell potential of the following cell: $\text{Mg}(\text{s}) \text{Mg}^{2+}(\text{aq}) \text{Ag}^+(\text{aq}) \text{Ag}(\text{s})$ iii). Can E° cell or $\Delta_r G^\circ$ for cell reaction ever be equal to zero?	
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ANSWER KEY		
SECTION A		
1	i) 1,2-Ethaneodioc acid -- $\text{CH}_2(\text{COOH})-\text{CH}_2(\text{COOH})$ ii) Pent-3-ene -2-one -- $\text{CH}_3\text{COCH}=\text{CHCH}_3$	1x2=2
2	$\text{Rate} = k [\text{X}]^2$ $r_1 = k [\text{X}]^2 \dots(\text{i})$ $r_2 = k [3\text{X}]^2 \dots(\text{ii})$ Dividing (ii) by (i), $r_2 = 9r_1$ Thus, rate of formation of Y will increase by nine times.	2
3	i) Carboxylic acids do not give characteristic reactions of carbonyl group because it is involved in resonance & is not free to give carbonyl group reactions ii). Formaldehyde does not undergo aldol condensation due to absence of alpha H.	1x2=2
SECTION B		
4	a)(i) Due to the presence of a lone pair of electrons on nitrogen atom, amines behave as nucleophiles. (ii) Pyridine and other bases are used to remove the side product, i.e., HCl from the reaction mixture. (iii) HNO_3 acts as a base in the nitrating mixture and provides the electrophile NO_2^+ . OR b) (i) Due to electron-donating effect (+R-effect) of $-\text{NH}_2$ group, the electron density on the benzene ring increases. As a result, aniline is easily oxidised on standing in air for a long time to form coloured products. (ii) Nitrogen is less electronegative than oxygen therefore lone pair of electrons on nitrogen is readily available for donation. Hence, MeNH_2 is more basic than MeOH (iii) To remove HX formed so that the reaction shifts in the forward direction.	1x3=3
5	Formulas of the coordination compounds: Ans. (i) $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]\text{Cl}_3$ (ii) $\text{K}_2\text{Ni}[(\text{CN})_4]$ (iii) $[\text{Cr}(\text{en})_3]\text{Cl}_3$ OR IUPAC names of the following coordination compounds: (i) hexaamminecobalt(III) chloride (ii) pentaamminechloridocobalt(III) chloride (iii) potassium hexacyanoferrate (III)	1x3=3
6	(i) (a) Cr, the highest melting point of Cr is attributed to the involvement of greater number of electrons(5) from 3d in addition to 4s electrons in interatomic metallic bonding.	1x3=3

	<p>(b) Mn, because the change from Mn^{3+} (d^4) to Mn^{2+} (d^5) results in the half filled configuration which has extra stability.</p> <p>(c) Zn, in Zn ($3d^{10} 4s^2$) all the electrons present in d-orbitals are paired and hence metallic bonds present in it are weak. That is why, it is soft</p>	
7	<p>a)(i) The reactivity in nucleophilic addition reactions increases in the order: Butanone < Propanone < Propanal < Ethanal</p> <p>(ii) the required order is as follows: Acetophenone < p-Tolualdehyde < Benzaldehyde < p-Nitrobenzaldehyde</p> <p>b) $CH_3CH_2CH_3 < CH_3OCH_3 < CH_3CHO < CH_3CH_2OH$</p>	1x3=3
8	<p>Physisorption It arises because of van der Waals' forces. It is not specific in nature. It is reversible in nature. It depends on the nature of gas. More easily liquefiable gases are adsorbed readily. Enthalpy of adsorption is low ($20-40 \text{ kJ mol}^{-1}$) in this case.. Low temperature is favourable for adsorption. (vii) No appreciable activation energy is needed. (viii) It results into multimolecular layers on adsorbent surface under high pressure.</p> <p>Chemisorption It is caused by chemical bond formation. It is highly specific in nature It is irreversible It also depends on the nature of gas. Gases which can react with the adsorbent show chemisorption. Enthalpy of adsorption is high ($80-240 \text{ kJ mol}^{-1}$) . It decreases with increase of temperature. High temperature is favourable for adsorption. It increases with the increase of temperature. High activation energy is sometimes needed. It results into unimolecular layer (Any 3 points)</p>	3
9	<p>(i) Carbylamine reaction (ii) Diazotisation (iii) Hofmann's bromamide reaction</p> <p>OR (i) Coupling reaction (ii) Ammonolysis (iii) Acetylation Correct equations</p>	1x3=3
10	<p>Radioactive decay follows first order kinetics. Steps Calculate K from $t_{1/2}$ $K = 0.693/t_{1/2}$ Cal t using formula $k = 2.303/t \log [A_0/A]$ = 1845 years (approx.)</p>	3
11	<p>a) In these oxoanions the oxygen atoms are directly bonded to the transition metal. Since oxygen is highly electronegative, the oxoanions bring out the highest oxidation state of the metal.</p> <p>b) Ce^{4+} has the tendency to attain +3 oxidation state which is more stable and so it is used as an oxidising agent in volumetric analysis.</p>	1+2

	<p>c) Zn^{2+} ion has all its orbitals completely filled whereas in Cu^{2+} ion there is one half-filled 3d-orbital. Therefore, due to d-d transition Cu^{2+} has a tendency to form coloured salts whereas Zn^{2+} has no such tendency.</p> <p style="text-align: center;">OR</p> <p>(i) Mn has +7 oxidation state in Mn_2O_7 and +2 in MnO. In low oxidation state of the metal, some of the valence electrons of the metal atom are not involved in bonding. Hence, it can donate electrons and behave as a base. On the other hand, in higher oxidation state of the metal, valence electrons are involved in bonding and are not available. Instead effective nuclear charge is high and hence it can accept electrons and behave as an acid.</p> <p>(ii) Copper exhibits +2 oxidation state wherein it will have incompletely filled d-orbitals ($3d^9$), hence a transition metal.</p> <p>(iii) This is because Eu^{2+} tends to change to Eu^{3+} as +3 is the common oxidation state of lanthanoids.</p>	
	SECTION C	
12	<p>a)</p> <p>i) The cell is represented as $Zn(s) Zn^{2+}(aq) Ag^+(aq) Ag(s)$</p> <p>ii) No, it is not safe to stir $AgNO_3$ solution with copper, because copper is more reactive than Ag and can displace Ag from $AgNO_3$ solution.</p> <p>b)</p> <p>i) The redox reaction will be $2MnO_4^- (aq) + 16H^+ (aq) + 5Sn^{2+}(aq) \rightarrow 2Mn^{2+}(aq) + 5Sn^{4+}(aq) + 8H_2O(l)$ $E_o \text{ Cell} = E_o \text{ Cathode} - E_o \text{ Anode} = 1.51 \text{ V} - 0.15 \text{ V} = 0.36 \text{ V}$, i.e., it will be positive. Hence, reaction will favour formation of products.</p> <p>ii) The factors that influence the value of cell potential are concentration of Mg^{2+} and Ag^+ ions in the solution and temperature.</p> <p>iii) No, E° cell or $\Delta_r G^\circ$ for cell reaction can never be zero. $\Delta G^\circ = -nFE^\circ$. E° is never zero hence ΔG° will also be not equal to zero.</p>	<p>1+1+3 =5</p>

