DIRECTORATE OF EDUCATION
Govt. of NCT, Delhi

SUPPORT MATERIAL

(2023-2024)

Class : XII

CHEMISTRY

Under the Guidance of

Shri Ashok Kumar
Secretary (Education)

Shri Himanshu Gupta
Director (Education)

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अशोक कुमार ,भा.प्र.से
सचिव (शिक्षा)
ASHOK KUMAR, IAS
Secretary (Education)

सत्यमेव जयते

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D.O. NO. : DE.5/228/Exam/Message/SM/2018/1095
Dated : 24.11.2023

Message

"Children are like wet cement, whatever falls on them makes an impression."
Haim Ginott

Embracing the essence of this quote, the Directorate of Education, GNCT of Delhi is unwavering in its commitment to its core mission of delivering high-quality education to all its students. With this objective in mind, DoE annually develops support materials meticulously tailored to suit the learning needs of students from classes IX to XII.

Every year, our expert faculty members shoulder the responsibility of consistently reviewing and updating the Support Material to synchronize it with the latest changes introduced by CBSE. This continuous effort is aimed at empowering students with innovative approaches and techniques, fostering their problem-solving skills and critical thinking abilities. I am confident that this year will be no exception, and the Support Material will greatly contribute to our students' academic success.

The support material is the result of unwavering dedication of our team of subject experts. The Support Material has been specially curated for our students, with the belief that its thoughtful and intelligent utilization will undoubtedly elevate the standards of learning and will continue to empower our students to excel in their examinations.

I wish to congratulate the entire team for their invaluable contribution in creating a highly beneficial and practical Support Material for our students.

I extend my best wishes to all our students for a promising and bright future.

24.11.23
(Ashok Kumar)

HIMANSHU GUPTA, IAS
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No. PS/DE/2023/349
Dated: 29/11/2023

सत्यमेव जयते

MESSAGE

It brings me immense pleasure to present the support material for students of classes IX to XII, meticulously crafted by our dedicated subject experts. Directorate of Education is committed to empower educators and students alike by providing these resources free of cost for students of all government and government aided schools of Delhi.

The support material is an appreciable effort to align the content with the latest CBSE patterns. It has been carefully designed as a resource to facilitate the understanding, acquisition and practice of essential skills and competencies outlined in the curriculum.

The core of this support material lies in providing a framework for adopting an analysis-based approach to learning and problem-solving. It aims to prompt educators to reflect on their teaching methodologies and create an interactive pathway between the child and the text.

In the profound words of Dr A.P.J. Abdul Kalam, **"Educationists should build the capacities of the spirit of inquiry, creativity, entrepreneurial and moral leadership among students and become their role model."**

The journey of education is ongoing; it's the process, not just the outcome, which shapes us. This support material endeavours to be that catalyst of change for each student of Directorate of Education.

Let us embark on this transformative journey together, ensuring that every student feels equipped not only with the knowledge but also, with the skills and mindset to thrive in the 21st century.

I wish you all the best for all your future endeavours.

(HIMANSHU GUPTA)

Dr. RITA SHARMA
Additional Director of Education
(School/Exam)

सत्यमेव जयते

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Directorate of Education
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D.O. No. DE.5/228/Exam/Message/SM/2018/1096
Dated: 24.11.2023

MESSAGE

The persistent efforts of the Directorate in making the course material more accessible and student-friendly are evident in the conscientious preparation of the Support Material. Our team consistently adapts to the evolving educational landscape, ensuring that the Support Material for the various subjects of classes 9 to 12 align with the latest CBSE guidelines and syllabi prescribed for the annual examinations.

The Support Material encapsulates crucial subject-specific points and facts, tailored to suit the students, all presented in a lucid language. It is our firm belief that these resources will significantly augment the academic prowess of our students, empowering them to excel in their upcoming examinations.

I extend my heartfelt congratulations to the diligent officials and teachers whose dedication and expertise have played a pivotal role in crafting this invaluable content/resource.

I convey my best wishes to all our students for a future brimming with success. Remember, every page you read is a step towards an enlightened tomorrow.

Rita Sharma

(Dr Rita Sharma)

DIRECTORATE OF EDUCATION
Govt. of NCT, Delhi

SUPPORT MATERIAL

(2023-2024)

CHEMISTRY

Class : XII

NOT FOR SALE

PUBLISHED BY : DELHI BUREAU OF TEXTBOOKS

भारत का संविधान

भाग 4क

नागरिकों के मूल कर्तव्य

अनुच्छेद 51 क

मूल कर्तव्य - भारत के प्रत्येक नागरिक का यह कर्तव्य होगा कि वह -

(क) संविधान का पालन करे और उसके आदर्शों, संस्थाओं, राष्ट्रध्वज और राष्ट्रगान का आदर करे;

(ख) स्वतंत्रता के लिए हमारे राष्ट्रीय आंदोलन को प्रेरित करने वाले उच्च आदर्शों को हृदय में संजोए रखे और उनका पालन करे;

(ग) भारत की संप्रभुता, एकता और अखंडता की रक्षा करे और उसे अक्षुण्ण बनाए रखे;

(घ) देश की रक्षा करे और आह्वान किए जाने पर राष्ट्र की सेवा करे;

(ङ) भारत के सभी लोगों में समरसता और समान भ्रातृत्व की भावना का निर्माण करे जो धर्म, भाषा और प्रदेश या वर्ग पर आधारित सभी भेदभावों से परे हो, ऐसी प्रथाओं का त्याग करे जो महिलाओं के सम्मान के विरुद्ध हों;

(च) हमारी सामासिक संस्कृति की गौरवशाली परंपरा का महत्त्व समझे और उसका परिरक्षण करे;

(छ) प्राकृतिक पर्यावरण की, जिसके अंतर्गत वन, झील, नदी और वन्य जीव हैं, रक्षा करे और उसका संवर्धन करे तथा प्राणिमात्र के प्रति दयाभाव रखे;

(ज) वैज्ञानिक दृष्टिकोण, मानववाद और ज्ञानार्जन तथा सुधार की भावना का विकास करे;

(झ) सार्वजनिक संपत्ति को सुरक्षित रखे और हिंसा से दूर रहे;

(ञ) व्यक्तिगत और सामूहिक गतिविधियों के सभी क्षेत्रों में उत्कर्ष की ओर बढ़ने का सतत् प्रयास करे, जिससे राष्ट्र निरंतर बढ़ते हुए प्रयत्न और उपलब्धि की नई ऊँचाइयों को छू सके; और

(ट) यदि माता-पिता या संरक्षक है, छह वर्ष से चौदह वर्ष तक की आयु वाले अपने, यथास्थिति, बालक या प्रतिपाल्य को शिक्षा के अवसर प्रदान करे।

Constitution of India

Part IV A (Article 51 A)

Fundamental Duties

It shall be the duty of every citizen of India —

(a) to abide by the Constitution and respect its ideals and institutions, the National Flag and the National Anthem;

(b) to cherish and follow the noble ideals which inspired our national struggle for freedom;

(c) to uphold and protect the sovereignty, unity and integrity of India;

(d) to defend the country and render national service when called upon to do so;

(e) to promote harmony and the spirit of common brotherhood amongst all the people of India transcending religious, linguistic and regional or sectional diversities; to renounce practices derogatory to the dignity of women;

(f) to value and preserve the rich heritage of our composite culture;

(g) to protect and improve the natural environment including forests, lakes, rivers, wildlife and to have compassion for living creatures;

(h) to develop the scientific temper, humanism and the spirit of inquiry and reform;

(i) to safeguard public property and to abjure violence;

(j) to strive towards excellence in all spheres of individual and collective activity so that the nation constantly rises to higher levels of endeavour and achievement;

*(k) who is a parent or guardian, to provide opportunities for education to his child or, as the case may be, ward between the age of six and fourteen years.

Note: The Article 51A containing Fundamental Duties was inserted by the Constitution (42nd Amendment) Act, 1976 (with effect from 3 January 1977).

*(k) was inserted by the Constitution (86th Amendment) Act, 2002 (with effect from 1 April 2010).

भारत का संविधान

उद्देशिका

हम, भारत के लोग, भारत को एक [1][**संपूर्ण प्रभुत्व-संपन्न समाजवादी पंथनिरपेक्ष लोकतंत्रात्मक गणराज्य**] बनाने के लिए, तथा उसके समस्त नागरिकों को :

सामाजिक, आर्थिक और राजनैतिक **न्याय,**

विचार, अभिव्यक्ति, विश्वास, धर्म

और उपासना की **स्वतंत्रता,**

प्रतिष्ठा और अवसर की **समता**

प्राप्त कराने के लिए,

तथा उन **सब में**

व्यक्ति की गरिमा और [2][**राष्ट्र की एकता**

और अखंडता] सुनिश्चित करने वाली **बंधुता**

बढ़ाने के लिए

दृढ़संकल्प होकर **अपनी इस संविधान सभा में** आज तारीख 26 नवंबर, 1949 ई. को **एतद्द्वारा इस संविधान को अंगीकृत, अधिनियमित और आत्मार्पित करते हैं।**

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1. संविधान (बयालीसवां संशोधन) अधिनियम, 1976 की धारा 2 द्वारा (3.1.1977 से) "प्रभुत्व-संपन्न लोकतंत्रात्मक गणराज्य" के स्थान पर प्रतिस्थापित।
2. संविधान (बयालीसवां संशोधन) अधिनियम, 1976 की धारा 2 द्वारा (3.1.1977 से) "राष्ट्र की एकता" के स्थान पर प्रतिस्थापित।

THE CONSTITUTION OF INDIA

PREAMBLE

WE, THE PEOPLE OF INDIA, having solemnly resolved to constitute India into a [1]**[SOVEREIGN SOCIALIST SECULAR DEMOCRATIC REPUBLIC]** and to secure to all its citizens :

JUSTICE, social, economic and political;

LIBERTY of thought, expression, belief, faith and worship;

EQUALITY of status and of opportunity; and to promote among them all

FRATERNITY assuring the dignity of the individual and the [2][unity and integrity of the Nation];

IN OUR CONSTITUENT ASSEMBLY this twenty-sixth day of November, 1949 do **HEREBY ADOPT, ENACT AND GIVE TO OURSELVES THIS CONSTITUTION.**

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1. Subs. by the Constitution (Forty-second Amendment) Act, 1976, Sec.2, for "Sovereign Democratic Republic" (w.e.f. 3.1.1977)
2. Subs. by the Constitution (Forty-second Amendment) Act, 1976, Sec.2, for "Unity of the Nation" (w.e.f. 3.1.1977)

CHEMISTRY
CLASS-XII
2023-2024

LIST OF MEMBERS WHO REVIEWED AND REVISED SUPPORT MATERIAL OF CHEMISTRY

S. No.	Name	Designation
1	**Dr. Hans Raj Modi** (Group Leader) (ID : 20025021)	PRINCIPAL GBSSS NO. 2 Model Town, Phase III
2	**Mr. Mukesh Kumar Kaushik** (Member) (ID : 20092607)	Lecturer RPVV, Narela (ID : 1310409)
3	**Mr. Harpreet Singh** (Member) (ID : 20092637)	Lecturer RPVV, Kishan Ganj (ID:1208092)
4	**Ms. Akshma** (Member) (ID : 20171208)	Lecturer SOE, Sector-22 Dwarka (ID : 1821282)
5	**Mohd Shahwez Siddiqui** (Member) (ID : 20192038)	Lecturer RPVV, Link Road Karol Bagh (ID : 2128031)

CONTENTS

SYLLABUS FOR SESSION 2023-24
CLASS XII (THEORY)

Time: 3 Hours **70 Marks**

S. No.	UNIT	No. of Periods	Marks
2	Solutions	10	7
3	Electrochemistry	12	9
4	Chemical Kinetics	10	7
8	d -and f -Block Elements	12	7
9	Coordination Compounds	12	7
10	Haloalkanes and Haloarenes	10	6
11	Alcohols, Phenols and Ethers	10	6
12	Aldehydes, Ketones and Carboxylic Acids	10	8
13	Amines	10	6
14	Biomolecules	12	7
	Total	108	**70**

Unit II Solutions

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

Unit III 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 and law of electrolysis (elementary idea), dry cell-electrolytic cells and Galvanic cells, lead accumulator, fuel cells, **corrosion.**

Unit IV 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), concept of collision theory (elementary idea, no mathematical treatment), activation energy, Arrhenius equation.

Unit VIII d and f Block Elements

General introduction, electronic configuration, occurrence and characteristics of transition metals, g6neral trends in properties of the first-row transition metals — metallic character, ionization enthalpy, oxidation states, ionic radii, colour, catalytic property, magnetic properties, interstitial compounds, alloy formation, preparation and properties of $K_2Cr_2O_7$ and $KMnO_4$.

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

Actinoids - Electronic configuration, oxidation states and comparison with lanthanoids.

Unit IX 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; structure and stereoisomerism, the importance of coordination compounds (in qualitative analysis, extraction of metals and biological system).

Unit X Haloalkanes and Haloarenes

Haloalkanes: Nomenclature, nature of C—X bond, physical and chemical properties, optical rotation mechanism of substitution reactions.

Haloarenes: Nature of C—X bond, substitution reactions (Directive influence of halogen in monosubstituted compounds only). Uses and environmental effects of - dichloromethane, trichloromethane, tetrachloromethane, iodoform, freons, **DDT.**

Unit XI Alcohols, Phenols and Ethers

Alcohols: Nomenclature, methods of preparation, physical and chemical properties (of primary alcohols only), identification of primary, secondary and tertiary alcohols, mechanism of dehydration, uses with special reference to methanol and ethanol.

Phenols: Nomenclature, methods of preparation, physical and chemical properties, acidic nature of phenol, electrophilic substitution reactions, uses of phenols.

Ethers: Nomenclature, methods of preparation, physical and chemical properties, uses.

Unit XII Aldehydes, Ketones and Carboxylic Acids **15 Periods**

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

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

Unit XIII Amines **14 Periods**

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

Diazonium salts: Preparation, chemical reactions and importance in synthetic organic chemistry.

Unit XIV Biomolecules **18 Periods**

Carbohydrates - Classification(aldoses and ketoses), monosaccharides (glucose and fructose), D-L configuration oligosaccharides (sucrose, lactose, maltose), polysaccharides (starch, cellulose, glycogen); Importance of carbohydrates,

Proteins -Elementary idea of - amino acids, peptide bond, polypeptides, proteins, structure of proteins - primary, secondary, tertiary structure and quaternary structures (qualitative idea only), denaturation of proteins; enzymes. Hormones - Elementary idea excluding structure.

Vitamins - Classification and functions.

Nucleic Acids: DNA and RNA.

QUESTION PAPER DESIGN CLASS-XII (2023-24)

S.No.	Domains	Marks	%
1	**Remembering and Understanding:** Exhibit memory of previously learned material by recalling fact, terms, basic concepts and answers. Demonstrate understanding of facts and **idea by organizing, comparing, translating, interpreting, giving** descriptions and stating main idea.	28	40
2	**Applying:** Solve problems to new situations by applying **acquired knowledge,** facts, techniques and rules in a different way.	21	30
3	**Analyzing, Evaluating and Creating:**Examine and break information into parts by identifying motives or causes. Make inferences and find evidence to support generalizations. Present and defend opinions by making judgments about information, the validity of ideas or quality of work based on a set of criteria. Compile information together in a **different way by combining elements in a new pattern** or proposing alternative solutions.	21	30

QUESTION WISE BREAK-UP

Sections	Type of Question	Marks per Question	Total No. of Question	Total Marks
A	MCQ	01	16	16
B	VSA	02	05	10
C	SA	03	07	21
D	CASE STUDY	04	02	08
E	LA	05	03	15
	TOTAL		**33**	**70**

Choice : There will be no overall choice in the question paper.
However, internal choice in 1 question each of section-B and C, 1 question each of case studies and all questions of section-E will be given.

UNIT 2

Solutions

Points to Remember

SOLUTION: A homogeneous mixture of two or more chemically non-reacting substances, whose composition can be varied within certain limits.

- A binary solution has two constituents one solute and one solvent.
- Solvent is the component present in largest amount and solute in smaller amount(in terms of moles).
- The solutions may be gaseous, liquid or solid depending upon the physical state of solvent.

CONCENTRATION OF SOLUTION

Mass% of a component (w/w)= (mass of solute/ total mass of solution)x100

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

Volume percentage (v/v)% volume of solute per 100 mL of solution Volume%=(volume of solute/total volume of solution)×100

Mole fraction(χ): Ratio of no. of moles of one component to the total no. of the components present in the solution.
$\chi_A = n_A/n_A+n_B$, $\chi_B = n_B/n_A+n_B$, $\chi_A+\chi_B=1$
No unit, independent of temperature

Molality(m): No. of moles of solute per kg of the solvent.
Molality(m)=moles of solute/ mass of solvent in kg
Unit:mol/kg
Preferred over molarity for expressing concentration as it is independent of temperature.

Molarity(M): The number of moles of solute per litre or per dm^3 of the solution.
M=Moles of solute/volume of solution(in L) Unit: mol/L
• **Changes with change in temperature due to change in volume of solution.**

Parts per million (ppm): part of a component per million (10^6) parts of the solution. ppm=no. of parts of the component $x10^6$/total no. of parts of all components of the solution. It is used when a solute is present in trace quantities

HENRY'S LAW: "The partial pressure of the gas in vapour phase (*p*) is proportional to the mole fraction of the gas (χ) in the solution"

$p=K_H\chi$. K_H is Henry's law constant.

Higher the value of K_H at a given pressure, the lower is the solubility of the gas in the liquid.

Applications of Henry's Law

(i) **Carbonated beverages:** To increase the solubility of CO_2 in soft drinks and soda water, the bottle is sealed under high pressure.

(ii) **In deep sea diving.** To avoid bends, toxic effects of high concentration of nitrogen in the blood, the tanks used by scuba divers are filled with air diluted with He.

(iii) **For climbers or people living at high altitude.** Concentration of O_2 in the blood and tissues is so low that they feel weak and are unable to think properly, a disease called anoxia.

RAOULT'S LAW

FOR A SOLUTION OF VOLATILE LIQUIDS: The partial vapour pressure of each component of the solution is directly proportional to its mole fraction present in solution. If A and B are the two volatile components of solution then

$$p_A = p_A^0 \chi_A$$

$$p_B = p_B^0 \chi_B$$

Where p_A and p_B are partial vapour pressure of component 'A' and 'B' respectively in solution. p_A^0 and p_B^0 are vapour pressure of pure components 'A' and 'B' respectively.

FOR A SOLUTION CONTAINING NON-VOLATILE SOLUTE: The vapour pressure of the solution is directly proportional to the mole fraction of the solvent.

$$p_A \propto \chi_A$$
$$p_A = p^0 \chi_A$$

Effect of adding non-volatile solute on vapour pressure of a liquid. The vapour pressure of a liquid decrease if some non-volatile solute is dissolved in it because some molecules of the solvent on the surface are replaced by the molecules of the non-volatile solute.

- **Raoults' law becomes a special case Henry's law** in which K_H becomes equal to P_A^0, i.e., vapour pressure of pure solvent.

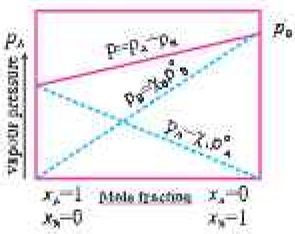
TYPES OF LIQUID-LIQUID SOLUTIONS ON THE BASIS OF RAOULT'S LAW
(Let A and B be the two liquids in solution.)

IDEAL SOLUTIONS

- Solutions which strictly obey Raoult's law over the entire range of concentration
- The interactions between solute and solvent are similar to those in pure components.

$$P_A = P_A^0 \chi_A,\ P_B = P_B^0 \chi_B$$
$$\Delta H_{mix} = 0$$
$$\Delta V_{mix} = 0$$

- Benzene + toluene, hexane + heptane, bromeothane + chloroethane



Graph for an ideal solution

NON-IDEAL SOLUTIONS

- Solutions which do not obey Raoult's law over the entire range of concentration
- The interactions between solute and solvent are different from those of pure components.

$$P_A \neq P_A^0 \chi_A,\ P_B \neq P_B^0 \chi_B$$
$$\Delta H_{mix} \neq 0$$
$$\Delta V_{mix} \neq 0$$

- Two types (i) Solutions showing positive deviations from Raoult's law.
  (ii) Solutions showing negative deviations from Raoult's law.

TYPES OF NON-IDEAL SOLUTIONS

NON-IDEAL SOLUTIONS SHOWING POSITIVE DEVIATION FROM RAOULT'S LAW

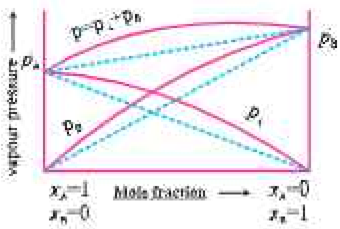
- solute - solvent interactions are weaker than solute - solute and solvent - solvent interaction

$p_A > p_A^0 \chi_A$; $p_B > p_B^0 \chi_B$

$\Delta_{mix}H > 0$

$\Delta_{mix}V > 0$

e.g. Acetone and ethanol, Water and ethanol, Acetone and benzene.



NON-IDEAL SOLUTIONS SHOWING NEGATIVE DEVIATION FROM RAOULT'S LAW

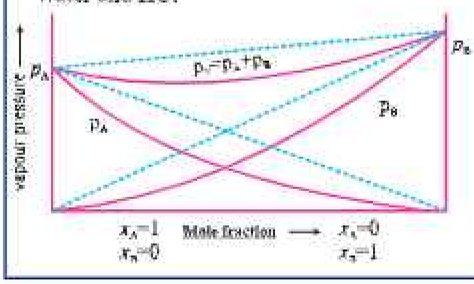
- solute - solvent interactions are stronger than solute - solute and solvent - solvent interaction

$p_A < p_A^0 \chi_A$; $p_B < p_B^0 \chi_B$

$\Delta_{mix}H < 0$

$\Delta_{mix}V < 0$

e.g. Acetone and aniline, Water and nitric acid, Water and HCl



AZEOTROPES

Liquid mixture, having the same composition, in liquid and vapour phase and boiling like a pure liquid is called a constant boiling mixture or an azeotropic mixture or an azeotrope.

MINIMUM BOILING AZEOTROPE

Minimum boiling azeotropes form when solutions exhibit positive deviation from Raoult's law. e.g. 95% ethanol - water mixture.

MAXIMUM BOILING AZEOTROPE

Maximum boiling azeotropes form when solutions exhibit negative deviation from Raoult's law. e.g. 68% nitric acid- water mixture.

COLLIGATIVE PROPERTIES

Physical properties of dilute solutions that depend upon the number of solute particles present in the solution irrespective of their nature.

RELATIVE LOWERING IN VAPOUR PRESSURE

$\chi_B = \frac{P_A^0 - P}{P_A^0}$

P_A^0 = Vapour pressure of solvent, P = Vapour pressure of solution

Where $P_A^0 - P/P_A^0$ is relative lowering in vapour pressure. χ_B = mole fraction of solute

$$\chi_B = \frac{n_B}{n_A + n_B}$$

For dilute solution, $n_B << n_A$, hence n_B is neglected in the denominator.

$$\frac{P_A^0 - P}{P_A^0} = \frac{n_B}{n_A}$$

$$\frac{P_A^0 - P}{P_A^0} = \frac{w_B}{M_B} \times \frac{M_A}{w_A}$$

w_B = mass of solute, M_B = molar mass of solute

w_A = mass of solvent, M_A = molar mass of solvent

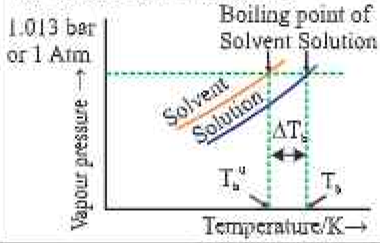
ELEVATION IN BOILING POINT (ΔT_b)

$\Delta T_b \propto m$, $\Delta T_b = k_b m$; m=molality

k_b = molal elevtion constant / Ebullioscopic constant. It is the elevation in boiling point when the molality of solution is unity. SI unit : K kg mol^{-1}

Elevation in boiling point and Molar mass of solute $M_B = k_b\, 1000 w_B/\Delta T_b W_A$

M_B=Molar mass of solute, w_B = mass of solute, w_A= mass of solvent (in gram)



COLLIGATIVE PROPERTIES

DEPRESSION IN FREEZING POINT (ΔT_f)

$\Delta T_f \propto m$, $\Delta T_f = K_f m$

K_f = molal depression constant / Cryoscopic constant. It is the depression in freezing point when the molality of solution is unity. SI unit : K kg mol^{-1}

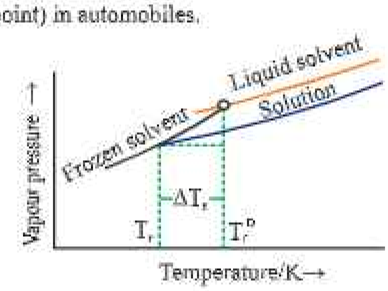
Depression in freezing point and Molar mass of solute

$M_B = k_f\, 1000 w_B/\Delta T_f w_A$

M_B= Molar mass of solute, w_B = mass of solute,

W_A=mass of solvent (in gram)

APPLICATION : Ethylene glycol is used as antifreeze (causes depression in freezing point) in automobiles.



n_B

OSMOTIC PRESSURE (π)

The excess pressure that must be applied to a solution side to prevent osmosis i.e. to stop the passage of solvent molecules into it through semi-permeable membrane is called osmotic pressure.

$\pi \propto C$, $\pi \propto T$, $\pi = CRT$,

C = Molarity of solution, $C = n_B/V$, V=volume of solution (L), n_B=no. of moles of solute

$\pi V = n_B RT$

$\pi = w_B RT/M_B V$

R=0.0821L atm K^{-1} mol^{-1} ; T=Temperature in Kelvin

ISOTONIC SOLUTIONS

Two solutions having same osmotic pressure at a given temperature are called isotonic solutions. **Hypertonic solution** have higher osmotic pressure and **Hypotonic solution** have lower osmotic pressure than the other solution. 0.91% of sodium chloride is isotonic with fluid present inside human red blood cells.

REVERSE OSMOSIS- If a pressure higher than osmotic pressure is applied on the solution the solvent will flow from the solution into the pure solvent through the semi permeable membrane. It is used in the desalination of sea water.

Abnormal Molar Masses

The molar mass of a substance determined by studying colligative properties comes out to be different from their normal values, the substance is said to show abnormal molar mass.

The anomalies in molar masses or colligative properties for electrolytes are mainly due to

(i) Dissociation of molecules (ii) Association of molecules

van't Hoff factor (i)

van't Hoff factor (i) is defined as the ratio of the experimental value of the colligative property to the calculated value of the colligative property.

$$i = \frac{\text{Observed colligative property}}{\text{Calculated colligative property}}$$

OR

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

OR

$$i = \frac{\text{Normal (calculated) molar mass}}{\text{Abnormal (observed) molar mass}}$$

Case I

In case of association, observed molar mass being more than the normal, the factor (i) has value less than 1 [$i < 1$]

Case II

In case of dissociation, observed mass being less than the normal molar mass, the factor *i* has value greater than 1. [$i > 1$]

Case III

In case there is no association or dissociation the value of *i* becomes equal to one.

OBJECTIVE TYPE QUESTIONS

I MULTIPLE CHOICE QUESTIONS

1. The molarity of 98% H_2SO_4 (density= 1.8 g/mL) by weight is:
   (a) 6 M (b) 18 M
   (c) 10 M (d) 4 M
2. Which of the following does not show positive deviation from Raoult's law?
   (a) benzene + chloroform (b) benzene + acetone
   (c) benzene + ethanol (d) benzene + CCl_4
3. Which solution will have least vapour pressure?
   (a) 1 M glucose (b) 2 M glucose
   (c) 3 M glucose (d) 4 M glucose
4. Which condition is not satisfied by an ideal solution?
   (a) $\Delta_{mix} H = 0$ (b) $\Delta_{mix} V = 0$
   (c) $\Delta_{mix} P = 0$ (d) $\Delta_{mix} S = 0$
5. Azeotrope mixture are:
   (a) mixture of two solids
   (b) those will boil at different temperature
   (c) those which can be fractionally distilled
   (d) constant boiling mixtures
6. Which is temperature independent term?
   (a) w/w% (b) v/v%
   (c) w/v% (d) Molarity
7. Solute when dissolve in water
   (a) increases the vapour pressure of water
   (b) decreases the boiling point of water
   (c) decrease the freezing point of water
   (d) All of the above
8. The plant cell will shrink when placed in:
   (a) water (b) a hypotonic solution
   (c) a hypertonic solution (d) an isotonic solution

9. Two aqueous solutions S_1 and S_2 are separated by a semi-permeable membrane. S_2 has lower vapour pressure than S1 of a non -volatile solute. Then
   a) more solvent will flow from S_1 to S_2
   b) more solvent will flow from S_2 to S_1
   c) solvent from S_1 and S_2 will flow at equal rates
   d) no flow will take place
10. Temperature dependent concentration term is :
    (a) M (b) m
    (c) x (d) All of these
11. Which of the following solutions would have the highest osmotic pressure:
    (a) M/10 NaCl (b) M/10 Urea
    (c) M/10 $BaCl_2$ (d) M/10 Glucose
12. 0.5 M aqueous solution of glucose is isotonic with:
    (a) 0.5 M KCl solution (b) 0.5 M $CaCl_2$ solution
    (c) 0.5 M Urea solution (d) 1 M solution of sucrose
13. Which of the following is true for Henry's constant ?
    (a) It decreases with temperature
    (b) It increases with temperature
    (c) Independent on temperature
    (d) It do not depend on nature of gases.
14. Which one is the best colligative property for determination of molecular mass of polymer?
    (a) osmotic pressure (b) elevation in boiling point
    (c) depression in freezing point (d) osmosis
15. An azeotropic solution of two liquids has boiling point lower than either of them when it
    a) shows negative deviation from Raoult's Law
    b) shows no deviation from Raoult's Law
    c) shows positive deviation from Raoult's Law
    d) is saturated
16. Henry's law constant K_H of CO_2 in water at 25°C is 3 x 10^{-2} mol/L atm^{-1}. Calculate the mass of CO_2 present in 100 L of soft drink bottled with a partial pressure of CO_2 of 4 atm at the same temperatrue.
    (a) 5.28 g (b) 12.0 g
    (c) 428 g (d) 528 g

17. If osmotic pressure of 1 M urea is π, what will be the osmotic pressure for 2 M urea?

(a) π (b) 0.1π

(c) 2π (d) 0.2π

18. The most likely an ideal solution is:

(a) $NaCl\text{-}H_2O$ (b) $C_2H_5OH\text{-}C_6H_6$

(c) $C_7H_{16}\text{-}H_2O$ (d) $C_7H_{16}\text{-}C_8H_{18}$

19. $\Delta_{mix}H$ for solution of $CHCl_3$ and CH_3COCH_3 is.

(a) positive (b) 0

(c) negative (d) None of these

20. The solutions A, B, C and D are respectively 0.1 M glucose, 0.05 M NaCl, 0.05 M $BaCl_2$ and 0.1 M $AlCl_3$. which one of the following pairs is isotonic?

(a) A & C (b) B & C

(c) C & D (d) A & B

21. Which one of the following pairs will form an ideal solution?

(a) Chloroform and acetone (b) Ethanol and acetone

(c) n-hexane and n-heptane (d) Phenol and aniline

22. An azeotropic solution of two liquids has a boiling point lower than either of the two when it ?

(a) shows a positive deviation from Raoult's law

(b) shows a negative deviation from Raoult's law.

(c) shows no deviation from Raoult's law.

(d) is saturated.

23. Which of the following formula represents Raoult's law for a solution containing non-volatile solute?

(a) $P_{solute} = P^0_{solute} \times X_{solute}$

(b) $P = K_{H.x}$

(c) $P_{Total} = P_{solvent}$

(d) $P_{solute} = P^0_{solvent} \times X_{solvent}$

24. On mixing 20mL of acetone with 30 mL of chloroform, the total volume of the solution is

(a) <50mL (b) =50mL

(c) >50mL (d) =10mL

25. Elevation of boiling point in inversely proportional to

(a) molal elevation constant(K_b) (b) molality (m)

(c) molar mass of solute(M) (d) weight of solute (w)

26. An unknown gas 'X' is dissolved in water at 2.5 bar pressure and has mole fraction 0.04 in solution. The mole fraction of 'X' gas when the pressure of gas is doubled at the same temperature is

(a) 0.08 (b) 0.04

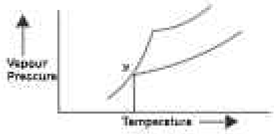
(c) 0.02 (d) 0.92

27. The boiling point of a 0.2 m solution of a non-eletrolyte in water is (k_b for water = 0.52 kg mol^{-1})

(a) 100°C (b) 100.52°C

(c) 100.104°C (d) 100.26°C

28. In the following diagram point, 'X' represents



(a) Boiling point of solution (b) Freezing point of solvent

(c) Boiling point of solvent (d) Freezing point of solution

29. A compound undergoes complete tetramerization in a given organic solvent. The van't Hoff factor 'i' is:

(a) 4.0 (b) 0.25

(c) 0.125 (d) 2.0

II FILL IN THE BLANKS

1. The sum of mole fractions of all the components i a three component system is equal to......................
2. A Solution which distill without change in composition is called ....
3. Desalination of sea water is based on the phenomenon of......................
4. Relative lowering in vapour pressure is equal to the mole fraction of ....
5. The evaporation of aqueous solution of glucose causes its molarity to ....
6. The boiling point of sea water at 1 atm pressure is .... that of distilled water.
7. The ratio of observed value of colligative property to the calculated value of colligative property is called ....
8. The most suitable colligative property to measure molecular mass of polymers is.............

9. People taking a lot of salt develop swelling or puffiness of their tissues. This disease is called..............

10. If observed molar mass of a solute is more than calculated molar mass, then the solute undergoes.................. in solution.

III ASSERTION REASON TYPE QUESTIONS

(a) Both assertion and reason are correct statements, and reason is the correct explanation of the assertion.

(b) Both assertion and reason are correct statements, but reason is not the correct explanation of the assertion.

(c) Assertion is correct, but reason is wrong statement

(d) Assertion is wrong, but reason is correct statement

1. **Assertion:** Molality is a better method to express concentration than molarity.
   Reason: Molality is defined in terms of mass of solvent and not volume of solution .

2. **Assertion:** Soda bottles are sealed under high pressure.
   Reason: High pressure increases the solubility of carbon dioxide gas in solution .

3. **Assertion:** Non-ideal solutions always form azeotropes.
   Reason: Boiling point of an azeotrope may be lower or higher than boiling points of both components.

4. **Assertion:** Benzene and hexane form an ideal solution.
   Reason : Both benzene and hexane are hydrocarbons.

5. **Assertion:** 1 molar NaCl solution has higher boiling point than one molar urea.
   Reason: NaCl dissociates into ions in solution .

6. **Assertion:** Two solutions having same osmotic pressures will also have same vapour pressures.
   Reason: Lowering of vapour pressure is not a colligative property .

7. **Assert ion :** Helium is mixed with nitrogen and oxygen in diving cylinders
   Reason: Helium has comparatively low solubility in blood.

8. **Assertion:** NaCl or $CaCl_2$ is used to clear snow on roads in the hills.
   Reason: The salts depress the freezing point of water.

9. **Assertion:** Molar mass of acetic acid in benzene calculated using colligative property is almost double the actual value.

   Reason: Acetic acid dimerises in solution.

10. **Assertion:** Vapour pressure of a solution is more that of the pure solvent.

    Reason: The solute particles occupy certain area of the surface of the solution which reduces the amount of vapour.

11. **Assertion:** When NaCl is added to water, a depression in freezing point is observed.

    Reason: The lowering of vapour pressure of a solution causes depression in the freezing point.

IV ONE WORD ANSWER TYPE QUESTIONS

1. Which of the following is a dimension less quantity : molarity, molality or mole fraction?
2. Liquid 'Y' has higher vapour pressure than liquid 'X' . Which of them will have higher boiling point?
3. N_2 and O_2 gases have K_H values 76.48 kbar an d 34.86 kbar respectively at 293 K temperature. Which one of these will have more solubility in water?
4. Name for k_b is___________.
5. Mention the unit of ebullioscopic constant (molal boiling point elevation constant).
6. What type of deviation from Raoult's law is exhibited the solution forming minimum boiling azeotrope?
7. For reverse osmosis to take place external pressure applied must be lesser than or greater than osmotic pressure?
8. Name the law which can explain the solubility of gases in liquids at different pressures.
9. Out of molarity and molality which is preferred for expressing the concentration of solution?
10. A decrease in temperature is observed on mixing ethanol and acetone. What type of deviation from Raoult's law is this?
11. What is the sum of the mole fractions of all the components in a three component system?
12. 10 cm^3 of a liquid A was mixed with 10 cm^3 of liquid B. The volume of the resulting solution was found to be 19.9 cm^3. What do you conclude?
13. Name the disease caused by low concentration of oxygen in the blood and tissues of people living at high altitude.
14. Mention a large scale use of reverse osmosis.
15. Under which conditon van't Hoff factor is less than one.

VERY SHORT ANSWER TYPE QUESTIONS (1 Mark Questions)

Q.1. What is van't Hoff factor ?

Ans. It is the ratio of normal molecular mass to observed molecular mass. It is denoted as *i*.

i = normal molecular mass/observed molecular mass

= no. of particles after association or dissociation/no. of particles before dissociation or association

Q.2. What is the van't Hoff factor in $K_4[Fe(CN)_6]$ and $BaCl_2$?

Ans. 5 and 3

Q.3. Why the molecular mass becomes abnormal ?

Ans. Due to association or dissociation of solute in given solvent.

Q.4. What role does the molecular interaction play in the solution of alcohol and water ?

Ans. Positive deviation from ideal behaviour.

Q.5. What is van't Hoff factor ? How is it related with :

(a) degree of dissociation (b) degree of association

Ans. It is the ratio of normal molecular mass to observed molecular mass. It is denoted as *i*.

i = normal molecular mass/observed molecular mass

i = no. of particles after association or dissociation/no. of particles before dissociation or association

(a) $\alpha = \dfrac{i-1}{n-1}$ (b) $\alpha = \dfrac{i-1}{1/n-1}$

Q.6. Why NaCl is used to clear snow from roads ?

Ans. It lowers freezing point of water.

Q.7. Why the boiling point of solution is higher than pure liquid ?

Ans. Due to lowering in vapour pressure.

Q.8. Henry's law constant for two gases are 21.5 and 49.5 atm, which gas is more soluble ?

Ans. K_H is inversely proportional to solubility.

Q.9. Define azeotrope. Give an example of maximum boiling azeotrope.

Hint: Refer "Points to remember"

Q.10. Calculate the volume of 75% of H_2SO_4 by weight (d = 1.8 gm/mL) required to prepare 1 L of 0.2 M solution.

Hint: $M_1 = \dfrac{\text{Mass \%} \times d \times 10}{98}$

$M_1V_1 = M_2V_2$

$= 14.5$ mL

Q.11. Why water cannot be completely separated from aqueous solution of ethyl alcohol ?

Ans. Due to formation of azeotrope at (95.4%).

Q.12. Why anhydrous salts like NaCl or $CaCl_2$ are used to clear snow from roads on hills ?

Hint : They depress freezing point of water.

Q.13. What is the effect on boiling and freezing point of a solution on addition of NaCl ?

Hint : Boiling point increases and freezing point decreases.

Q.14. Why osmotic pressure is considered as colligative property ?

Hint : It depends upon number of moles of solute present in solution.

Q.15. Liquid A and B on mixing produce a warm solution. Which type of deviation does this solution show ?

Hint : — ve deviation for from Raoult's law

Q.16. Give an example of a compound in which hydrogen bonding results in the formation of a dimer.

Hint : Carboxylic acids

Q.17. What role does the molecular interaction play in solution containing chloroform and acetone ?

Hint : H-bonding formed, results in negative deviation from Raoult's law.

Q.18. What is meant by 5% Na_2CO_3 solution (w/w)?

Ans. 5% *w*/w means 5g Na_2CO_3 dissolves in 100 g solution.

Q.19. What will be the mole fraction of C_2H_5OH in aqueous solution of C_2H_5OH when solution contain equal number of moles of water and C_2H_5OH?

Ans. Solution is equimolar, it means mole fraction of each component is 0.5.

Q.20. If at the same temperature, hydrogen is more soluble in water than helium, which of them will have a higher value of K_H?

Ans. As H_2 is more soluble than helium, so H_2 will have lower value of K_H than that of helium.

Q.21. State the formula relating to the pressure of a gas with its mole fraction in a liquid solution in contact with it

Hint: $p = K_H . x$

Q.22. If K_f for water is 1.86 K kgmol^{-1}, what is the boiling point of 0.01 molal aqueous solution of a substance which undergoes neither association nor dissociation?

Ans. $\Delta T_b = i\, K_b \, . \, m$

$$\Delta T_b = 1 \times 1.86 \times 0.01 = 0.0186$$
$$= 100.0186°C$$

Q.23. Why does sodium chloride solution freeze at a lower temperature than water?

Hint: NaCl being non-volatile solute , decreases the vapour pressure and therefore decreases the freezing point.

Q.24. Out of 0.1 molal solution of glucose and NaCl, which one will have a higher boiling point and why?

Ans. 0.1 m NaCl solution will have higher boiling point because it dissociates in the solution. As a result, number of moles of the solute in solvent is higher in case of NaCl than glucose.

Q.25. Ionic compounds are soluble in water but they are insoluble in organic solvents.

Give reason.

Hint: "Like dissolves like"

SHORT ANSWER TYPE QUESTIONS (2 or 3 Marks Questions)

Q.1. State Henry's law. What is the significance of K_H ?

Ans. **Henry's Law:** It states that "the partial pressure of the gas in vapour phase (p) is directly proportional to the mole fraction of the gas (x) in the solution", and is expressed as : $p = K_H x$ where, K_H is the Henry's Law constant

Significance of K_H : Higher the value of Henry's law constant K_H, the lower is the solubility of the gas in the liquid.

Q.2. How is that measurement of osmotic pressure is more widely used for determining molar masses of macromolecules than the elevation in boiling point or depression in freezing point of their solutions?

Ans : The osmotic pressure method has the advantage over elevation in boiling point or depression in freezing point for determining molar masses of macromolecules because

1. Osmotic pressure is measured at the room temperature and the molarity of solution is used instead of molality.

2. Compared to other colligative properties, its magnitude is large even for very dilute solutions.

Q.3. Equal moles of liquid P and Q are mixed. What is the ratio of their moles in the vapour phase? Given that $P_P° = 2 \times P_Q°$.

Hint: Since equal moles of P and Q are mixed

$\Rightarrow$ Mole fraction of P = Mole fraction of Q = x = 1/2

$P_P = p°_P \times 1/2 = 2 \times P_Q° \times 1/2 = P_Q°$

$P_Q = P°_Q \times 1/2 = P_Q°/2$

- In vapour phase, let the total pressure be P

$\Rightarrow$ $y_1 = P_P / P = P_Q^0 / p$

$\Rightarrow$ $y_2 = P_Q / P = (P°_Q/2) / P$

$\Rightarrow$ $y_1/y_2 = 2/1$

- Ratio of moles of P and Q in vapour phase = $y_1 : y_2 = 2 : 1$

$\Rightarrow$ **P:Q = 2:1**

Q.4. On mixing liquid X and Y, volume of the resulting solution decreases. What type of deviation from Raoult's law is shown by the resulting solution ? What change in temperature would you observe after mixing liquids X and Y ?

Hint: Negative; Increase in temp.

Q.5. Explain the significance of Henry's constant (K_H). At the same temperature, hydrogen is more soluble in water than helium. Which of them will have higher value of K_H and why ?

Hint: Significance of K_H Higher the value of Henry's law constant K_H ,the lower is the solubility of the gas in the liquid ; He has higher value of K_H

Q.6. How many grams of KCl should be added to 1 kg of water to lower its freezing point to — 8.0°C ? (K_f=1.86 K kg mol^{-1})

Ans. Since KCl dissociate in water completely, $i = 2$.

$$\Delta T_f = iK_f . m$$

$$m = \Delta T_f / i K_f$$

$$= \frac{8}{2 \times 1.86}$$

$$m = 2.15 \text{ mol/kg}$$

Grams of KCl = 2.15 × 74. = 160.2 g/kg

Q.7. Why is freezing point depression of 0.1 M sodium chloride solution nearly twice that of 0.1 M glucose solution?

Hint: Colligative properties α number of particles.

NaCl is a strong electrolyte and gives two particles on dissociation, but glucose being non-electrolyte does not dissociate and remains as a single particle

Q.8. a) Why is an increase in temperature observed on mixing chloroform and acetone?

b) Why does sodium chloride solution freeze at a lower temperature than water?

Ans: a) The bonds between chloroform molecules and molecules of acetone are dipole-dipole interactions but on mixing, the chloroform and acetone molecules, they start forming hydrogen bonds which are stronger bonds resulting in the release of energy. This gives rise to an increase in temperature.

b) When a non- volatile solute is dissolved in a solvent, the vapour pressure decreases. As a result, the solvent freezes at a lower temperature.

Q.9. Define reverse osmosis. Write its one use.

Hint: If the pressure applied on the solution is greater then the osmotic pressure than the solvent molecules start to move from solution into solvent through a semipermeable membrane this process called the reverse osmosis. ; Desalination of water.

Q.10.Why does an azeotropic mixture distills without any change in composition ?

Hint : It has same composition of components in liquid and vapour phase.

Q.11.Under what condition Van't Hoff factor is :

(a) **equal to 1 ? (b) less than 1 ? (c) more than 1 ?**

Hint: (a) When the solute neither associates nor dissociates in solution , i is equal to I.

(b)When the solute under goes association in solution , i is less than 1.

(c) When the solute under goes dissociation in solution , i is more than 1.

Q.12. An aqueous solution of 2% non-volatile exerts a pressure of 1.004 Bar at the normal boiling point of the solvent. What is the molar mass of the solute ?

Hint:

$$\frac{P^{\circ}_A - P_A}{P^{\circ}_A} = \frac{W_B \times m_A}{m_B \times W_A}$$

$$\frac{1.013 - 1.004}{1.013} = \frac{2 \times 18}{m_B \times 98}$$

$$m_B = 41.35 g/mol$$

Q.13. Why is it advised to add ethylene glycol to water in a car radiator in hill station ?

Hint: Anti-freeze.

Q.14. Calculate the molarity of pure water (*d* = 1 g mL^{-1}).

Ans. Density of water = 1 g mL^{-1}

Mass of 1000 mL of water = V × *d*

= 1000 mL × **1** g/mL

= 1000 g

Moles of water = $\frac{1000}{18}$ = 55.55 mol

Now, mole of H_2O present in 1000 mL or **1 L** of water.

So, molarity = 55.55M

Q.15. Define Henry's law. Give their two application.

Hint: Refer"Points to remember"

Q.16. The dissolution of ammonium chloride in water is endothermic process. What is the effect of temperature on its solubility ?

Ans. Since dissolution of NH_4Cl in water is endothermic process, its solubility increases with rise in temperature (*i.e.,* Le-Chatelier process).

Q.17. Two liquids A and B boil at 145°C and 190°C respectively. Which of them has higher vapour pressure at 80°C ?

Ans. Lower the boiling point more volatile is the respective compound. Therefore, liquid A will have higher vapour pressure at 80°C.

Q.18. Why is liquid ammonia bottle first cooled in ice before opening it ?

Ans. At room temperature, the vapour pressure of liquid ammonia is very high. On cooling vapour pressure decreases, therefore the liquid ammonia will not splash out.

Q.19 Determine the amount of $CaCl_2$ dissolved in 2.5L at 27°C such that its osmotic pressure is 0.75 atm at 27°C. (*i* for $CaCl_2$ = 2.47)

Ans. For $CaCl_2$,

$$i = 2.47$$

$$\pi = iCRT$$

$$= i\frac{n_B}{V} \times RT$$

$$0.75 = \frac{2.47 \times n_B \times 0.082 \times 300}{2.5}$$

$$n = \frac{0.75 \times 2.5}{2.47 \times 0.082 \times 300}$$

$$n_B = 0.0308 \text{ mol}$$

Amount of $CaCl_2$ = 0.0308 mol × 111g mol^{-1}

= 3.418g

Q.20. Determine the osmotic pressure of a solution prepared by dissolving 25 mg of K_2SO_4 in 2 litre of water at 25°C assuming that it is completely dissociated.

Ans. If K_2SO_4 is completely dissociated,

$$K_2SO_4 \Rightarrow 2K^+ + SO_4^{2-}$$

$$i = 3$$

Mol mass of K_2SO_4 = 2 × 39 + 32 + 4 × 16= 174 g mol^{-1}

$$\pi = iCRT$$

$$= \frac{W_B \times RT}{M_B \times V}$$

$$= \frac{3 \times 25 \times 10^{-3} \times 0.082 \times 298}{174 \times 2.0}$$

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

Q.21. If the solubility product of CuS is 6 x 10^{-16}, calculate the maximum molarity of CuS in aqueous solution.

Ans. K_{sp} of CuS = 6 × 10^{-16}

If S is the solubility, then

CuS —> $Cu^{2+} + S^{2-}$

$[Cu^{2+}]$ = S, $[S^{2-}]$ = S

K_{sp} = $[Cu^{2+}][S^{2-}]$ = S × S = S^2

Solubility S = $\sqrt{K_{sp}} = \sqrt{6 \times 10^{-16}}$

= 2.45 × 10^{-8} M

Highest molarity = 2.45 × 10^{-8} M

Q.22 Suggest the most important type of intermolecular attractive interaction in the following pairs:

(a) n-hexane and n-octane (b) I_2, and CCl_4

(c) $NaC1O_4$ and water

Ans. (a) van der Waals interaction

(b) van der Waals interaction

(C) Ion-dipole interaction

23. The vapour pressure of water is 12.3 kPa at 300K. Calculate vapour pressure of 1 molal solution of a non-volatile solute in it.

Ans. Mole fraction of solute =

$$\frac{1}{1+\frac{1000}{18}} = 0.0177$$

$$\frac{P_A^0 - P}{P_A^0} = 0.0177$$

$$\frac{12.3 - P_A}{12.3} = 0.0177$$

$$P_A = 12.08 \text{ Kpa}$$

Q.24. 6.90M solution of KOH in water contains 30% by mass of KOH. Calculate the density of the KOH solution. (Molar mass of KOH = 56 g mol^{-1})

Ans. Mass of KOH = 30 g

$$M = \frac{n_B}{v(mL)} \times 1000$$

$$= \frac{W_B}{M_B \times V(mL)} \times 1000 = \frac{30}{56 \times V} \times 1000$$

$$6.90 = \frac{30 \times 1000}{56 \times V}$$

$$V = \frac{30 \times 10000}{56 \times 6.90} = 81.43mL$$

$$d = \frac{M}{V}$$

$$= \frac{100}{81.43} = 1.28gmL^{-1}$$

Q.25. An anti-freeze solution is prepared from 222.6 g of ethylene glycol $C_2H_4(OH)_2$ and 200 g of water. Calculate the molality of the solution. If the density of this solution be 1.072 g L^{-1}, what will be the molarity of the solution ?

Ans. M_B of $C_2H_4(OH)_2 = 62\ gmol^{-1}$

$$\text{Molality} = \frac{n_B}{W_A} \times 1000 = \frac{W_B}{M_B x W_B} \times 1000 = \frac{222.6x1000}{56 \times 200}$$

$$= 17.95m$$

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}}$$

$$\text{So. Volume} = \frac{\text{Mass}}{\text{Density}} = \frac{422.6}{1.072} = 394.22\ mL$$

$$M = \frac{n_B}{V} \times 1000$$

$$= \frac{222.6}{394.22 \times 62} \times 1000 = 9.11M$$

Q.26. What would be the molar mass of compound if 6.21 g of it is dissolved in 24.0g of $CHCl_3$ from a solution that has a boiling point of 68.04°C. The boiling point of pure chloroform is 61.7°C and the boiling point elevation constant K_b for chloroform is 3.63°C/m.

Ans. Elevation in boiling point $\Delta T_b = 68.04 - 61.7 = 6.34°C$

Mass of substance $W_B = 6.21$ g

Mass of $CHCl_3$, $W_A = 24.0$ g

$K_B = 3.63$ °C/m

$$M_B = \frac{K_b \times W_B \times 1000}{\Delta T_b \times W_A} = \frac{3.63 \times 6.21 \times 1000}{6.34 \times 24}$$

$$= 148.15 g\ mol^{-1}$$

Q.27 A solution of glycerol ($C_3H_8O_3$) in water was prepared by dissolving some glycerol in 500 g of water. This solution has a boiling point of 100.42°C while pure water boils at 100°C. What mass of glycerol was dissolved to make the solution ? (K_b= 0.512 K kg mol^{-1})

Ans. Given w_1= 500g

Boiling point of solution(T_b)=100.42^{0}C

$K_b(H_2O)$=0.512Kkgmol^{-1}

$M_2(C_3H_8O_3)=3\times12+8\times1+3\times16=92gmol^{-1}$

$\Delta T_b=T_b-T_b^0=373.42-373K=0.42K$

As we know $$\Delta T_b = \frac{K_b.w_2\times1000}{M_2\times w_1} \Rightarrow w_2 = \frac{\Delta T_b\times M_2\times w_1}{K_b\times100}$$

$$w_2= \frac{0.42K\times92g\ mol^{-1}\times500g}{0.512\ Kkg\ mol^{-1}\times1000gkg^{-1}} =37.73g$$

Q.28. 18 g of glucose ($C_6H_{12}O_6$) (molar mass = 180 g mol^{-1}) is dissolved in 1 kg of water in a saucepan. At what temperature will this solution boil ? for water = 0.52 K kg pure water = 373.1 K)

Ans. According to question,

M_1=18g mol^{-1}

M_2=180g mol^{-1}

w_1=1kg=1000g

w_2=18g K_b=0.52 K kg mol^{-1}

We know that $\Delta T_b= K_b.\ \frac{w_2}{M_2}\times\frac{1000}{w_1}$

or $$\Delta T_b=0.52\ K\ kg\ mol^{-1}\times\frac{18g}{180g\ mol^{-1}}\times\frac{1000kg^{-1}}{1000g}=0.052K$$

Since water boils at 373.15 K at 1.013 bar pressure, therefore, the boiling point of solution will be 373.15+0.052=373.202 K

LONG ANSWER TYPE QUESTIONS (5 Marks)

Q.1 (a) Define Raoult's law of binary solution containing non-volatile solute in it.

(b) On dissolving 3.24 g of sulphur in 40 g of benzene, boiling point of solution was higher than that of benzene by 0.81K (K_b = 2.53 K kg mol^{-1}). What is molecular formula of sulphur ? (Molar mass of sulphur = 32 g mol^{-1})

Ans.(a) At a given temperature, the vapour pressure of a solution containing non-volatile solute is directly proportional to the mole fraction of the solvent.

(b)
$$M_B = \frac{K_b.w_2 x1000}{\Delta T_b x W_A} = \frac{2.53x3.24 \times 1000}{0.81x40}$$

$$= 253 \text{ g mol}^{-1}$$

Let the molecular formula of sulphur = S_x

Atomic mass of sulphur = 32

Molecular mass = $32 \times x$

$32x = 253$

$x = 7.91 \approx 8$

Molecular formula of sulphur = S_8

Q.2(a) Outer shells of two eggs are removed. One of the egg is placed in pure water and the other is placed in saturated solution of NaCl. What will be observed and why ?

(b) A solution prepared by dissolving 8.95 mg of a gene fragment in 35.0 ml of water has an osmotic pressure of 0.335 torr at 25°C.Assuming the gene fragment is a non-electrolyte, determine the molar mass.

Ans. (a) In pure water the egg swells and in saturated solution of NaCl it will shrinks.

(b) Mass of gene fragment = 8.95 mg

$= 8.95 \times 10^{-3}$g

Volume of water = 35.0 mL = 35×10^{-3} L

π = 0.335 torr = 0.335/760 atm

Temp = 25 + 273 = 298 K

$$\pi = \frac{W_B RT}{M_B \times V}$$

$$\frac{0.335}{760} = \frac{8.95 \times 10^{-3} \times 0.0821 \times 298}{M_B \times 35 \times 10^{-3}}$$

$$M_B = 14193.3 \text{ g mol}^{-1}$$

Q.3 (a) **Define van't Hoff factor.**

(b) Calculate the freezing point depression expected for 0.0711M aqueous solution of Na_2SO_4. If this solution actually freezes at — 0.320°C, what would be the value of van't Hoff factor ?(K_f= 1.86°C mol^{-1})

Ans.(a) **van't Hoff factor :** It is the ratio of the normal molar mass to the observed molar mass of the solute.

(b) $\Delta T_f = K_f \times m$

$\Delta T_f = 1.86 \times 0.0711 = 0.132$

Observed freezing point = 0 – (–0.320) = 0.320°C

$$i = \frac{\text{Observed freezing point}}{\text{Calculate freezing point}}$$

$$= \frac{0.320}{0.132} = 2.42$$

Q.4. (a)**What is the value of *i* when solute is associated and dissociated ?**

(b)**Calculate the freezing point of an aqueous solution containing 10.50 g of $MgBr_2$ in 200 g of water. (Molar mass of $MgBr_2$ = 184, K_f = 1.86 K kg mol^{-1})**

Ans. (a) $i < 1$ when solute is associated and

$i > 1$ when solute is dissociated.

(b) $$m = \frac{n_B \times 1000}{W_A(g)}$$

$$= \frac{W_b \times 1000}{W_B \times W_A} = \frac{10.50 \times 1000}{184 \times 200} = 0.2853M$$

$MgBr_2$ ionizes as $MgBr_2 \rightarrow Mg^{2+} + 2Br^-$

$i = 3$

$\Delta T_f = i \times K_f \times m$

$= 3 \times 1.86 \times 0.2853$

$= 1.59$

Freezing point = 0 – 1.59°C = –1.59°C

Q.5 (a) What is the value of i for $Al_2(SO_4)_3$ when it is completely dissociated ?

(b) Calculate the boiling point of a solution prepared by adding 15.00 g of NaCl to 250 g of water. (K_b = 0.512 K kg mol^{-1} and molar mass of NaCl = 58.44 g mol^{-1})

Ans. (a) $Al_2(SO_4)_3 \rightarrow 2Al^{3+} + 3SO_4^{2-}$

$$i = 5$$

(b) $$\Delta T_b = \frac{iK_b \times 1000 \times W_B}{W_A \times M_B}$$

$NaCl \rightarrow Na^+ + Cl^-$

$$i = 2$$

$$\Delta T_b = \frac{2 \times 0.512 \times 1000 \times 15}{250 \times 58.44}$$

$$= 1.05$$

Boiling Point of solution = 100 + 1.05 = 101.05°C

Q.6 (a) Calculate the freezing point of solution when 1.9 g of $MgCl_2$ (M = 95g mol^{-1}) was dissolved in 50g of water, assuming $MgCl_2$ undergoes complete ionization. (K_f for water = 1.86K kg mol^{-1}).

(b) *(i)* Out of 1 M glucose and 2 M glucose, which one has a higher boiling point and why?

ii*)* What happens when the external pressure applied becomes more than the osmotic pressure of solution?

Ans. (a)

$$\Delta T_f = \frac{iK_f \times w_B \times 1000}{M_B \times w_A}$$

$$\Delta T_f = 3 \times (1.86 \times 1.9/95 \times 50) \times 1000 = 2.23K$$

$$T_f^\circ - T_f = 2.25 \text{ K}$$

$$273.15 - T_f = 2.23$$

$$T_f = 270.92 \text{ K}$$

(b) (i) 2 M glucose; More number of particles/less vapour pressure

(ii) Reverse osmosis

Q.7. (a) When 2.56 g of sulphur was dissolved in 100 g of CS_2, the freezing point lowered by 0.383 K. Calculate the formula of sulphur S_x [K_f for CS_2 = 3.83 K Kg mol^{-1}. Atomic mass of sulphur = 32 g mol^{-1}]

(b) Blood cells are isotonic with 0.9% sodium chloride solution. What happens if we place blood cells in *a* solution containing.

(i) 1.2% sodium chloride solution?

(ii) 0.4% sodium chloride solution?

Ans. (a)

$$\Delta T_f = \frac{K_f \times w_b \times 1000}{M \times w_a}$$

$$0.383 = \frac{3.83 \times 2.56 \times 1000}{M \times 100}$$

$$M = 256$$

Let molecular formula of sulphur = Sx, its mol mass = 32x

$$\therefore \quad 32x = 256$$

$$x = 8, \quad S_8$$

(b) (i) Shrinks (ii) Swells

Q.8. (a) How will you determine the molecular mass from the relative lowering of vapour pressure?

(b)) At 298 K, the vapour pressure of water is 23.75 mm Hg. Calculate the vapour pressure at the same temperature over 5% aqueous solution of urea NH_2CONH_2.

Hint: (i) Refer "Points To Remember"

(ii) According the Raoult's law,

Subtituting the values, we have $\frac{P^0 - P_s}{P^\circ} = \frac{w_2}{M_2} \times \frac{M_1}{w_1}$

$$\frac{23.75 - P_s}{23.75} = \frac{5 \times 18}{60 \times 95}$$

$$\Rightarrow \quad 23.75 - P_s = \frac{5 \times 18}{60 \times 95} \times 23.75 = 0.375$$

$$\therefore \quad P_s = 23.75 - 0.375 = 23.375 \text{ mm}$$

Q9. (a) List three points of differences between ideal solution and non-ideal solution.

(b) Calculate the boiling point elevation for a solution prepared by adding 10 g of $CaCl_2$ to 200 g of water. (K_b for water = 0.512 K kg mol^{-1}, Molar mass of $CaCl_2$ =111 g mol^{-1})

(a) Refer " Points to remember"

(b) $\Delta T_f = i\,K_b\,m = i\,K_b \cdot \frac{w_2}{M_2} \times \frac{1000}{w_1}$

For $CaCl_2$: $i = 2$

$K_b = 0.512$ K kg mol^{-1}

$$\Delta T_b = 2 \times 0.512 \times \frac{10}{111} \times \frac{1000}{200}$$

$\therefore \quad \Delta T_b = 0.461K$

Q10. (i) Give reason for the following:

(a) Cold drink bottles are *sealed* at high pressure CO_2

(b) Aquatic species are more comfortable in cold water than in warm water.

(ii) Calculate the amount of KCl which must be added to 100 g of water so that water freezes at - 2.0°C. Assume that KCl undergoes complete dissociation. [Given, K_f for water 1.86 K/m]

Ans. (a) CO_2 is less soluble water, so according to Henry's law to increase its solubility bottles are sealed at high pressure of CO_2

(b) In warm water K_H value of CO_2 greater than cold water, consequently solubility of CO_2 in water increases with decrease of temperature. Hence aquatic species are more comfortable in cold water rather than in warm water.

(ii) $KCl \rightarrow K^+ + Cl^-$

van't Hoff factor (i) = $\frac{2}{1} = 2$

According to formula $\Delta T_f = iK_f\,m \Rightarrow 2 = 2 \times 1.86 \times m$

$\therefore \quad m = \frac{1}{1.86} = 0.538$ m

Amount of KCl dissolved in 100g $= \frac{0.538}{1000} \times 100 \times 74.5 = 4.0008g$

[Molar mass of KCl = 74.5 g mol^{-1}]

CASE STUDY BASED QUESTION

1. **Read the passage given below and answer the qu est ions that follow:**

Dissolution of solids in water can be accompanied by absorption or evolution of heat i.e. dissolution process may be exothermic or endothermic in nature but dissolution of gases in water is an exothermic process. Dissolution of a substance in water is either due to ion dipole interaction or by hydrogen bond formation.

Dissolution of gases in water is highly affected by pressure. The quantitative relationship between the solubility of gas in liquid and pressure is given by Henry's law in the form of mathematical relationship $p=K_H\chi_B$.

(A) **Dissolution of glucose in water can be explained by:**

(a) Hydrogen bond (b) ion-ion interaction

(c) vander Waals' force (d) ion- dipole interaction

(B) **Solubility of KCl in water increases with the rise in temperature. This means that enthalpy of dissolution of KCl in water:**

(a) $=0$ (b) <0

(c) >0 (d) unpredictable

(C) **The value of K_H for N_2 gas in water at 298K is 86.76k bar, the value of K_H for N_2 in water at 303K in kbar is :**

(a 86.76 (b) >86.7 6

(c) <86.76 (d) unpredictable

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

Many biological processes depend on osmosis, which is a spontaneous process by which the solvent molecules pass through a semi permeable membrane from a solution of lower concentration to a solution of higher concentration. The name osmosis is derived from the Greek word 'osmosis' which means 'to push'. It is also important to know that the semipermeable membrance selectivity allows certain molecules in the solution to pass through it but not others. Two solutions having same osmotic pressure at a given temperature are called isotonic solutions. When such solutions are separated by a semipermeable membrane, solvent flow between one to the other one in either direction is same, i.e. the net solvent flow between the two isotonic solution is zero.

In the following questions a statement of assertion followed by a statement or reason is given. Choose the correct answer out of the following choices.

a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

b) Assertion and reason both are correct statements reason is not correct explanation for assertion.

c) Assertion is correct statement but reason is wrong statement.

d) Assertion is wrong statement but reason is correct statement.

(A) **ASSERTION:** Among all the colligative properties, osmotic pressure measurement provides better method for determination of the molecular mass of the solute.

REASON: Osmotic pressure measurement cannot be carried at room temperature.

(B) **ASSERTION**: The osmotic pressure of 0.1 M urea solution is less than 0.1 M NaCl solution.

REASON : Osmotic pressure is not a colligative property.

(C) **ASSERTION** : The molecular mass of polymers cannot be calculated using the boiling point or freezing point method.

REASON : The boiling point method for determining the molecular mass is used for compounds stable at high temperature.

(D) **ASSERTION** : The elevation in boiling point for two isotonic solutions is same.

REASON : The boiling point depends upon concentration of solute.

3. **Read the passage given below and answer the questions that follow:**

The colligative property of a solution is a property that depends only on the number of solute particles present, not on their identity. An ideal solution is a solution in which all components obey Raoult's law (i.e., $P_A = x_A P^0_A$) throughout the composition range. The vapour pressure of a binary volatile mixture is $P = P^0_B + (P^0_A - P^0_B)\chi_A$. The composition of the vapour is given by $Y_A = x_A P_A^0 / P_B^0 + (P_A^0 - P_B^0)x_A$ and $Y_B = 1 - Y_A$. The total vapour pressure of a mixture is $P = P_A^0 P_B^0 / P_A^0 + (P_B^0 - P_A^0)Y_A$. Azeotrope is a mixture that boils without change in composition. In colligative properties, the elevation of boiling point is given by $\Delta T_b = k_b m$ and the depression of freezing point by $\Delta T_f = k_f m$. During dissociation of ionic electrolytes, the van't Hoff factor equals, $i = 1 + (n-1)\alpha$.

During association of electrolytes, $i = 1 - \beta + \beta/n$

Here α and β are the degrees of dissociation and association, respectively, of electrolytes.

(A) **The vapour-phase compositions in two binary liquid mixtures follow:**

(a) Boyle's law (b) Dalton's law

(c) Raoult's law (d) Henry's law

(B) **The mole fraction of a solute is 0.4. The relative lowering of vapour pressure is :**

(a) 60% (b) 80%

(c) 40% (d) 20%

(C) **Which is not a colligative property?**

(a) Elevation in boiling point (b) Boiling point

(c) Depression in freezing point (d) Osmotic pressure

(D) **The most accurate method for the measurement of molar mass is:**

(a) osmotic pressure (b) ebullioscopy

(c) cryoscopy (d) Raoult's law

ANSWERS

I MULTIPLE CHOICE QUESTIONS

1.	(b)	2.	(a)	3.	(d)	4.	(d)	5.	(d)	6.	(a)	7.	(c)
8.	(c)	9.	(a)	10.	(a)	11.	(c)	12.	(c)	13.	(b)	14.	(a)
15.	(c)	16.	(d)	17.	(c)	18.	(d)	19.	(c)	20.	(d)	21	(c)
22	(a)	23.	(c)	24.	(a)	25.	(c)	26.	(a)	27.	(c)	28.	(d)
29.	(b)												

II FILL IN THE BLANKS

1.	One	2.	Azeotropic mixture	3.	Reverse osmosis
4.	Solute	5.	Increase	6.	Greater than
7.	van' t Hoff factor	8.	Osmotic pressure	9.	Edema
10	Association				

III ASSERTION REASON TYPE QUESTIONS

1. (a)	2. (a)	3. (d)	4. (c)	5. (a)	6. (d)
7. (a)	8. (a)	9. (a)	10. (d)	11. (a)	

IV ONE WORD ANSWER TYPE QUESTIONS

1. Mole fraction	2. X	3. 0_2
4. Molal elevation constant	5. K kg mol^{-1}	6. Positive deviation
7. Greater	8. Henry's law	9. Molality
10. Positive	11. One	12. Negative deviation1
13. Anoxia	14. Desalination of sea water	
15. Association		

CASE STUDY BASED QUESTIONS:

1.	(A) a	(B) b	(C) b	
2.	(A) c	(B) c	(C) a	(D) c
3.	(A) c	(B) c	(C) b	(D) a

UNIT TEST - 1
CHAPTER-2
SOLUTIONS

TIME ALLOWED: 1 HR. **M.M. 20**

1. 250g fluoride is present in 1000 kg toothpaste sample, concentration of fluoride in ppm is 1

   (a) 250 ppm (b) 25 ppm

   (c) 2500 ppm (d) 4 ppm

2. At a given temperature, the osmotic pressure of a concentrated solution of a substance 1

   (a) is higher than that of a dilute solution.

   (b) is lower that of a dilute solution

   (c) is same as that of a dilute solution

   (d) cannot be compared with osmotic pressure of dilute solution.

3. The value of Henry's law constant K_H is: 1

   (a) Greater for gases with higher solubility

   (b) greater for gases with lower solubility

   (c) constant for all gases

   (d) not related with the solubility of gases

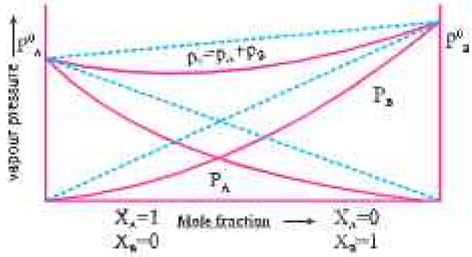
4. What type of deviation from Raoult's law is shown by the liquid mixture forming minimum boiling azeotrope? 1

5. Justify that relative lowering in vapour pressure is a colligative property. 1

6. Draw the graph between vapour pressure and temperature and explain the elevation in boiling point of a solvent in solution. 2

7. CCl_4 and water are immiscible whereas ethanol and water are miscible in all proportions. Explain . 2

8. The graphical representation of vapour pressures of two component system as a function of composition is given below. On the basis of graph answer the questions that follow: 3



(i) Are the A-B interactions weaker, stronger or of the same magnitude as A-A and B-B?

(ii) Name the type of deviation from Raoult's law exhibited by this solution.

(iii) Predict the sign of $\Delta_{mix}H$ for this system.

(iv) Predict the sign of $\Delta_{mix}V$ for this solution.

(v) Give one example of such a solution.

(vi) What type of azeotrope will this system form?

9. A solution containing 1.9g per 100 mL of KCl (molar mass=74.5 $gmol^{-1}$) is isotonic with a solution containing 3g per 100 mL of urea (molar mass=60$gmol^{-1}$). Calculate the degree of dissociation of KCl solution. Assume that both the solutions have same temperature. 3

10. (i) Boiling point is not a colligative property but elevation in boiling point is a colligative property. Comment. 5

(ii) What happens when we place the red blood cell in distilled water?

(iii) State Raoult's law for a solution containing non-volatile solute.

(iv) Define Cryoscopic constant.

UNIT TEST -2
CHAPTER-2
SOLUTION

TIME ALLOWED:1 HR. **M.M. 20**

1. Which of the following is a dimensionless quantity: molarity, molality or mole fraction? (1)
2. N_2 and O_2 gases have K_H values 76.48 kbar and 34.86 kbar respectively at 293 K temperature. Which one of these will have more solubility in water? (1)
3. Liquid 'Y' has higher vapour pressure than liquid 'X'. Which of them will have higher boiling point? (1)
4. Mention the unit of ebulioscopic constant (molal elevation constant). (1)
5. What is the maximum value of van't Hoff factor *(i)* for $Na_2SO_4.10H_20$? (1)
6. Define the term osmosis and osmotic pressure. What is the advantage of using osmotic pressure as compared to other colligative properties for the determination of molar masses of solutes in solutions? (2)
7. Account for the following: (2)
   (a) Aquatic species are more comfortable in winter than summer.
   (b) Solution of acetone and $CHCl_3$ is not an ideal solution.
8. Define isotonic solutions. A 5% solution of cane sugar (Molar mass = 342 g mol^{-1}) is isotonic with 0.887% solution of urea. Find the molar mass of urea. (3)
9. A solution containing 8 g of a substance in 100 g of diethyl ether boils at 36.86°C, whereas pure ether boils at 35.6°C. Determine the molar mass of the] solute. [For diethyl ether K_b = 2.02 K kg mol^{-1}] (3)
10. (a) How will you determine the molecular mass from the relative lowering of vapour pressure?
    (b) At 298 K, the vapour pressure of water is 23.75 mm Hg. Calculate the vapour pressure at the same temperature over 5% aqueous solution of urea NH_2CONH_2. (5)

UNIT 3

Electrochemistry

Points to Remember

Galvanic cells: A galvanic cell is a device in which chemical energy is converted into electrical energy.e.g. Daniell cell.

- Daniell cell consists of two beakers containing $CuSO_4$ and $ZnSO_4$ solutions. A zinc rod is dipped into $ZnSO_4$ while a copper rod is dipped into $CuS0_4$ solution. In this cell zinc reacts with copper (II) ions and produces metallic copper and zinc (II) ion according to the reaction :

  $Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$

  Electrons flow from anode to cathode in the external circuit. The solutions of two beakers are connected by salt bridge.

  Functions of salt bridge :

  (i) It allows the flow of current by completing the electrical circuit.

  (ii) It maintains electrical neutrality of the cell.

  Electrode Potential

  The potential difference that develops between the metal and its electrolyte is known as electrode potential.

  (a) **Oxidation potential:** The tendency of an electrode to lose electrons or to get oxidised is called oxidation potential. For example, $M(s) \longrightarrow M^{n+}(aq) + ne^-$

  (b) **Reduction potential:** The tendency of an electrode to gain electrons or to get reduced is called reduction potential. For example, $M^{n+}(aq) + ne^- \longrightarrow M(s)$

  According to latest IUPAC convention, the half reactions are always written as reduction half reaction and their potentials are represented by reduction potentials

  $$\boxed{E^o_{ox} = -E^o_{red}}$$

  Cell potential of a cell

  The potential difference between the two electrodes of galvanic cell is called the cell potential and is measured in volts.

  $$\boxed{E^o_{cell} = E^o_{cathode} - E^o_{anode}}$$

- Half cell potential or electrode potential of M^{n+}/M cannot measured directly because a half cell whether oxidation or reduction half cell cannot work on its own we cannot determine the absolute electrode potential of an electrode. To solve this problem, a reference electrode standard hydrogen electrode (SHE) or normal hydrogen electrode (NHE) is used, its standard electrode potential (oxidation as well as reduction) is arbitrarily taken as zero.

Electrochemical series or e.m.f. series

Arrangement of different electrodes in the order (increasing or decreasing) of their standard electrode potentials.

Applications of the electrochemical series:

1. **To compare the relative oxidising and reducing powers:** substances with higher reduction potentials are stronger oxidising agents.
2. **Calculation of standard emf of electrochemical cell (E°_{cell}) :**
   $E^\circ_{cell} = E^\circ_{Cathode} - E^\circ_{anode}$
3. **Comparison of the reactivity of metals:** A metal with smaller reduction potential has a strong tendency to get oxidised and can displace metals having greater reduction potential from the aqueous solution of their salts.
4. **To predict whether a metal displace hydrogen from acids :** Metals having a negative reduction potential value can displace hydrogen from acid.
5. **To predict the spontaneity of a redox reaction:** E_{cell} should be positive. If emf comes out to be negative, the direct reaction as given cannot take place, the reverse reaction may takes place.

Effect of opposing potential on the cell reaction

Consider a Daniell cell: $Zn_{(s)} \mid Zn^{2+}_{(aq)} \parallel Cu^{2+}_{(aq)} \mid Cu$

- When Subscript $E_{ext} < 1.1V$, Electrons flow from Zn rod to Cu rod hence current flows from Cu to Zn.
- When $E_{ext} > 1.1$ V, flow of current in this case occurs from zinc electrode to copper electrode, the cell now **electrolytic cell.**

NERNST EQUATION FOR SINGLE ELECTRODE

For the electrode reaction $M^{n+}(aq) + ne^- \longrightarrow M(s)$

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

Concentration of pure solid [M] should be taken as unity

$$E_{M^{n+}/M} = E^\circ_{M^{n+}/M} - \frac{2.303\ RT}{nF} \log \frac{1}{[M^{n+}]} \quad (\text{since } \log_e = 2.303 \log_{10})$$

At 298 K

$$E_{M^{n+}/M} = E^\circ_{M^{n+}/M} - \frac{0.059}{n} \log \frac{1}{[M^{n+}]}$$

Calculation of cell potential using Nernst Equation

$$E_{cell} = E^{\circ}_{cell} - \frac{2.303RT}{nF} \log_{10} \frac{[PRODUCTS]}{[REACTANTS]} \quad \text{At 298K}$$

$$E_{cell} = E^{\circ}_{cell} - \frac{0.059}{n} \log_{10} \frac{[PRODUCTS]}{[REACTANTS]}$$

EQUILIBRIUM CONSTANT (Kc) FROM NERNST EQUATION

$$E^{\circ}_{cell} = \frac{2.303RT}{nF} \log_{10} K_c$$

$$E^{\circ}_{cell} = \frac{0.059}{n} \log_{10} K_c \quad \text{at 298 K}$$

GIBB'S ENERGY CHANGE AND CELL POTENTIAL

$\Delta_r G = -nF E_{cell}$

$\Delta_r G^{\circ} = -nF E^{\circ}_{cell}$

$\Rightarrow$ **For cell reaction to be spontaneous, ΔG° must be negative, the value of E°_{cell} must be positive.**

FREE ENERGY CHANGE AND EQUILIBRIUM CONSTANT

$\Delta_r G^{\circ} = -2.303\, RT \log_{10} K_c$

CONDUCTORS: Substances that allow the flow of electric current through them are called electrical conductors .

Metallic / electronic Conductor

- Flow of electricity due to movement of electrons
- No chemical change as there is no transfer of matter.
- Faraday's law is not followed
- Conduction decreases with temperature because kernels start vibrating faster which interfere in the flow of electrons.

Electrolytic conductor

- Flow of electricity due to movement of ions
- Ions are oxidised or reduced at the electrodes, hence involve transfer of matter .
- Faraday's law is followed
- Conduction increase with temperature because dissociation increases and viscosity decreases

FACTOR AFFECTING ELECTROLYTIC CONDUCTANCE

1. **Interionic interactions**: Greater the interionic interactions lesser is the mobility of the ions, hence lesser will be conductance.
2. **Solvation of ions:** More the solvation of the ions, the lesser will be the electrical conductivity.
3. **Viscosity of the solvent:** Higher the viscosity of the solvent, lesser is the mobility of ions.
4. **Temperature:** As the temperature of the electrolytic solution is increased, the kinetic energy of the ions in the solution increases, hence their mobility increases. This results in the increase of electrical conductance of the electrolytic solution.
5. **Effect of concentration of solution:** More the concentration of electrolytic solution smaller will be its electrical conductivity.
   - Weak electrolyte ionise to a lesser extent in concentrated solution, on dilution ionisation increases which causes increase in conductivity.
   - Strong electrolyte ionise completely. On dilution interionic attraction decreases, so mobility of ions increases, consequently conductance increases.

Electrolytic conduction

Resistance (R) : A measure of obstruction in the flow of current. Unit: ohm (Ω)

$R \, \alpha \frac{l}{A} \qquad R = \rho \frac{l}{A}$

ρ, constant of proportionality, known as specific resistance or resistivity.

Resistivity or specific resistance (ρ) :

$\rho = R \, \frac{A}{l}$

Resistivity may be defined as the resistance offered by the conductor of 1 m length with area of cross section equal to 1 m^2

Unit : ohm. m or Ω. m

Conductance (G): Conductance is a measure of the ease with which current flows through the conductor. It is reciprocal of electrical resistance.

$$G = 1/R$$

Units: ohm^{-1} or Ω^{-1} *i.e.*, Siemen (S). $\qquad 1S = 1\Omega^{-1}$

Specific conductance or conductivity (κ): conductivity is the reciprocal of resistivity.

$$\kappa = 1/\rho = \frac{1}{R}.\frac{l}{a}$$, l/a is known as cell constant (G*)

κ = G. G* i.e. $\boxed{\textbf{Conductivity = Conductance x cell constant}}$

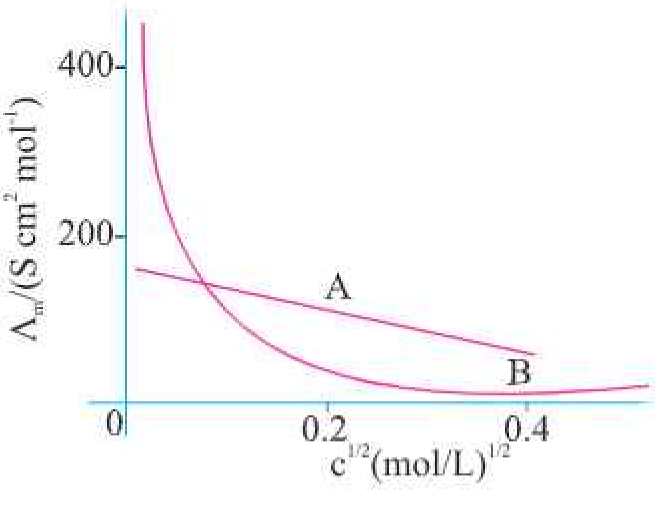
Units of k = $ohm^{-1} cm^{-1}$ or SI units are $ohm^{-1} m^{-1}$ or $S\,m^{-1}$

- **Molar conductivity (Λ_m)** - of a solution is the conductance of all the ions produced from one mole of the electrolyte dissolved in a given volume of the solution when the electrodes are one cm apart and the area of the electrodes is so large that the whole of the solution is contained between them.

  $\boxed{\Lambda_m = \kappa \times 1000/\text{Molarity}}$, Unit: $ohm^{-1}cm^{2}mol^{-1}$ (Scm^2mol^{-1}), SI unit= Sm^2mol^{-1}

- **Effect of dilution**. Conductance increases (because total no. of ions increase), conductivity decreases (because no. of ions per unit volume decreases), molar conductivity increase with dilution.
- **Variation of molar conductivity with concentration**. For a strong electrolyte, it is given by **Debye - Huckel - Onsager equation**: $\Lambda_m = \Lambda^\circ_m - A\sqrt{c}$ where A is a constant depending upon the nature of the solvent and temperature. Λ°_m **is limiting molar conductivity and it is defined as the molar conductivity of electrolyte when concentration appproaches zero i.e. at infinite dilution.**

  <u>**Graphical representation of the variation of Λ_m vs $\sqrt{c}$**</u>



It can be seen that if we plot Λ_m against $c^{1/2}$, we obtain a straight line with intercept equal to Λ^0m and slope equal to '- A'.

Reasons for increase of Λ_m with dilution.

- (Molar conductivity of a strong electrolyte increases with dilution because interionic attractions decrease with dilution. Small deviations at higher concentration are due to large interionic attractions.)
- (Molar conductivity of a weak electrolyte increases with dilution because dissociation increases with dilution.)

Inability to determine limiting molar conductivity experimentally for a weak electrolyte. Molar conductivity at infinite dilution for a strong electrolyte can be found by extrapolation to zero concentration but that of weak electrolyte cannot be thus found.

KOHLRAUSCH LAW OF INDEPENDENT MIGRATION OF IONS

The law states that limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte.

For e.g. $Al_2(SO_4)_3$ $\qquad \Lambda^0_m[Al_2(SO_4)_3] = 2\lambda^0_m(Al^{3+}) + 3\lambda^0_m(SO_4^{2-})$

Applications of Kohlrausch's Law

a) In calculation of limiting molar conductivity of weak electrolyte

b) In calculation of degree of dissociation, i.e., $\alpha = \Lambda_m/\Lambda^0_m$

c) In calculation of dissociation constant (K_c) by using value of a, $K_c = c\alpha^2/1-\alpha$

ELECTROLYTIC CELLS : The device in which conversion of electrical energy into chemical energy is done is known as electrolytic cell.

PRODUCTS OF ELECTROLYSIS: If an electrolytic solution consists of more than two ions then during electrolysis all the ions are not discharged simultaneously but certain ions are liberated at the electrode in preference to the others. This is based on the principle of preferential discharged theory which states that the ion which requires least energy is discharged first.

Batteries and Fuel Cells :

Batteries are classified as two types:

Primary: use oxidation-reduction reactions that cannot be reversed very easily

Secondary : reactions of these batteries can be reversed (rechargeable batteries)

Primary Cells :

(i)Dry cell :

Anode(-) $Zn(s) \rightarrow Zn^{2+} + 2e^-$

Cathode(+) $2MnO_{2(s)} + 2NH_4^+ + 2e^- \rightarrow Mn_2O_3 + 2NH_3 + H_2O$

(ii) Mercury Cell :

Anode(-) $Zn(Hg) + 2OH^- \rightarrow ZnO + H_2O + 2e^-$

Cathode(+) $HgO + H_2O + 2e^- \rightarrow Hg + 2OH^-$

Overall reaction —$Zn + HgO \rightarrow ZnO + Hg$

Secondary Cells :

(i)Lead storage battery

Anode(-) $Pb(s) + SO_4^{2-} \rightarrow PbSO_4 + 2e^-$

Cathode(+) $PbO_2(s) + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$

Cell reaction- $Pb(s) + PbO_2(s) + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O$

On recharging cell reaction is reversed.

(ii)**Nickel — Cadmium cell.**

Anode (-) $Cd + 2OH^- \rightarrow Cd(OH)_2 + 2e^-$

Cathode (+) $NiO(OH) + H_2O + e^- \rightarrow Ni(OH)_2 + OH^-$

Cell reaction — $Cd(s) + 2Ni(OH)_3(s) \rightarrow CdO(s) + 2Ni(OH)_2(s) + H_2O_{(l)}$

Cell reaction is reversed on recharging.

FUEL CELLS :

It is an electrochemical device used to convert free energy of a chemical reaction to electrical energy. Fuel used are in gaseous state(H_2,CH_4,CO etc)

e.g. **H_2- O_2 fuel cell.**

Reactions are

Anode (-) $2[H_{2(g)} + 2OH^-_{(aq)} \rightarrow 2H_2O_{(aq)} + 2e^-]$

Cathode(+) $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-_{(aq)}$

Cell reaction $2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)}$

Advantages

1) Efficient than any conventional source.

2) No pollution.

3) Electrodes are not affected

CORROSION : It involves the slow destruction of a metal as a result of its reaction with moisture and gases present in atmosphere. More reactive metals corrode more easily. Corrosion of Iron is called rusting.

Mechnism of Rusting

Electrochemical theory of rusting :

Impure surface of iron act as an electrochenical cell. Pure Iron act as anode and impure iron as cathode. Carbonic acid act as the electrolyte(It provide H^+ ion).

(i) $H_2O + CO_2 \longrightarrow H_2CO_3 \rightleftharpoons 2H^+ + CO_3^{2-}$

Setting up of Electrochemical cell on Iron surface

(ii) $Fe(s) \longrightarrow Fe^{2+} + 2e^-$ **(Anode)** $E° = -0.44\ V$

(iii) $O_2 + 4H^+ \longrightarrow 2\,H_2O$ **(Cathode)** $E° = +1.23\ V$

$$2Fe(s) + O_2 + 4H^+ \longrightarrow 2Fe^{2+} + 2\,H_2O \quad E_{cell} = 1.67\ V$$

Cathode is further oxidised by atmospheric oxygen to form rust. $Fe_2O_3.x\,H_2O$

(iv) $4Fe^{2+} + O_2 + 4H_2O \longrightarrow 2\,Fe_2O_3 + 8\,H^+$

$$Fe_2O_3 + xH_2O \longrightarrow Fe_2O_3.xH_2O \text{ (Rust)}$$

Prevention of corrosion :

1) **Barrier protection** — By coating with a suitable material —paint, oil, grease etc

2) Sacrificial protection — Coating with a more reactive metal. The process of coating the surface of iron with Zinc is called Galvanization. More reactive metal act as anode.

3) Alloying with metals that form oxide coats.

4) **Antirust solutions** — Alkaline phosphate or chromate solutions are applied on iron surface to form a heat resistant iron phosphate or chromate coating which prevent corrosion.

4) **Cathodic protection** - Here metal to be protected is set as cathode by attaching a more reactive metal to it. Now the more reactive metal undergo oxidation. for ex. Zn, Al or Mg can be used for cathodic protection.

OBJECTIVE TYPE QUESTIONS

I. MULTIPLE CHOICE QUESTIONS

1. The potential of a hydrogen electrode at pH=10 is :

   (a) 0.591 V (b) 0.00 V

   (c) -0.591 V (d) -0.059 V

2. How many coulomb are required for the oxidation of 1 mol of H_2O_2 to O_2?

   (a) 9.65×10^4C (b) 93000 C

   (c) 1.93×10^5C (d) 19.3×10^2C

3. KCl is used in salt bridge because:

   (a) It forms a good jelly with agar -agar

   (b) It is a strong electrolyte

   (c) It is a good conductor of electricity

   (d) Migration factor of K^+ and Cl^- ions are almost equal

4. For a spontaneous reaction the ΔG, equilibrium constant (K) and E^0cell will be respectively.

   (a) -ve, < 1, - ve (b) - ve, > 1, - ve

   (c) - ve, > 1, + ve (d) + ve, > 1, - ve

5. If a salt bridge is removed between the half cells, the voltage:

   (a) drops to zero (b) does not change

   (c) increase gradually (d) increases rapidly

6. The process in which chemical change occurs on passing electricity is termed :

   (a) Ionisation (b) neutralisation

   (c) electrolysis (d) hydrolysis

7. The charge required for the reduction of 1 mol of MnO_4^- to MnO_2 is:

   (a) 1F (b) 3F

   (c) 5F (d) 4F

8. The value of Λ_m^0 for NH_4Cl, NaOH and NaCl are 129.8, 248.1 and 126.4 $Ohm^{-1}cm^2mol^{-1}$ respectively. Calculate Λ_m^0 for NH_4OH solution.

   (a) 215.5 $Ohm^{-1}cm^2 mol^{-1}$ (b) 251.5 $Ohm^{-1}cm^2 mol^{-1}$

   (c) 244.7 $Ohm^{-1}cm^2 mol^{-1}$ (d) 351.5 $Ohm^{-1}cm^2 mol^{-1}$

9. In a Galvanic cell the electrical work done is equal to :
   (a) Free energy change (b) mechanical work done
   (c) thermodynamic work done (d) all of the above
10. Zn cannot displace following ions from their aqueous solution :
   (a) Al^{3+} (b) Cu^{2+}
   (c) Fe^{3+} (d) Na^{+}
11. Electrical work done is equal to :
   (a) $-nFE^{0}_{cell}$ (b) nFE^{0}_{cell}
   (c) nE^{0}_{cell} (d) None of these
12. Which are not the following decrease with increase in concentration?
   (a) Conductance (b) Molar conductance
   (c) Conductivity (d) All of the above
13. The standard electrode potential values of three metallic cations, X, Y, Z are 0.52, -3.03 and -1.18V, respectively. The order of reducing power of the corresponding metals is
   (a) Y>Z>X (b) X>Y>Z
   (c) Z>Y>X (d) Z>X>Y
14. How is elctrical conductance of a conductor related with length and area of cross section of the conductor?
   (a) $G=k.l.a^{-1}$ (b) $G=l.a.k^{-1}$
   (c) $G=k.a.l^{-1}$ (d) $G=k.l.a^{-2}$
15. What will happen during the electrolysis of aqueous solution of $CuSO_4$ in the presence of Cu electrodes?
   (a) Copper will deposit at cathode. (b) Copper will dissolve at anode.
   (c) Oxygen will be released at anode. (d) Copper will deposit at anode.
16. The cell constant of a conductivity cell __________________.
   (a) changes with change of electrolyte. (b) changes with change of concentration of electrolyte.
   (c) changes with temperature of electrolyte. (d) remains constant for a cell.
17. An electrochemical cell can behave like an electrolytic cell when
   (a) $E_{cell}=0$ (b) $E_{cell}>E_{ext}$
   (c) $E_{ext}>E_{cell}$ (d) $E_{cell}=E_{ext}$
18. Which of the following statement is not correct about an inert electrode in a cell?
   (a) It does not participate in the cell reaction.
   (b) It provides surface either for oxidation or for reduction reaction.
   (c) It provides surface for conduction of electrons.
   (d) It provides surface for redox reaction.

19. The difference between the electrode potentials of two electrodes when no current is drawn through the cell is called
    (a) Cell potential
    (b) Cell emf
    (c) Potential difference
    (d) Cell voltage
20. The positive value of the standard electrode potential of Cu^{2+} /Cu indicates that :
    (a) this redox couple is a stronger reducing agent than the H^+/H_2 coupl e.
    (b) this redox couple is a stronger oxidising agent than H^+/H_2.
    (c) Cu can displace H_2 from acid.
    (d) Cu cannot displace H_2 from acid.

II FILL IN THE BLANKS:

1. The conductance of a solution placed between two opposite faces of a centimetre cube is called...................... .
2. Strong electrolytes give almost a linear plot of Λ_m versus............................ .
3. In a galvanic cell, the electrons flow from .... to..................through connecting wire.
4. The unit of resistivity is ....
5. For the spontaneous cell reaction, E^0 should be........................ .
6. Conductivity of an electrolytic solution........................with increase in dilution.
7. The unit of cell constant is........................
8. An aqueous solution of copper nitrate.....................be stored in iron vessel.
9. Protection of iron by coating with zinc is called ....
10. To deposit two mol of Ca from $CaCl_2$,.................................electricity is required .

III ASSERTION REASON TYPE QUESTIONS

(a) Both assertion and reason are correct statements, and reason is the correct explanation of the assertion.
(b) Both assertion and reason are correct statements, but reason is not the correct explanation of the assertion.
(c) Assertion is correct, but reason is wrong statement.
(d) Assertion is wrong, but reason is correct statement.

1. **Assertion:** When aqueous sodium chloride solution is electrolysed, Oxygen gas is produced at the anode.

   Reason : It is due to the overpotential for oxidation of water to oxygen.

2. **Assertion:** Molar conductivity of an electrolyte increases with decrease in concentration.

   Reason: The mobility of ions decrease with increase in concentration.

3. **Assertion:** Reduction of 1 mole of Cu^{2+} ions require 2 faraday of charge.

   Reason: 1 Faraday is equal to the charge of 1 mole of electrons.

4. **Assertion:** Lechlanche cell gives constant voltage throughout its life.

   Reason: The overall reaction of button cell does not involve any ion in solution whose concentration can change during its life time.

5. **Assertion:** Coating iron with zinc prevents rusting.

   Reason: The coating of zinc prevents moist air to come in contact with the metal.

6. **Assertion:** More negative the electrode potential greater is the power to act as oxidising agent .

   Reason: As the electrode potential becomes more negative there is greater tendency to undergo oxidation.

7. **Assertion:** Secondary cells are cells which can be recharged after use.

   Reason: The products are electrolysed back to the initial reactants during recharge of the cell.

8. **Assertion :** Kohlrausch law helps to find the molar conductivity of weak electrolyte at infinite dilution.

   Reason : Molar conductivity of a weak electrolyte at infinite dilution cannot be determined experimentally.

9. **Assertion :** Fluorine is the best oxidising agent.

   Reason : Fluorine has highest reduction potential.

10. **Assertion:** Λ_m for weak electrolytes shows a sharp increase when the electrolyte solution is diluted.

    Reason: For weak electrolytes degree of dissociation increases with dilution of solution.

IV ONE WORD ANSWER TYPE QUESTIONS

1. How much charge in Faraday is required for the reduction of 1 mol Al^{3+} to Al?
2. What is the effect of increase of temperature on ionic conductance?
3. What flows in the internal circuit of a Galvanic cell?
4. Name of the reference electrode in determining the standard electrode potential.
5. Can E^0_{cell} for a cell reaction ever be equal to zero?
6. Name the quantity which is reciprocal of resistivity.
7. How will pH of brine (aqueous NaCl solution) be affected when it is electrolysed?
8. What is the name given to the constant quantity of charge carried by one mole electrons?
9. Name of reference electrode used for determination of E^0 instead of NHE/SHE.
10. What is the effect of presence of salt in water on the rate of rusting of iron?
11. Name the type of cell which was used in Apollo Space Programme for providing electrical power.
12. Under what condition is $E_{cell} = 0$ or $\Delta_r G = 0$?
13. How is equilibrium constant of a reaction related to standard cell potential?
14. Mention the direction of flow of electrons in the following cell:
    $Zn_{(s)} | Zn^{2+}_{(aq)} || Ag^{+}_{(aq)} | Ag_{(s)}$
15. A galvanic cell has electrical potential of 1.1 V. If an opposing potential of 1.1 V is applied to this cell. What will happen to the cell reaction and current flowing through the cell ?

VERY SHORT ANSWER TYPE QUESTIONS (1 Mark Questions)

Q. 1. Why is it not possible to measure single electrode potential ?

Ans. Because the half cell containing single electrode cannot work independently, as charge cannot flow on its own in a single electrode.

Q. 2. Name the factors on which emf of a cell depends.

Ans. Emf of a cell depends on following factors :

(a) Nature of reactants

(b) Concentration of solution in two half cells

(c) Temperature

Q. 3. What is the effect of temperature on the electrical conductance of metal ?

Ans. Temperature increases, electrical conductance decreases.

Q. 4. What is the effect of temperature on the electrical conductance of electrolyte ?

Ans. Temperature increases, electrical conductance increases.

Q. 5. What is the relation between conductance and conductivity ?

Ans. $\Lambda_m^c = \dfrac{k}{C}$

Q. 6. Reduction potentials of 4 metals A, B, C and D are – 1.66 V, + 0.34 V, + 0.80 V and – 0.76 V. What is the order of their reducing power and reactivity ?

Ans. A > D > B > C

Q.7. Why does a dry cell become dead even if it has not been used for a long time?

Ans. NH_4Cl is acidic in nature. It corrodes zinc container

Q.8. Why Na cannot be obtained by the electrolysis of aqueous NaCl solution ?

Ans. Due to low reduction potential, Na^+ ions are not reduced at cathode. Instead, H^+ are reduced and H_2 is obtained.

Q.9. What is the use of platinum foil in the hydrogen electrode ?

Ans. It is used for the in and out flow of electrons.

Q.10. Why Λ_m^o for CH_3COOH cannot be determined experimentally ?

Ans. Molar conductivity of weak electrolytes keeps on increasing with dilution and does not become constant even at very large dilution.

Q.11. Why is it necessary to use a salt bridge in a galvanic cell?

Ans. To complete the inner circuit and to maintain electrical neutrality of the electrolytic solutions of the half cells.

Q.12. Why does mercury cell gives a constant voltage throughout its life?

Ans. This is because the overall cell reaction does not have any ionic concentration in it.

Q.13. What is the role of $ZnCl_2$ in a dry cell ?

Ans. $ZnCl_2$ combines with the NH_3 produced to form a complex salt $[Zn(NH_3)_2]Cl_2$.

Q.14. Why does the conductivity of a solution decrease with dilution ?

Ans. Conductivity of a solution is dependent on the number of ions per unit volume. On dilution, the number of ions per unit volume decreases, hence the conductivity decreases.

Q.15. Suggest two materials other than hydrogen that can be used as fuels in fuel cells.

Ans. Methane and methanol.

Q.16. How does the pH of Aq-NaCl solution be affected when it is electrolysed ?

Ans. When Aq-NaCl solution is electrolysed, H_2 is liberated at cathode, Cl_2 at anode and NaOH is formed in the solution. Hence pH of solution increase.

Q.17. Which reference electrode is used to measure the electrode potential of other electrodes?

Ans. Standard hydrogen electrode (SHE) whose electrode potential is taken as zero.

Q.18. Out of zinc and tin, which one protects iron better even after cracks and why ?

Ans. Zinc protects better because oxidation potential of zinc is greater but that of tin is less than that of iron.

Q.19. Define corrosion. What is the chemical formula of rust ?

Ans. Corrosion is the slow eating away of the surface of the metal due to attack of atmospheric gases. $Fe_2O_3.xH_2O$

20. What is the electrolyte used in a dry cell?

Ans. A paste of NH_4Cl

21. How much electricity is required in Coulomb for the oxidation of 1 mole of FeO to Fe_2O_3 ?

Ans. $Fe^{2+} \rightarrow Fe^{3+} + e^{-1}$

So, $1F = 1F \times 96500C = 96500\,C$

22. Two metals A and B have reduction potential values - 0.76 V and +0.34V respectively. Which of these will liberate H_2 from dil. H_2SO_4 ?

Ans. Metal having higher oxidation potential will liberate H_2 from H_2SO_4. Thus, A will liberate H_2 from H_2SO_4.

23. How does conc. of sulphuric acid change in lead storage battery when current is drawn from it ?

Ans. Concentration of sulphuric acid decreases.

24. Why is alternating current used for measuring resistance of an electrolytic solution ?

Ans. The alternating current is used to prevent electrolysis so that the concentration of ions in the solution remains constant.

Q.25. E° values of MnO_4^-, Ce^{4+} and Cl_2 are 1.507, 1.61 and 1.358 V respectively. Arrange these in order of increasing strength as oxidizing agent.

Ans. $Cl_2 < MnO_4^- < Ce^{4+}$

26. Explain Kohlrausch's law of independent migration of ions.

Ans. It states that at infinite dilution , molar conductivity of an electrolyte is equal to sum of contributions due to cation as well as anion.

$$\Lambda^\circ_{Na_2SO_4} = 2\Lambda^\circ_{Na^+} + \Lambda^\circ_{SO_4^{2-}}$$

27. Give products of electolysis of an equeous solution of $AgNO_3$ with silver electrode.

Ans. At anode: $Ag_{(s)} \longrightarrow Ag^+_{(aq)} + e^-$

At cathode: $Ag^+_{(aq)} + e^- \longrightarrow Ag_{(s)}$

SHORT ANSWER TYPE QUESTIONS (2 or 3 Marks)

1. How can you increase the reduction potential of an electrode for the reaction :

$$M^{n+}(aq) + ne^- \rightarrow M(s)$$

Ans. Nernst equation is :

$$E_{M^{n+}/M} = E^{\theta}_{M^{n+}/M} - \frac{0.0591}{n}\log\frac{1}{[M^{n+}]} \text{ at } 298k$$

$E_{M^{n+}/M}$ can be increased by

(a) Increase in concentration of M^{n+} ions in solution.

(b) By increasing the temperature.

2. Calculate emf of the following cell at 298 K :

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

The Nernst equation for the cell is :

[Given : $E^{\theta}_{cell} = 3.17$ V]

Ans.

$$E_{cell} = E^{\theta}_{cell} - \frac{0.059}{2}\log\frac{[Mg^{2+}]}{[Ag^+]^2}$$

$$= 3.17 - \frac{0.059}{2}\log\frac{.130}{(.0001)^2}$$

$$= 3.17 - 0.21 = 2.96V$$

Q.3. Suggest a way to determine the $\wedge^{\circ}_{m}$ value of water

Ans. $\wedge^{\circ}_{m}(H_2O) = \Lambda^{\circ}_{m}(H^+) + \Lambda^{\circ}_{m}(OH^-)$

It can be determine from the value of

$\wedge^{\circ}_{m}(HCl)$, $\wedge^{\circ}_{m}(NaOH)$-$\wedge^{\circ}_{m}(NaCl)$. then,

$\wedge^{\circ}_{m}(H_2O) = \wedge^{\circ}_{m}(HCl) + \wedge^{\circ}_{m}(NaOH) - \wedge^{\circ}_{m}(NaCl)$

Q. 4. How much electricity in term of Faraday is required to produce 40 gram of Al from Al_2O_3 ? (Atomic mass of Al = 27 g/mol)

Ans.

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

27 gram of Al require electricity = 3F

40 gram of Al require electricity = $\frac{3F}{27} \times 40 = 4.44$ F

Q.5. Predict the product of electrolysis of an equeous solution of $CuCl_2$ with an inert electrode.

Ans. $CuCl_2(s) + aq \longrightarrow Cu^{2+} + 2Cl^-$

$H_2O \rightarrow H^+ + OH^-$

At cathode (Reduction): Cu^{2+} will be reduced in preference to H^+ ions.

$Cu^{2+} + 2e^- \rightarrow Cu(s)$

At anode (Oxidation): Cl^- will be reduced in preference to OH- ions.

$Cl^- \rightarrow 1/2Cl_2 + 1e^-$

Q.6. Calculate Λ°_m for $CaCl_2$ and $MgSO_4$ from the following data : $\Lambda^\circ_m(Ca^{2+})$=119.0,Scm^2 mol^{-1}, Mg^{2+}=106.0, Cl^- = 76.3 and SO_4^{2-} = 160.0Scm^2 mol^{-1}

$$\Lambda^\circ_{m(CaCl_2)} = \Lambda^\circ_{m(Ca^{2+})} + 2\Lambda^\circ_{m(Cl^-)} \quad = 119 + (2 \times 76.3) = 271.6 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\Lambda^\circ_{m(MgSO_4)} = \Lambda^\circ_{m(Mg^{2+})} + \Lambda^\circ_{m(SO_4^{2-})} \quad = 106 + 160 = 266 \text{ S cm}^2 \text{ mol}^{-1}$$

Q. 7. Calculate the potential of hydrogen electrode in contact with a solution whose pH is 10.

Ans. $H^+ + e^- \rightarrow ½H_2 \quad n = 1$

$$E = E^\ominus - \frac{0.0591}{n}\log\frac{1}{[H^+]}$$

$$E = 0 - \frac{0.0591}{1} \times pH$$

$$E = -0.0591 \times 10 \text{ v}$$

$$E = -0.591 \text{ V}$$

Q. 8. If a current of 0.5 amp flows through a metallic wire for 2 hours, how many electrons would flow through the wire ?

Ans. $q = i \times t = 0.5 \times 2 \times 60 \times 60 = 3600$ C

96500 Coulombs are equal to $6.022 \times 10^{23} e^-$

So, 3600 Coulombs = $\dfrac{6.022 \times 10^{23}}{96500} \times 3600 = 2.246 \times 10^{22}$ electrons

Q.9. Calculate the electrode potential of a copper wire dipped in 0.1M $CuSO_4$ solution at 25°C. The standard electrode potential of copper is 0.34 Volt.

Ans. The electrode reaction written as reduction potential is

$$Cu^{2+} + 2e^- \rightarrow Cu \qquad n = 2$$

$$E_{Cu^{2+}/Cu} = E^0_{Cu^{2+}/Cu} - \frac{0.0591}{2}\log\frac{1}{[Cu^{2+}]} = 0.34 - \frac{0.0591}{2}\log\frac{1}{0.1} = 0.3104 \text{ V}$$

Q.10. The conductivity of a 0.20M solution of KCl at 298K is 0.0248 S cm^{-1}. Calculate molar conductivity.

Ans. Molar conductivity $= \dfrac{k \times 1000}{M} = \dfrac{0.0248 \text{ S cm}^{-1} \times 1000 \text{ cm}^3 \text{ L}^{-1}}{0.2 \text{ mol L}^{-1}}$

$= 124.0 \text{ S cm}^2 \text{ mol}^{-1}$

Q.11. Define conductivity and molar conductivity for a solution of an electrolyte.

Ans. Conductivity is defined as ease with which current flows through electrolyte. It is reciprocal of specific resistance. Molar conductivity is conductance of all the ions produced by one mole of electrolyte when electrodes are at unit distance apart and have sufficient area of cross-section to hold electrolyte.

Q.12. The resistance of a conductivity cell containing 0.001M KCl solution at 298 K is 1500 Ω. What is the cell constant if conductivity of 0.001M KCl solution at 298 K is 0.146 × 10^{-3} S cm^{-1} ?

Ans. Cell constant $= k \times R$

$= 0.146 \times 10^{-3} \times 1500$

$= 0.219 \text{ cm}^{-1}$

Q.13. Indicate the reaction which take place at cathode and anode in fuel cell.

Ans. At cathode: $O_2(g) + 2H_2O + 4e^- \rightarrow 4OH^-(aq)$

At anode: $2H_2(g) + 4OH^-(aq) \rightarrow 4H_2O + 4e^-$

The overall reaction is : $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$

Q.14. The standard reduction potential for the Zn^{2+} (aq)/Zn (s) half cell is – 0.76V. Write the reactions occurring at the electrodes when coupled with standard hydrogen electrode (SHE).

Ans. At anode : $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

At cathode : $2H^+ + 2e^- \rightarrow H_2(g)$

$$Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$$

Q.15. What type of a battery is lead storage cell ? Write the anode and cathode reaction and overall reaction occuring in a lead storage battery during discharging and recharging cell.

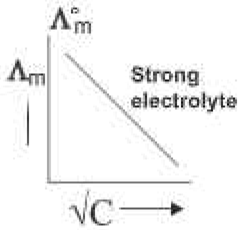
Ans. It is a secondary cell.

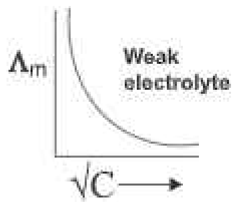
Anode reaction: $Pb+SO_4^{2-} \rightarrow PbSO_4+2e^-$

Cathode reaction: $PbO_2+4H^+ +SO_4^{2-}+2e^- \rightarrow PbSO_4+2H_2O$

$Pb(s)+PbO_2(s)+2H_2SO_4 \underset{\text{Recharging}}{\overset{\text{Discharging}}{\rightleftharpoons}} 2PbSO_{4(s)}+2H_2O(l)$

Q.16. Draw a graph between $\Lambda^\circ m$ and $\sqrt{C}$ for strong and weak electrolyte.





Q.17. Predict the products of electrolysis in each of the following:

(a) An aqueous solution of $AgNO_3$ with platinum electrodes.

(b) An aqueous solution of $Cu\,Cl_2$ with Pt electrodes.

Ans. (a) At Anode (Oxidation)

$4OH^- - 4e^- \rightarrow 2H_2O+O_2$

At cathode (Reduction)

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

(b) At anode (Oxidation)

$Cl^- \rightarrow \frac{1}{2}Cl_{(g)}+e^-$

$\frac{1}{2}Cl+Cl \rightarrow Cl_2$

At cathode (Reduction)

$Cu^{2+}+2e^- \rightarrow Cu(s)$

Q.18. Determine the values of equilibrium constant K_c and ΔG^θ for the following reaction :

$$Ni\ (s) + 2Ag^+\ (aq) \rightarrow Ni^{2+}\ (aq) + 2Ag\ (s) \qquad E^\theta = 1.05\ V$$

Ans.

$$\Delta G^\theta = -nFE^\theta_{cell}$$

$$n = 2,\ E^\theta_{cell} = 1.05\ V$$

$$F = 96500\ C\ mol^{-1}$$

$$\Delta G^\theta = -2 \times 1.05 \times 96500$$

$$= -202.650\ kJ$$

$$\Delta G^\theta = -RT\ \ln K_c$$

$$\ln K_c = -\frac{\Delta G^\theta}{RT} = \frac{-202.650 \times 10^3}{8.314 \times 298}$$

$$K_c = 3.32 \times 10^{35}$$

Q.19. The K_{sp} for AgCl at 298 K is 1.0×10^{-10}. Calculate the electrode potential for Ag^+/Ag electrode immersed in 1.0M KCl solution. Given $E^\circ Ag^+/Ag$=0.80 V.

Ans.

$$AgCl\ (s) \rightleftharpoons Ag^+ + Cl^-$$

$$K_{sp} = [Ag^+][Cl^-]$$

$$[Cl^-] = 1.0\ M$$

$$[Ag^+] = \frac{K_{sp}}{\left[Cl^-\right]} = \frac{1 \times 10^{-10}}{1} = 1 \times 10^{-10}\ M$$

Now, $Ag^+ + e^- \rightarrow Ag\ (s)$

$$E = E^\theta - \frac{0.059}{1} \log \frac{1}{\left[Ag^+\right]} \qquad = 0.80 - \frac{0.059}{1} \log \frac{1}{10^{-10}}$$

$$= 0.80 - 0.059 \times 10 = 0.21\ V$$

Q.20. Estimate the minimum potential difference needed to reduce Al_2O_3 at 500°C. The free energy change for the decomposition reaction :

$$\frac{2}{3}Al_2O_3 \rightarrow \frac{4}{3}Al + O_2 \text{ is } \Delta G = +960 \text{ kJ, F} = 96500 \text{ C mol}^{-1}.$$

Ans.

$$\frac{2}{3}Al_2O_3 \rightarrow \frac{4}{3}Al + O_2$$

$$n = \frac{6 \times 2}{3} = 4e^-$$

$$\Delta G = -nFE$$

$$\Delta G = 960 \times 10^3 \text{ J}, n = 4, F = 96500 \text{ C mol}^{-1}$$

$$960 \times 10^3 = -4 \times 96500 \times E$$

$$E = -2.487 \text{ V}$$

Minimum potential difference needed to reduce Al_2O_3 = – 2.487 V.

Q.21. Two electrolytic cells containing silver nitrate solution and copper sulphate solution are connected in series. A steady current of 2.5 amp was passed through them till 1.078 g of Ag were deposited . How long did the current flow ? What weight of copper will be deposited ? (Ag = 107.8 u, Cu = 63.5 u)

Ans. $W = z \times i \times t$

$$t = \frac{W}{z \times i}$$

$$t = \frac{1.078 \times 1 \times 96500}{107.8 \times 2.5} = 386 \text{ Seconds}$$

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

$$w = \frac{63.5}{2 \text{x} 96500} \text{ x } 2.5 \text{x} 386 = 0.3175 \text{ gram}$$

Q.22. A solution of Ni $(NO_3)_2$ is electrolysed between platinum electrodes using a current of 5.0 amp for 20 minutes . What mass of the nickle will be deposited at the cathode ? (Ni = 58.7u)

Ans. $W = z \times i \times t$

$$z = \frac{58.7}{2 \text{ x } 96500}$$

w = 1.825 gram

Q.23. The cell in which the following reaction occurs :

$$2Fe^{3+}(aq) + 2I^{-}(aq) \rightarrow 2Fe^{2+}(aq) + I_2(s) \text{ has } E^0_{cell} = 0.236\ V.$$

Calculate the standard Gibbs energy and the equilibrium constant of the cell reaction.

Ans.

$$n = 2$$

$$\Delta G^o = -nFE^0_{cell} = -2 \times 96500 \times 0.236\ J = -45.55\ kJ/mol$$

$$\Delta G^o = -2.303\ RT \log K_c$$

$$\log K_c = \frac{\Delta G^o}{-2.303RT} = \frac{45.55 \times 10^3}{2.303 \times 8.314 \times 298} = 7.983$$

$$K_c = \text{antilog}(7.983) = 9.616 \times 10^7$$

Q.24. The molar conductivity of 0.025 mol L^{-1} methanoic acid is 46.1 S cm^2 mol^{-1}. Calculate its degree of dissociation and dissociation constant. Given $\Lambda^o(H^+)$ = 349.6 S cm^2 mol^{-1}, $\Lambda^o(HCOO^-)$ = 54.6 S cm^2 mol^{-1}.

Ans.

$$\Lambda^o_m(HCOOH) = \Lambda^o_m(H^+) + \Lambda^o_m(HCOO^-)$$

$$= 349.6 + 54.6\ S\ cm^2\ mol^{-1} = 404.2\ S\ cm^2\ mol^{-1}$$

$$\Lambda^o_m = 46.1\ S\ cm^2\ mol^{-1}$$

$$HCOOH \rightleftharpoons HCOO^- + H^+$$

$$\alpha = \frac{\Lambda^c_m}{\Lambda^o_m} = \frac{46.1}{404.2} = 0.114$$

	$HCOOH$ $\rightleftharpoons$	$HCOO^-$ +	H^+
Initial conc.	C mol L^{-1}	0	0
At equil.	$C(1-\alpha)$	$C\alpha$	$C\alpha$

$$K_a = \frac{C\alpha^2}{1-\alpha} = \frac{0.025 \times (0.114)^2}{1-0.114}$$

$$= 3.67 \times 10^{-4}$$

Q.25. Calculate the standard cell potentials of galvanic cells in which the following reaction take place:

$2Cr(s) + 3Cd^{2+}(aq) \rightarrow 2Cr^{3+}(aq) + 3Cd(s)$

Also calculate ΔG° and equilibrium constant of the reaction.

Ans. $E^{0}_{cell} = E^{0}_{cathode} - E^{0}_{anode}$

$= 0.40-(-0.74)=0.34V$

$\Delta G^{0} = -nFE^{0}_{cell} = -6x96500x0.34 = -196860$

$= -196860\ j\ mol^{-1} = -196.86kJ/mol$

$-\Delta G^{0} = 2.303XRT \log K_c$

$196860 = 2.303 X 8.314 X 298 \log K_c$

or

$\log K_c = 34.5014$

$K_c = \text{antilog } 34.5014 = 3.193 X 10^{34}$

Q.26. Calculate the potential of the following ce

$Sn^{4+}(1.5 M) + Zn \rightarrow Sn^{2+}(0.5) + Zn^{2+}(2M)$.

Given : $E^{0}_{Sn^{4+}/Sn^{2+}} = 0.13V$, $E^{0}_{Zn^{2+}/Zn} = -0.76V$

Will the cell potential increase or decrease, if the concentration of Sn^{4+} is increased?

Ans.

$$E_{cell} = E^{\theta}_{cell} - \frac{0.0591}{n}\log\frac{[Sn^{2+}][Zn^{2+}]}{[Sn^{4+}][Zn]}$$

$$= 0.89 - \frac{0.0591}{2}\log\frac{0.5\times 2}{1.5\times 1} \quad = 0.89 - \frac{0.0591}{2}\log\frac{1}{1.5} \quad = 0.895\ V$$

On increasing the concentration of Sn^{4+}, EMF of the cell will increase.

Q.27. $E^{\circ}(Cu^{2+}/Cu)$ and $E^{\circ}(Ag^{+}/Ag)$ is + 0.337 V and + 0.799 V respectively. Make a cell whose EMF is +ve. If the concentration of Cu^{2+} is 0.01M and E_{cell} at 25°C is zero, calculate the concentration of Ag^{+}.

Ans. Cu is more reactive than silver, so that the cell is as $Cu|Cu^{2+}$ (0.01M) || Ag^{+}(C) | Ag or cell reaction

$$Cu + 2Ag^+ \rightarrow Cu^{2+} + 2Ag$$

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{n}\log\frac{\left[Cu^{2+}\right]\left[Ag\right]^2}{\left[Cu\right]\left[Ag^+\right]^2}$$

$$= E^{\circ}_{cell} - \frac{0.0591}{n}\log\frac{(0.01)\times 1^2}{1\times\left[Ag^+\right]^2}$$

Or $\quad [Ag^+] = 1.47 \times 10^{-9}$ M

Q.28. Calculate the potential of the cell at 298 K :

$Cd \mid Cd^{2+}$ (0.1M) $\parallel$ H^+ (0.2M) $\mid$ Pt, H_2 (0.5 atm)

Given E° for Cd^{2+}/Cd = – 0.403 V, R = 8.314 J^{-1} mol^{-1}, F = 96500 C mol^{-1}.

Ans. The cell reaction is $Cd + 2H^+$ (0.2M) $\rightarrow Cd^{2+}$ (0.1M) + H_2 (0.5 atm)

$$E^{o}_{cell} = 0 - (-0.403) = +0.403 \text{ V}$$

$$E_{cell} = 0.403 - \frac{2.303RT}{nF}\log\frac{\left[Cd^{2+}\right]\times P_{H_2}}{\left[Cd\right]\left[H^+\right]^2}$$

$$= 0.403 - \frac{2.303\times 8.314\times 298}{2\times 96500}\log\frac{0.1\times 0.5}{(0.2)^2}$$

$$E_{cell} = 0.403 - 0.003 = 0.40 \text{ V}$$

Q.29. The electrical resistance of a column of 0.05M NaOH solution of diameter 1 cm and length 50 cm is 5.55 × 10^3 ohm. Calculate its resistivity, conductivity and molar conductivity.

Ans. Diameter = 1 cm, radius = 0.5 cm

$$\text{Area} = \pi r^2 = 3.14 \times (0.5)^2 = 0.785 \text{ cm}^2$$

$$\rho = \frac{R\times A}{l} = \frac{5.55\times 10^3\times 0.785}{50} = 87.135 \text{ ohm cm}$$

$$\text{Conductivity (k)} = \frac{1}{\rho} = \frac{1}{87.135} = 0.01148 \text{ ohm}^{-1}\text{ cm}^{-1} = 0.01148 \text{ ohm cm}$$

$$\text{Molar conductivity } \Lambda^c_m = \frac{k\times 1000}{M} = \frac{0.01148\times 1000}{0.05} = 29.6 \text{ S cm}^2\text{ mol}^{-1}$$

Q.30. Name the cell which:

(a) was used in Apollo Space programme.

(b) is used in automobiles and inverters.

(c) is suitable for hearing aids and watches.

(d) does not give a steady potential and is used in transistors.

Ans. (a) Fuel cell

(b) Lead storage cell

(c) Mercury cell

(d) Dry cell

LONG ANSWER TYPE QUESTIONS (5 Marks)

Q. 1. Conductivity of 0.00241M acetic acid is 7.896 × 10^{-5} S cm^{-1}. Calculate its molar conductivity and if Λ^{o}_{m} for acetic acid is 390.5 S cm^2 mol^{-1}, what is its dissociation constant ?

Ans. $$\Lambda_m = \frac{k \times 1000}{M}$$

$$= \frac{7.896 \times 10^{-5} \text{ S cm}^{-1} \times 1000 \text{ cm}^3 \text{ L}^{-1}}{0.00241 \text{ mol L}^{-1}} = 32.76 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\alpha = \frac{\Lambda_m}{\Lambda^{o}_{m}} = \frac{32.76}{390.5} = 8.39 \times 10^{-2}$$

$$K_a = \frac{C\alpha^2}{1-\alpha} = \frac{0.00241 \times \left(8.39 \times 10^{-2}\right)^3}{1 - 8.39 \times 10^{-2}} = 1.86 \times 10^{-5}$$

Q.2. Three electrolytic cells A, B, C containing solution of $ZnSO_4$, $AgNO_3$ and $CuSO_4$ respectively all connected in series. A Steady current of 1.5 amperes was passed through then until 1.45g of silver deposited at the cathode of cell B How long did the current flow? What mass of copper and of zinc were deposited ?

Ans. 108 g of silver is deposited by $Ag^+ + e^- \rightarrow Ag_{(s)}$ is 96500C.

1.45 g silver is deposited by $= \frac{96500 \times 1.45}{108} = 1295.6C$

$$Q = I \times t$$
$$1295.6 = 1.5xt$$
$$t = \frac{12956}{1.5} = 863 \text{ s}$$

In cell A, the electrode reaction is

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

2F of electricity deposit Zn = 65.3 g

In cell A, the electrode reaction is

$Zn^{2+} + 2e^- \longrightarrow Zn$

2F of electricity deposit Zn=65.3g

1295.6 of electricity deposit Zn = $\frac{65.3 \times 1295.6}{2 \times 96500}$

=0.438 g

In cell C, the electrode reaction is

$Cu^{2+} + 2e \longrightarrow Cu(s)$

2F of electricity deposit Cu = 63.5g

1295.6 of electricity deposit Cu = $\frac{63.5 \times 1295.6}{2 \times 96500}$

= 0.426g

Q. 3. (a) State Kohlraush's law.

(b) Suggest a way to determine the Λ°_m for CH_3COOH.

(c) The Λ°_m for sodium acetate, HCl, NaCl are 91.0, 425.9 and 126.4 S cm^2 mol^{-1} respectively at 298 K. Calculate Λ°_m for CH_3COOH.

Ans. (a) The molar conductivity at a infinite dilution for a given salt can be expressed as the sum of the individual contribution from the ions of electrolyte.

(b) $\Lambda^\circ\ CH_3COOH = ?$

$$\lambda^\circ\ CH_3COO^- + \lambda^\circ\ H^+ = \lambda^\circ\ CH_3COO^- + \lambda^\circ\ Na^+ + \lambda^\circ\ H^+$$

$$+ \lambda^\circ\ Cl^- - \lambda^\circ\ Na^+ - \lambda^\circ\ Cl^- \quad ...(i)$$

$$\Lambda^\circ_m\ CH_3COOH = \Lambda^\circ\ CH_3COONa + \Lambda^\circ\ HCl - \Lambda^\circ\ NaCl$$

(c) $$\Lambda^\circ_m\ CH_3COOH = \Lambda^\circ\ CH_3COONa + \Lambda^\circ\ HCl - \Lambda^\circ\ NaCl$$

$$= 91.0 + 425.9 - 126.4$$

$$= 390.5\ S\ cm^2\ mol^{-1}$$

Q.4. **(a) Define weak and strong electrolytes**

(b) The E° values corresponding to the following two reduction electrode processes are:

(i) $Cu^+/Cu = 0.52V$ (ii) $Cu^{2+}/Cu^+ = 0.16V$

Formulate the galvanic cell for their combination . Calculate the cell potential and ΔG° for the cell reaction.

Ans. (a) Weak electrolyte: the substance which partially ionized in solution is known as weak electrolyte. Example: NH_4OH

Strong electrolyte: The substance which completely ionized in solution is known as strong electrolyte. Example: NaCl.

(b) $Cu^{+} + e^{-}$ Cu

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

Overall cell reaction: $2Cu^{+} \rightarrow Cu + Cu^{2+}$

$Cu^{+}|Cu^{2+}||Cu^{+}|Cu$

$E^{0}cell = 0.52 - 0.16 = 0.36V$

$\Delta G^{o} = -nFE^{o}_{Cell}$

$= -1X96500x0.36$

$= -34740 \text{ J mol}^{-1}$

Q.5. **Calculate emf and ΔG^{o} for the following cell at 298K.**
$Mg(s) | Mg^{2+}(10^{-3} M) || Cu^{2+} (10^{-4} M) | Cu(s)$
[Given : $E^{o}\ Mg^{2+}/Mg = -2.36$ V; $E^{o}\ Cu^{2+}/Cu = 0.34$ V; 1 F = 96500 C mol^{-1}]

Ans. $E_{cell} = E^{o}_{cell} - \frac{0.059}{2} \log \frac{[Mg^{2+}]}{[Cu^{2+}]}$

$$E_{cell} = 0.34-(-2.36)- \frac{0.059}{2} \log \frac{10^{-3}}{10^{-4}}$$

$$= 2.70 - 0.02655 = 2.67V$$

$\Delta G^{o} = -nF\ E^{o}_{cell} = -2X96500X2.71$

$= -5.23X10^{2} \text{ kJ mol}^{-1}$

Q.6. **(a) Give the units of conductivity and molar conductivity**
(b) Write down Nernst equation and calculate the emf of the following cell at 298 K:
$Cu(s) | Cu^{2+} (0.13 M) || Ag^{+}(10^{-4} M) | Ag(s)$
Given: $E^{o}\ (Cu^{2+}/Cu) = +0.34$ V and $E^{o}\ (Ag^{+}/Ag) = +0.80$ v.
Hint: (a) Conductivity Scm^{-1} cm, Molar conductivity $Scm^{-2}\ mol^{-1}$

(b) $Q = \frac{[Cu^{2+}]\ [Ag]^{2}}{[Cu]\ [Ag+]^{2}} \quad \frac{0.13 \times 1^{2}}{1 \times (10^{-4})^{2}} = 0.13\ X10^{8}$

$$E = E^{o} - \frac{0.0591}{n} \log_{10}Q$$

$$= 0.46 - \frac{0.0591}{2} \log_{10}(0.13X10^{8}) = 0.25V$$

Q.7. **(a) Calculate the emf of the following concentration cell:**
$Zn_{(s)} | ZnSO_4(0.001\ M) || ZnSO_4(0.01\ M) |\ Zn(s)$
(b) How can the reduction potential of an electrode be increased ?

Hint: (a)

$$E = E^{o} - \frac{0.0591}{n} \log_{10}Q$$

$$= 0 - \frac{0.0591}{n} \log 10 = 0.0295 \text{ Volt}$$

(b) $M^{n+}\ ne^{-} \rightarrow M$

$$E_{M^{n+}/M} = E^{o}_{M^{n+}/M} - \frac{2.303\ RT}{nF} \log \frac{1}{[M^{n+}]}$$

or

$$E_{M^{n+}/M} = E^{o}_{M^{n+}/M} + \frac{2.303\ RT}{nF} \log [M^{n+}]$$

From the above relation it is clear that the reduction potential can be increased either by increasing temperature or by increasing the concentration of metal ion.

Q.8. **(i) The conductivity of 0.02M solution of NaCl is 2.6×10^{-2} S cm^{-1}. What is its molar conductivity ?**

(ii) Give reasons:

(a) Rusting of iron pipe can be prevented by joining it with a piece of magnesium.

(b) Dry cell become dead after a long time, even if it has not been used?

Ans.

$K = 2.6 \times 10^{-2}$ S cm^{-1}

$C = 0.02M$

$$\Lambda m = \frac{k \times 1000}{C(M)}$$

$$= \frac{2.6 \times 10^{-2} \times 1000}{0.02}$$

$$= \frac{26 \times 100}{0.02 \times 100} = \frac{26 \times 10^{2}}{2}$$

$$= 13 \times 10^{2} \text{ S cm mol}^{-1}$$

(ii) (a) It is due to cathodic protection in which magnesium metal is oxidised in preference to iron and acts as the anode.

(b) A dry cell becomes dead after a long time because the acidic NH_4Cl corrodes with the zinc container of dry cell.

Q.9. **(i) Depict the galvanic cell in which the reaction**

$Zn(s) + 2Ag^{+}(aq) \rightarrow Zn^{2+}(aq) + 2Ag(s)$

take place. Further show :

(a) Which of the electrode is negatively charged?

(b) The carriers of the current in the cell.

(c) Individual reaction at each electrode?

(ii) A solution of $CuSO_4$ is electrolysed for 10 mins. With a current of 1.5 amperes. What is the mass of copper deposited at the cathode ?

Ans. (i) $Zn_{(s)} | Zn^{2+}_{(aq)} \parallel Ag^{+}_{(aq)} | Ag_{(s)}$

(a) Zn electrode (anode)

(b) Ions are carriers of the current in the cell.

(c) At anode:

$Zn(s) \rightarrow Zn^{2+} + 2e^{-}$

At cathode:

$Ag^{+} + e^{-} \rightarrow Ag(s)$

(ii) $I = 1.5$ Ampere

Time: $10 \times 60s = 600s$

$Q = I \times t = 1.5 \times 600 = 900$ C

$Cu^{2+} + 2e^{-} \rightarrow Cu(s)$

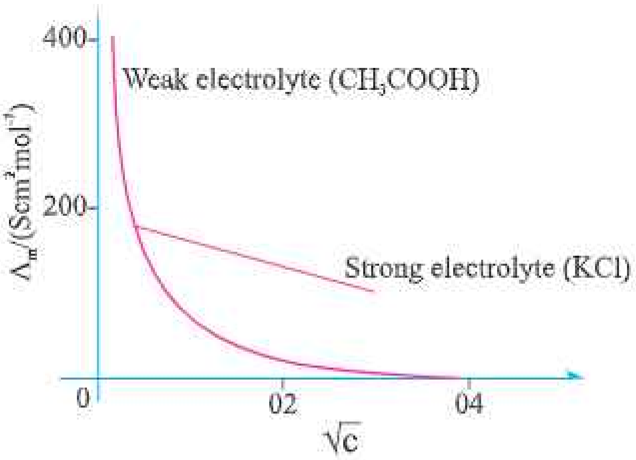
2F amount of electricity deposit copper = 63.5g

900 C amount of electricity deposit copper = $\frac{63.5 \times 900}{2 \times 96500} = 0.296g$

CASE STUDY BASED QUESTIONS

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

The study of the conductivity of electrolyte solution is important for the development of electrochemical devices, for the characterisation of the dissociation equilibrium of weak electrolytes and for the understanding of charge transport by ions. The conductivity of electrolyte is measured for electrolyte solution with concentration in the range of 10^{-3} to 10^{-4} mol/L, as solution in this concentration range can be easily prepared. The variation in molar conductivity (Λ_m) of strong electrolyte with concentration is given by equation $\Lambda_m = \Lambda^0_m - A\sqrt{C}$ Where Λ^0_m is the molar conductivity at infinite dilution and Cis the concentration for solution. Following graph shows the, variation of molar conductivity with concentration for both weak and strong electrolytes.



Limiting molar conductivity cannot be determined by extrapolation of Λ_m versus $\sqrt{C}$ curve. Molar conductivity at infinite dilution can be calculated by sum of contributions of each ion. $\Lambda^0_m = v^+\lambda_0^+ + v\lambda_0^-$

Where λ_0^+ and λ_0^- are the limiting ionic conductivities of positive and negative ions respectively and v^+ and v^- are their stoichiometric coefficients in the salt molecular formula.

In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

a) Assertion and reason both are correct statements and reason is correct explanation for assertion .

b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

c) Assertion is correct statement but reason is wrong statement.

d) Assertion is wrong statement but reason is correct statement.

(A) **ASSERTION**: For CH_3COOH Λ^0_m cannot be determined experimentally.

REASON: CH_3COOH is a weak acid and Debye Huckel Onsager equation cannot be used. Extrapolation method cannot be employed.

(B) **ASSERTION** : The ratio of conductivity to the observed conductance does not depend upon the concentration of the solution taken in the conductivity cell.

REASON : Conductivity of solution decreases with dilution whereas observed conductance increases with dilution.

(C) **ASSERTION** : Molar conductance of all electrolytes decrease with increasing concentration.

REASON : Lesser no. of ions are available per unit volume of solution at higher concentration.

(D) **ASSERTION** : 0.1 M NH_4OH at 25°C has lesser conductance than at 50 °C.

REASON : Conductance of a weak electrolyte decreases with increase in temperature.

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

In the Daniell cell, the copper electrode is the anode. The electrons leave the cell from the zinc and enter into the copper electrode. To complete the circuit a salt bridge (an inverted U-tube) is used. Salt bridge consists of a concentrated solution of agar-agar + KCl/ KNO_3/NH_4NO_3. The mobility of cations and anions are the same. The maximum electrical work is given by $W_{max} = -\Delta G$. This ΔG is related to emf as $\Delta G = -nFE$. The extent of reaction is measured by ΔG. The emf of a cell is determined by the Nernst equation,

$$E = E^0 - \frac{0.0591}{n} \log Q.$$

The Nernst equation is also used to calculate the emf of concentration cell.

$M|M^+_{(aq)} || M^+_{(aq)} |M$. When a given cell is at equilibrium, $Q = K_{eq}$.

To calculate the standard electrode potential of a half cell like Ag/Ag^+, Cu/Cu^{2+}, one has to complete it with SHE e.g.

$Pt/H_2(g)\ /H^+_{(aq)}$ its $E^0 = 0$ (by convention). From the emf study, we can calculate E^0, pH, valency, K_{eq}, K_s, thermodynamic parameters, etc.

(A) An electrochemical cell stops working after some time because

(a) Electrode potential of both the electrodes becomes zero.

(b) Electrode potential of both the electrodes becomes equal.

(c) One of the electrode is eaten away.

(d) The reaction start s proceeding in opposite direction.

(B) Which of the following statements is correct for a galvanic cell?

(a) Reduction occurs at cathode. (b) Oxidation occurs at anode.

(c) Electrons flow from anode to cathode. (d) All statements are correct.

(C) What is correct when net cell reaction is spontaneous?

(a) E°_{cell} is negative (b) $E_{cell} > 0$

(c) $E_{cell} = E^0_{cell}$ (d) $\Delta G < 0$

(D) The function of salt bridge is to:

(a) allow ions to move from anode to cathode

(b) allow solutions from one half cell to the other half cell

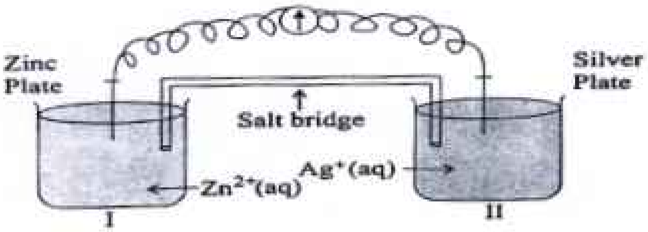
(c) allow the current to flow through the cell and keep the solutions electrically neutral

(d) keep the level of solutions same.

3. Read the passage given below and answer the questions that follow:

Oxidation-reduction reactions are commonly known as redox reactions. They involve transfer of electrons from one species to another. In a spontaneous reaction, energy is released which can be used to do useful work. The reaction is split into two half reactions. Two different containers are used and a wire is used to drive the electrons from one side to the other and a Voltaic/Galvanic cell is created. It is an electrochemical cell that uses spontaneous redox reactions to generate electricity. A salt bridge also connects to the half cells. The reading of the voltmeter gives the cell voltage or cell potential or electromotive force. If E°cell is positive the reaction is spontaneous and if it is negative the reaction is non-spontaneous and is referred to as electrolytic cell. Electrolysis refers to the decomposition of a substance by an electric current. One mole of electric charge when passed through a cell will discharge half a mole of a divalent metal ion such as Cu^{2+}. This was first formulated by Faraday in the form of laws of electrolysis.

The conductance of material is the property of materials due to which a material allows the flow of ions through itself and thus conducts electricity. Conductivity is represented by k and it depends upon nature and concentration of electrolyte, temperature etc. A more common term molar conductivity of a solution at a given concentration is conductance of the volume of solution containing one mole of electrolyte kept between two electrodes with the unit area of cross-section and distance of unit length. Limiting molar conductivity of weak electrolytes cannot be obtained graphically.



(A) Which plate zinc or silver is going to act as cathode of the cell?

(B) What will happen if the salt bridge is removed?

(C) When does electrochemical cell behaves like an electrolytic cell?

(D) (i) What will happen to the concentration of Zn^{2+} and Ag^{+} when $E_{cell}=0$

(ii) Why does conductivity of a solution decreases with dilution?

OR

(D) The molar conductivity of a 1.5 M solution of an electrolyte is found to be 138.9 S cm^2 mol^{-1} Calculate the conductivity of this solution.

ANSWERS

I MULTIPLE CHOICE QUESTIONS

1. c 2. c 3. d 4. c 5. a 6. c 7. b 8. b 9. a 10. a, d
11. a 12. a,b 13. a 14. a 15. a, b 16. d 17. c 18. d 19. b 20. b,d

II FILL IN THE BLANKS

1.	Conductivity	2.	$c^{1/2}$	3.	Anode to cathode
4.	ohm metre	5.	positive	6.	decreases
7.	m^{-1}	8.	cannot	9.	galvanisation
10.	4F				

III ASSERTION REASON TYPE QUESTIONS

1. a 2. a 3. a. 4. d 5. c.
6. d. 7. a 8. a 9. a 10. a

IV ONE WORD ANSWER TYPE QUESTIONS

1.	3F	2.	Increases	3.	ions
4.	Standard hydrogen electrode	5.	No	6.	Conductivity
7.	increases	8.	Faraday constant		
9.	Calomal electrode	10.	increases	11.	Fuel Cell
12.	At equilibrium	13.	$E^0 cell = \frac{0.0591}{n} \log K_c$		
14.	From Zinc to Silver	15.	Equilibrium state is attained		

CASE STUDY BASED QUESTIONS

1: (A) a (B) b (C) c (D) c
2: (A) b (B) d (C) b,d (D) c
3: (A) Cathode (B) voltage will drop to zero (C) When $E_{ext} > E_{cell}$
(D) (i) Increasing concentration of Zn^{2+} and decreasing concentration of Ag^+ reaches to an equilibrium
(ii) Due to decrease in no. of ions per unit volume.

OR

(D) $\Lambda_m = K \times \frac{1000}{M}$

$138.9 = K \times \frac{1000}{1.5}$

$K = 0.208\ ohm^{-1} cm^{-1}$

UNIT TEST-1

CHAPTER-3

ELECTROCHEMISTRY

TIME ALLOWED :1 HR. **M.M. 20**

1. What does the negative sign in the expression $E^0_{(Zn^{2+}/Zn)} = -0.76$ V mean? 1

2. Write unit of molar conductivity. 1

3. Suggest a way to determine the Λ_m^0 value of water. 1

4. Write the nernst equation of the following cell

   $Mg(s)|Mg^{2+}(0.001M) || Cu^{2+}(0.001M)|Cu(s)$ 1

5. Why is it not possible to measure single electrode potential? 1

6. Calculate emf of the following cell 2

   $Cd|Cd^{2+}(0.10M) || H^+(0.20M)|H_2(0.5\ atm)/Pt$

   (Given E^0 for $Cd^{2+}/Cd = -0.403V$)

7. Why on dilution Λ_m of CH_3COOH increases drastically while that of CH_3COONa increases gradually? 2

8. Conductivity of 2.5×10^{-4} M methanoic acid (HCOOH) is 5.25×10^{-5} Scm^{-1}. Calculate its molar conductivity and degree of dissociation. 3

   Given: $\lambda^0(H^+) = 349.5\ Scm^2mol^{-1}$ and $\lambda^0(HCOO^-) = 50.5\ Scm^2mol^{-1}$.

9. (i) The conductivity of an aqueous solution of NaCl in a cell is 92 ohm^{-1}, the resistance offered by the cell is 247.8 ohm. Calculate the cell constant. 3

   (ii) What is the effect of dilution on the conductivity of an electrolytic solution?

10. Calculate EMF and ΔG for the following cell at 298K:

    $Mg(s) | Mg^{2+}(0.01M) || Ag^+(0.0001M) | Ag(s)$

    Given : $E^0_{(Mg^{2+}/Mg)} = -2.37V$, $E^0_{(Ag^+/Ag)} = +0.80V$ 5

UNIT TEST-2

CHAPTER-3

ELECTROCHEMISTRY

TIME ALLOWED :1 HR. **M.M. 20**

1. Express the relation between conductivity and molar conductivity of the solution. 1
2. Name any two metals which can be used for cathodic protection of iron. 1
3. Name a battery used in Apollo space programme. 1
4. Write the correct representation of the cell: 2
   2. $Cr_{(s)} + 3Cd^{2+}_{(aq)} \rightarrow Cr^{3+}_{(aq)} + 3Cd_{(s)}$
5. How many Faradays of charge are required to convert 1 mole of Fe^{2+} to Fe? 1
6. How does molar conductivity vary with dilution for 2
   (i) weak electrolyte and for
   (ii) strong electrolyte? Give reasons for these variations.
7. The conductivity of 0.2 M solution of KCl at 298 K is 0.025 S cm^{-1}. Calculate the molar conductivity. 2
8. Account for the following: 2
   (i) Alkaline medium inhibits the rusting of iron.
   (ii) Iron does not rust even if the zinc coating is broken in a galvanised iron pipe.
9. Calculate the emf for the given cell at 25°C. 3
   $Cr \mid Cr^{3+}(0.1M) \parallel Fe^{2+}(0.01M) \mid Fe$
   [Given: $E^0_{Cr^{3+}/Cr} = -0.74$ V, $E^0_{Fe^{2+}/Fe} = -0.44$ V]
10. (a) Write the cell reactions which occur in lead storage battery 3
    (i) When the battery is in use and
    (ii) When the battery is on charging.
    (b) Mention two advantages of fuel cells.
11. Molar conductivities at infinite dilution for NH_4Cl, NaOH and NaCl solutions at 298 K are respectively 129.8, 217.4 and 108.9 S cm^2 mol^{-1} and the molar conductivity of a 10^{-2} M solution of NH_4OH is 9.33 S cm^2 mol^{-1} Calculate the degree of dissociation (a) of NH_4OH in the above mentioned solution. 3

UNIT 4

Chemical Kinetics

Points to Remember

RATE OF REACTION:-

For a reaction $R \rightarrow P$

Rate of reaction = change of conc. of R or P / Time interval

Rate = $-\Delta[R]/\Delta t = \Delta[P]/\Delta t$, This is average rate of reaction.

For expressing the rate of such a reaction where stoichiometric coefficients of reactants or products are not equal to one, rate of disappearance of any of the reactants or the rate of appearance of products is divided by their respective stoichiometiric coefficients.

For e.g. for a chemical reaction: $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

$r_{e.g} = -\Delta[N_2]\,\Delta t = -1/3\,(\Delta[H_2]/\Delta t) = ½(\Delta[NH_3]/\Delta t)$

Units of rate of a reaction:-

Concentration $time^{-1}$

- if concentration is in mol L^{-1} and time is in seconds then the units will be mol $L^{-1}s^{-1}$.

- In gaseous reaction, when the concentration of the gases is expressed in terms of their partial pressure, then the units will be atm s^{-1}.

INSTANTANEOUS RATE is defined as the rate of change in concentration of any one of reactant or product at a particular instant of time.

when $\Delta t \rightarrow 0$; $r_{inst} = -d[R]/dt = d[P]/dt$

Factors affecting rate of a reaction:

(a) **Nature of the reacting species:** Chemical reaction is a process in which new chemical bonds are formed and old bonds are broken. Therefore, the strength of these bonds affect the rate of the reaction.

(b) **Concentration of reactants:** The rate of reaction increases with increase in concentration of reactants.

(c) **Effect of temperature:** The rate of reaction is nearly double for every 10^0C rise in temperature.

(d) **Catalyst:** generally catalyst increases the rate of reaction.

(e) **Effect of radiations:** The rates of some reactions are enhanced due to absorption of radiation. These reactions are called photochemical reactions.

LAW OF MASS ACTION:

The rate of a chemical reaction is directly proportional to the product of the molar concentrations of the reactants.

$$aA + bB \rightarrow \text{Products}$$

According to law of mass action $\quad$ Rate $\alpha\ [A]^a[B]^b$,

$$\text{Rate} = k[A]^a[B]^b$$

- **RATE CONSTANT OF A REACTION**

  at a given temperature may be defined as rate of the reaction when the molar concentration of each of the reactants is unity.

- **CHARACTERISTICS OF RATE CONSTANT**

(i) Rate constant is a measure of the rate of the reaction.

(ii) Larger the value of k, faster is the reaction.

(iii) Different reactions have different values of k.

(iv) For a particular reaction, the rate constant is independent of concentration.

(v) At a particular temperature, the value of k is constant. However, it changes with temperature.

- **RATE LAW** is the expression in which reaction rate is given in terms of molar concentration of reactants with each term raised to some power, which may or may not be same as the stoichiometric coefficient of the reacting species in a balanced chemical equation. It is determined experimentally.

- **ORDER OF A REACTION:** The sum of powers of the concentration of the reactants in the rate law expression is called the order of the chemical reaction.

  For the rate law expression

  Rate $= k[A]^x[b]^y$

  Order $= x + y$

- **UNITS OF RATE CONSTANTS:** Units of rate constant are different from reaction of different order : $(molL^{-1})^{1-n}$ time^{-1} where 'n' is order of reaction. For gas phase reaction unit of rate constant is (atm of bar)$^{1-n}s^{-1}$

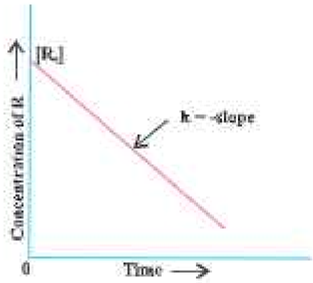
Reaction	Order ($\alpha+\beta$)	Units of rate constant
Zero order reaction	0	$\frac{molL^{-1}}{s} x \frac{1}{(molL^{-1})^0} = molL^{-1}s^{-1}$
First order reaction	1	$\frac{molL^{-1}}{s} x \frac{1}{(molL^{-1})^1} = s^{-1}$
Second order reaction	2	$\frac{molL^{-1}}{s} x \frac{1}{(molL^{-1})^2} = mol^{-1}L^{-1}s^{-1}$

MECHANISM AND RATE LAW:

The reactions taking place in one step are called **elementary reactions.** When a sequence of elementary reactions, (called mechanism) gives us the products, the reactions are called **Complex reactions.** In complex reactions, the rate of the reaction is determined by the slowest step in the sequence. The slowest step is called **rate determining step** in the proposed mechanism.

ZERO ORDER REACTION

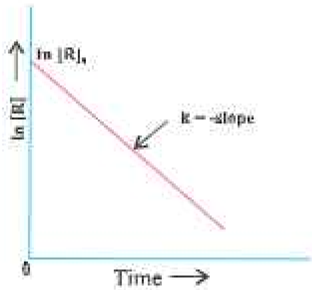
Integrated rate equation $k=[R]_0-[R]/t$

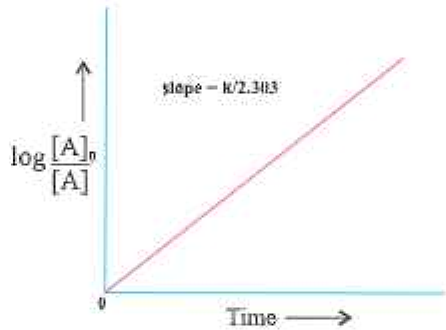


INTEGRATED RATE EQUATION FOR FIRST ORDER REACTION:

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

where $[R]_0$ is initial concentration of reactants and $[R]$ is concentration at time t.





For a typical first order gas phase reaction: $A(g) \rightarrow B(g) + C(g)$

Where p_i is the initial pressure of A and P_t the total pressure at time 't'.

- **HALF-LIFE PERIOD** ($t_{1/2}$): The half-life of a reaction is the time in which the concentration of a reactant is reduced to one half of its initial concentration.

$$k = \frac{2.303}{t} \log \frac{p_i}{(2p_i - p_t)}$$

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

For first order reaction : $t_{1/2} = 0.693/k$

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

- **PSEUDO FIRST ORDER REACTIONS.** Chemical reactions which are not truly of the first order but under certain conditions become first order reactions are called e.g. A bimolecular reaction, in which one reactant is present in large excess and rate of reaction is independent of its concentration, the reaction follows first order kinetics.

  For example, ester hydrolysis, where water is taken in excess.

  $CH_3COOCH_2CH_3 + H_2O \rightarrow CH_3COOH + CH_3CH_2OH$ is a bimolecular but first order reaction.

- **Activation energy :** The minimum extra amount of energy absorbed by reactant molecules so that their energy becomes equal to the threshold energy is called activation energy.

  Activation energy = Threshold energy - Kinetic energy

- **Temperature coefficient:** the ratio of rate constant at two temperatures having difference of 10 K is called temperature coefficient.

  Temperature coefficient = Rate constant at T + 10°C/Rate constant at T°C

- **Arhenius Equation:**

  $k = Ae^{-Ea/RT}$

  where, k = Rate constant

  A = Arrhenius energy (Frequency factor or pre-exponential factor)

  E_a = Activation energy

  R = Rate constant

  T = Temperature

  = Fraction of molecules having energy equal to or more than activation energy

  $\log k = \log A - \frac{E_a}{RT}$

  $\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2}\right]$

  $\log \frac{k_2}{k_1} = \frac{E_a}{2.303x\ 8.314} \left[\frac{T_2}{T_2} - \frac{T_1}{T_2}\right]$ Where R = 8.314 JK^{-1} mol^{-1}

OBJECTIVE TYPE QUESTIONS

I MULTIPLE CHOICE QUESTIONS

1. The initial concentration of the reactant is doubled, the time for half reaction is also doubled. Then the order of the reaction is

(a) Zero (b) one (c) Fraction (d) none

2. Which of the following statements is correct?

(a) The rate of a reaction decreases with passage of time as the concentration of reactants decreases

(b) The rate of a reaction is same at any time during the reaction

(c) The rate of a reaction is independent of temperature change

(d) The rate of a reaction decreases with increase in concentration of reactants(s)

3. The rate constant of a reaction is $5.8 \times 10^{-21} s^{-1}$. The order of the reaction is.

(a) First order (b) zero order (c) Second order (d) Third order

4. A second order reaction between A and B is elementary reaction: A+B→Product rate law expression of this reaction will be:

(a) Rate=k[A][B] (b) Rate=$k[A]^0[B]^2$ (c) Rate=$k[A]^2[B]^0$ (d) Rate = $k[A]^{3/2}[B]^{1/2}$

5. Which of the following is pseudo first order reaction?

(a) $2H_2O_2 \rightarrow 2H_2O+O_2$

(b) $2O_3 \rightarrow 3O_2$

(c) $CH_3COOC_2H_5+NaOH \rightarrow CH_3COONa+C_2H_5OH$

(d) $CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$

6. A large increase in the rate of reaction for rise in temperature is due to:

(a) Increase in the number of collisions

(b) Increase in the number of activated molecules

(c) Lowering of activation energy

(d) Shortening of the mean free path.

7. **Radioactive decay is an example of:**

   (a) first order (b) zero order (c) second order (d) 0.5 order

8. **For a zero order reaction, the plot of concentration of reactant vs time is (intercept refers to concentration axis)**

   (a) linear with +ve slope and zero intercept

   (b) linear with -ve slope and zero intercept

   (c) linear with -ve slope and non-zero intercept

   (d) linear with positive slope and non-zero inercept

9. **The rate constant of nth order has units**

   (a) $litre^{1-n} mol^{n} s^{-1}$ (b) $mol^{1-n} litre^{1-n} s^{-1}$

   (c) $mol^{1-n} litre^{n} s^{-1}$ (d) $mol^{1-n} lire^{n-1} s^{-1}$

10. **A hypothetical reaction $A_2 + B_2 \rightarrow 2\,AB$ follows the mechanism as given below:**

    $A_2 \rightarrow A + A$ (fast)

    $A + B_2 \rightarrow AB + B$ (slow)

    $A + B \rightarrow AB$ (Fast)

    The order of reaction is:

    (a) 2 (b) 0 (c) 1½ (d) 1

11. **In a first order, the concentration of the reactant reduced to 1/4 in 60 minutes. What will be its half life?**

    (a) 120 min (b) 40 min

    (c) 30 min (d) 25 min

12. **For a complex reaction________________________**

    (a) order of overall reaction is same as molecularity of the slowest step.

    (b) order of overall reaction is less than the molecularity of the slowest step.

    (c) order of overall reaction is greater than molecularity of the slowest step.

    (d) molecularity of the slowest step is never zero or non integer.

13. **Which of the reaction ends in infinite time?**

    (a) Zero order (b) First order

    (c) Second order (d) Third order

14. **Which one is correct for first order reaction.**

    (a) $t_{75\%}/t_{50\%}=1.5$ (b) $t_{75\%}/t_{50\%}=2$ (c) $t_{99.9\%}/t_{50\%}=10$ (d) $t_{99.9\%}/t_{50\%}=2$

15. The rate constant of a zero order reaction is :

(a) Independent upon initial concentration

(b) Inversely proportional to concentration

(c) Does not depend upon concentration

(d) None of these

16. For the elementary reaction M→N, the rate of dissappearance of M increases by a factor of 8 upon doubling the concentration of M. The order of the reaction with respect to M is:

(a) 4 (b) 3 (c) 2 (d) 1

17. When initial concentration of a reactant is doubled in a reaction, its half life period is not affected. The order of the reaction is.

(a) Second (b) more than zero but less than first

(c) Zero (d) First

18. Which of the following influences the rate of reaction?

(a) Temperature (b) Concentration

(c) Light (d) All of these

19. Higher order(>3) reactions are rare due to

(a) shifting of equilibrium towards reactants due to elastic collisions

(b) loss of active species on collisions

(c) low probability of simultaneous collision of all the reacting species

(d) increase in entropy and activation energy as more molecules are involved.

20. Half life period of a first order reaction is:

(a) directly proportional to the initial concentration of the reactant

(b) half of the rate constant

(c) same for all reactions

(d) independent of initial concentration of reactants

21. The half-life for a zero order reaction equals:

(a) $\frac{2k}{R}$ (b) $\frac{1}{2}\frac{k}{R^2}$

(c) $\frac{R^2}{2k}$ (d) $\frac{R}{2k}$

Where R is the initial concentration.

II FILL IN THE BLANKS

1. Hydrolysis of ethyl acetate in an acidic solution is an example of .... order reaction.

2. If the activation energy of the reaction is low, it proceeds at .... rate.

3. In a multi step reaction, the .... step determines the rate of reaction.

4. For a first order reaction, the half life period is equal to ....

5. The order and molecularity of a complex reaction............................be same.

6. The inversion of cane sugar is a .... order reaction though its molecularity is...........

7. The difference of energy between activated complex and that of the reactants is called.......................................

8. The unit of first order rate constant when concentration is Measured in terms of pressure and time in minutes is...................................

9. A first order reaction has $t_{1/2} = 6.93$min. The rate constant is ....

10. Increase in temperature increases the number of ....

III ASSERTION REASON TYPE QUESTIONS

(a) Both assertion and reason are correct statements, and reason is the correct explanation of the assertion.

(b) Both assertion and reason are correct statements, but reason is not the correct explanation of the assertion.

(c) Assertion is correct, but reason is wrong statement.

(d) Assertion is wrong, but reason is correct statement.

1. **Assertion:** Hydrolysis of methyl ethanoate is a pseudo first order reaction.

Reason: Water is present in large excess and therefore its concentration remains constant throughout the reaction.

2. **Assertion:** The slowest elementary step in a complex reaction decides the rate of the reaction.
Reason: The slowest elementary step always has the smallest molecularity.
3. **Assertion:** A catalyst increases the rate of a reaction.
Reason: The catalyst increases the activation energy which in tum increases the rate of the reaction.
4. **Assertion:** Activation complex for the forward reaction reaction will have lower energy than that for the backward reaction in an exothermic reaction.
Reason: Reactants have greater energy than products for an exothermic reaction.
5. **Assertion:** Increase in temperature increases rate of reaction.
Reason: More colliding molecules will have energy greater than threshold energy.
6. **Assertion:** Unit of rate constant is independent of order of reaction.
Reason: The power of concentration terms in the rate equation keep changing with change in order.
7. **Assertion:** In zero order reaction , the conc. versus time graph is a straight line.
Reason: The rate of change of concentration per unit time in zero order reaction remains constant
8. **Assertion:** Half-life period is always independent of initial concentration
Reason: Half-life period is inversely proportional to rate constant
9. **Assertion:** The rate of reaction is the rate of change of concentration of a reactant or a product.
Reason: Rate of reaction remains constant during the course of reaction.
10. **Assertion:** Rate constants determined from Arrhenius equation are fairly accurate for simple as well as complex reactions.
Reason: Reactant molecules undergo chemical change irrespective of their orientation during collision

IV ONE WORD ANSWER TYPE QUESTIONS

1. For reactions of which order the units of rate constant and rate of reaction are same?
2. What is the difference in energy between the energy of activated complex and the average energy of reactants called?
3. A reaction is 50% complete in 2 hours and 75% complete in 4 hours. What is the order of reaction?
4. What is the effect of catalyst on activation energy of reaction?
5. For a reaction half-life is observed to be independent of the initial concentration of the reactants. What is the order of reaction?
6. What is the effect of catalyst on Gibb's energy change (ΔG) of a reaction?
7. For which type of reaction, order and molecularity have the same value?
8. Identify the order of reaction from the following unit of rate constant: $Lmol^{-1}s^{-1}$
9. What is the effect of increase in surface area of reactants on rate of reaction?
10. E_1 and E_2 are the activation energies of the reactant and product respectively. If $E_2 > E_1$, predict the nature of reaction (Exothermic or Endothermic)?

11. The reaction, $A + 2B \rightarrow C$ obeys the rate equation.
Rate $= K[A]^{1/2}[B]^{3/2}$
What is the order of a reaction?
12. Express the rate of the following reaction in terms of disapperance of hydrogen in the reaction.
$3H_2(g)+N_2(g)\ 2\,NH_3(g)$
13. For the reaction, $A \rightarrow B$, the rate of reaction becomes twenty seven times when the concentration of A is increased three times. What is the order of the reaction ?
14. The decomposition reaction of ammonia gas on platinum surface has a rate constant $= 2.5 \times 10^{-4}$ mol L^{-1} s^{-1}. What is the order of the reaction?
15. An endothermic reaction $A \rightarrow B$ has an activation energy of 15 kcal/mole and the energy of the reactant is 5 kcal/mol. What is the activation energy for the reaction $B \rightarrow A$?

VERY SHORT ANSWER TYPE QUESTIONS (1 MARK)

1. The rate law for a reaction is Rate=K [A][B]$^{3/2}$
Can the reaction be an elementary process? Explain.

Ans. No, an elementary process would have a rate law with orders equal to its molecularities and therefore must be in integral form.

2. For the reaction $3H_2 + N_2 \rightarrow 2NH_3$, how are the rate of reaction expression - d$[H_2]$/dt and d$[NH_3]$/dt **inter-related?**

Ans.-1/3 d$[H_2]$/dt = 1/2 d $[NH_3]$/dt

3. Identify the order of a reaction from the following rate constant :
$=2.3 \times 10^{-5}$ L mol^{-1} s^{-1}

Ans. Second order

4. After five half-life periods for a first order reaction, what fraction of reactant remains?

Ans. 1/32

5. What is the effect of adding catalyst on the free energy of a reaction?

Ans. No change in ΔG.

6. What value of k is predicted for the rate constant by Arrhenius equation is $T \rightarrow \infty$? Is this value physically reasonable?

Ans. From the equation $k=Ae^{-Ea/RT}$ if $T \rightarrow \infty$ $k = A$, so that $Ea = 0$. This is not feasible

7. Determine the roder of reaction?
Step 1. $2NO+H_2 \rightarrow N_2+H_2O_2$ (Slow)
Step 2. $H_2O_2+H_2 \rightarrow 2H_2O$ (Fast)

Ans. Rate $= k[NO]^2\,[H_2]$
Order $= 2+1$
$= 3$

8. What is the order of reaction whose rate constant has the same units as the rate of reaction?

Ans. Zero order

9. **Why are reactions of higher order less in number ?**

Ans. Reaction takes place due to collide of molecules. The chances for a large number of molecules or ions to collide simultaneously are less. Hence, the reactions of higher order are less.

10. **What will be the effect of temperature on rate constant?**

Ans. Rate constant of a reaction is nearly doubled with rise in temperature by 10^0C.

11. **State a condition under which a bimolecular reaction is kinetically first order reaction.**

Ans. A bimolecular reaction becomes first order reaction when one of the reactants is in excess.

12. **Why can't molecularity of any reaction be equal to zero?**

Ans. Molecularity of a reaction means the number of molecules of the reactants taking place in an elementary reaction. Since at least one molecule must be present, so that molecularity will be atleast one.

13. **The rate constant of a reaction is $3x10^2$ min^{-1}. What is its order of reaction ?(On the basis of units of rate constant)**

Ans. First order reaction.

14. **Three-fourth of a reaction is completed in 32 minutes. What is the half life period of this reaction?**

Ans. 16 minutes.

15. **What is meant by an elementary reaction?**

Ans. A reaction which takes place in one step is called an elementary reaction. For example: $H_2 + I_2 \rightarrow 2HI$.

16. **Give one example of a reaction where order and molecularity are equal?**

Ans. $2HI \rightarrow H_2 + I_2$ (Order = Molecularity = 2)

17. **For a reaction R→P, the rate becomes 2 time when the concentration of the reactant A is increased 4 times. What is the order of reaction ?**

Ans. $r=k(a)^n$ $2r=k(4a)^n$ $2=4^n=0.5$

18. **The rate constant of a zero order reaction in A is 0.003 mol L^{-1} sec^{-1}. How long will it take for the initial concentration of A to fall from 0.10M to 0.075 M?**

Ans. $t=[R]_0-[R]/k=0.10-0.075/0.003=8.3$ second

19. **In a reaction 2A → Products, the concentration of A decreases from 0.5 mol L^{-1} to 0.4 mol L^{-1} in 10 minutes. Calculate the rate during this interval.**

Ans. Average rate: $-\Delta[A]/2\Delta t = -\frac{1}{2}(0.4-0.5/10) = 5x10^{-3}$M min^{-1}

20. **In some cases large number of colliding reactant molecules have energy more than threshold energy even then the reaction is slow. Why**

Ans. Because resultant molecules do not collide in proper orientation

21. **Give an example of a reaction having fractional order.**

Ans. Decomposition of acetaldehyde (order = 1.5)

$CH_3CHO \rightarrow CH_4 + CO$

22. Decomposition reaction of ammonia on Pt surface has rate constant = 2.5 x 10^{-4} mol L^{-1} sec^{-1}. What is order of reaction ?

Ans. Unit of k explain that it is zero order reaction.

23. What is order of radioactive decay?

Ans. First order

24. For a reaction A+B $\rightarrow$ product, the rate law is given by $r=k[A]^{1/2}[B]^{2}$. What is the order of the reaction ?

Ans. Order of reaction = 1/2 + 2 = 2.5

25. For a chemical reaction half life period cannot depend on concentration of solution. What is order of reaction?

Ans. First order reaction

SHORT ANSWER TYPE QUESTIONS (2 or 3 Marks)

Q. 1. The rate of a particular reaction quadruples when the temperature changes from 293 K to 313 K. Calculate activation energy.

Ans. $k_2/k_1 = 4$

$T_1 = 293$ K, $T_2 = 313$ K

$$\log\frac{k_2}{k_1} = -\frac{E_a}{2.303R}\left[\frac{1}{T_1}-\frac{1}{T_2}\right]$$

Thus, on calculating and substituting values, we get :

$E_a = 52.86$ kJ mol^{-1}

Q. 2. If the decomposition of nitrogen oxide as

$$2N_2O_5 \rightarrow 4NO_2 + O_2$$

follows a first order kinetics.

(a) Calculate the rate constant for a 0.05M solution if the instantaneous rate is 1.5×10^{-6} mol/l/s ?

(b) What concentration of N_2O_5 would give a rate of 2.45×10^{-5} mol L^{-1} s^{-1} ?

Ans. (a) Rate $= k[N_2O_5]$

$$k = \frac{\text{Rate}}{[N_2O_5]} = \frac{1.5\times10^{-6}}{0.05}$$

$$k = 3.0 \times 10^{-5}$$

(b) Rate $= 2.45 \times 10^{-5}$ mol L^{-1} s^{-1}

$$[N_2O_5] = \frac{\text{Rate}}{k} = \frac{2.45\times10^{-5}}{3.0\times10^{-5}} = 0.82\text{ M}$$

Q. 3. Write the difference between order and molecularity of reaction.

Ans.

Order	Molecularity
1. It is the sum of the powers of concentration terms in the rate law expression.	It is the number of reacting species undergoing simultaneously collision in a reaction.
2. It is determined experimentally.	2. It is a theoretical concept.
3. Order of reaction need not to be a whole number.	3. It is whole number only.
4. Order of reaction can be zero.	4. It can't be zero or fractional.

Q. 4. Consider the decomposition reaction :

$$2H_2O_2 \xrightarrow{OH^-/I^-} 2H_2O + O_2$$

This reaction takes place in two steps as given below :

Step 1. $H_2O_2 + I^- \rightarrow H_2O + IO^-$ **(slow)**

Step 2. $H_2O_2 + IO^- \rightarrow H_2O + I^- + O_2$ **(fast)**

(a) Determine rate law expression.

(b) Determine the order of reaction.

Ans. (a) Rate = $k[H_2O_2][I^-]$ because second step is rate determining step.

(b) Order = 1 + 1 = 2

Q. 5. The decomposition of hydrocarbon follows the equation K = $(4.5 \times 10^{11}\ s^{-1})$ $e^{28000k/T}$. Calculate E_a.

Ans. $k = (4.5 \times 10^{11}\ s^{-1})\ e^{-28000k/T}$

Comparing the equation with Arrhenius equation,

$$k = Ae^{-Ea/RT}$$

$$-\frac{E_a}{R} = -28000\ K$$

$$E_a = 28000 \times 8.314$$

$$= 232192\ J\ mol^{-1}$$

Q.6. A reaction is of second order with respect to a reactant. How is the rate of reaction affected if the conc. of the reactant is reduced to half. What is the unit or rate constant for such a reaction?

Ans. Rate = $k[A]^2$

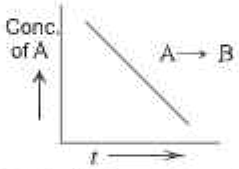
New rate will be 1/4 of initial rate

$k = mol^{-1}\,LS^{-1}$

Q.7. For a first order reaction time taken for half of the reaction to complete is t_1 and ¾ of the reaction to complete is t_2. How are t_1 and t_2 related ?

Ans. $t_2 = 2t_1$ because for 3/4th of the reaction to complete time required is equal to two half lives.

Q.8.



(A) Why is the order of the reaction ?

(b) What is the slope of the curve ?

Ans. (a) Zero order reaction.

(b) $[R] = [R]_o - kt$ $\therefore$ Slope = $-k$

Q.9. Derive an expression to calculate time required for completion of zero order reaction.

Ans. For a zero order reaction,

$$R = [R]_0 - kt$$

For completion of the reaction [R] =0

$$\therefore \quad kt = [R]_0 \qquad t = \frac{[R]_0}{k}$$

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

Q.10. The rate of a gaseous reaction becomes half when volume of the vessel is doubled. What is the order of reaction ?

Ans. Suppose, order of reaction is n and the reaction is A (g) → Products

$$\text{Rate} = k[A]^n \qquad ...(i)$$

When volume is doubled, molar conc. becomes half and rate of reaction gets halved.

$$\frac{\text{Rate}}{2} = k\left(\frac{A}{2}\right)^n \qquad ...(ii)$$

Dividing equation (i) by equation (ii),

$$(2)^1 = (2)^n \qquad n = 1$$

Q.11. A reaction which is first order with respect to A has rate constant 6 min^{-1}. If we start with [A] = 0.5 mol L^{-1}, when would [A] reach the value of 0.05 mol L^{-1}

Ans. $$k = \frac{2.303}{t}\log\frac{[A]_0}{[A]}$$

$k = 6\text{ min}^{-1}$, $[A]_0 = 0.5$, $[A] = 0.05$, $t = ?$

$$t = \frac{2.303}{6}\log\frac{0.5}{0.05} = \frac{2.303}{6}\log 10 = 0.3838\text{ min}$$

Q.12. The conversion of the molecules X to Y follows second order kinetics. If the concentration of X is increased to three times, how will it affect the rate of formation of Y ?

Ans. 9 times

Q.13. A first order reaction has a rate constant 1.15 × 10^{-3} s^{-1}. How long will 5 gram of this reactant take to reduce to 3 grams ?

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

$$t = \frac{2.303}{(1.15\times10^{-3})\text{s}^{-1}}\log\left(\frac{5}{3}\right)$$

$$= \frac{2.303}{(1.15\times10^{-3})\text{s}^{-1}}[\log 5 - \log 3]$$

$$= 444\text{s}$$

Q.14. Distinguish between rate expression and rate constant of a reaction.

Ans. Rate expression is the way to express rate of reaction in terms of concentration of reactants. for a chemical reaction aA+bB→cC+dD Rate = $k[A]^x[B]^y$

Rate constant (k) is defined as the rate of reaction when the concentration of reactants are taken as unity.

Q.15. Consider a certain reaction A → Product with k = 2.0 × 10^{-2} s^{-1}. Calculate the concentration of A remaining after 100 s, if the initial concentration of A is 1.0 mol L^{-1}.

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

$$2 \times 10^{-2} = \frac{2.303}{100}\log\frac{1}{[R]}$$

$$\log\frac{1}{[R]} = \frac{2}{2.303} = 0.8684$$

$$\frac{1}{[R]} = \text{Antilog }(0.8684)$$

$$= 7.3853$$

$$[R] = \frac{1}{7.3853} = 0.135\text{M}$$

Q.16. For the reaction $NO_2 + CO \rightarrow CO_2 + NO$, the experimentally determined rate expression below 400K is rate= $k[NO_2]^2$. What mechanism can be proposed for this reaction?

Ans. $NO_2 + NO_2 \xrightarrow{\text{Slow}} NO + NO_3$

$NO_3 + CO \xrightarrow{\text{Fast}} NO_2 + CO_2$

Q.17. The half life period of a first order reaction is 60 min. What % will be after 240 mins?

Hint: No. of half lives (n) = 240/60 = 4

% of A left = $\frac{[A]_0}{2^n} = \frac{[A]_0}{2^4} = 6.25\%$

Q.18. Time for half change for a first order reaction is 40 min. What % will be left after 240 mins. ?

Ans.

No. of half lives = $\frac{240}{40} = 6$

% of A left = $\frac{[A]_0}{2^n} = \frac{[A]_0}{2^6}$

$= 1.56\%$

Q.19. The following data were obtained during the first order thermal decomposition of N_2O_5 at constant volume :

$$2N_2O_5 \rightarrow 2N_2O_4 + O_2$$

S. No.	Time per second	Total pressure (atm)
1	0	0.5
2	100	0.512

Calculate rate constant.

Ans.

	N_2O_5	N_2O_4	$+ 1/2O_2$
Initial	0.5	0	0
Final	(0.5-x)	x	x/2

$P_t = 0.5 - x + x + x/2 = 0.5 + x/2$

$0.5 + x/2 = 0.512$

$x = 0.024$

$$k = \frac{2.303}{t} \log \frac{p_i}{p_{N_2O_5}}$$

$$k = \frac{2.303}{100} \log \frac{0.5}{0.5 - 0.0240}$$

$k = 4.92 \times 10^{-4} s^{-1}$

Q.20. The decomposition of A into product has value of k as $4.5 \times 10^3 s^{-1}$ at $10^\circ C$ and energy of activation 60 KJ mol. At what temperature would k be $1.5 \times 10^4 sec^{-1}$.

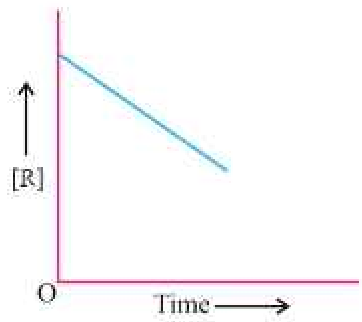
Ans.

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

$$\log\left(\frac{1.5 - 10^4}{4.5X10^3}\right) = \frac{60000}{2.303X\ 8.314}\left[\frac{T_2 - 283}{283\ T_2}\right]$$

$T_2 = 297K$

Q.21. For a chemical reaction R → P, the variation in the concentration (R) vs time (*t*) plot is given :



(a) Predict the order of reaction.

(b) Write down its rate law.

(c) What is the slope of the curve?

Ans. (a) Zero

(b) Rate = $k[R]^0$

(c) Slope = - k

Q.22. (a)Write rate law and order of the following reaction:

$AB + C_2 \rightarrow AB_2C + C$ (slow)

$AB_2 + C \rightarrow AB_2C$ (fast)

(b) define energy of activation of a reaction

(c) What is the relationship between rate constant and activation energy of a reaction?

Ans. (a) Rate = k [AB][C_2], Order = 1+1=2

(b) Refer 'points to remember"

(c) $k = Ae^{-Ea/RT}$

Q.23. The rate constant for first order reaction is 60/s , How much time will it take to reduce the concentration of the reaction to 1/10 of its initial value ?

Ans.

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

$$t = \frac{2.303}{60} \log \frac{[R]_0}{[R]_0/10}$$

$$t = \frac{2.303}{60} \log 10$$

$$t = \frac{2.303}{60}$$

$$= 3.38 \times 10^{-2} s^{-1}$$

Q.24. The rate of most of reaction double when their temperature is raised from 298K to 308K. Calculate the activation energy of such a reaction .

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$E_a = \frac{2.303 \times 8.314 \times 298 \times 308 \times 0.3010}{1000}$$

$$E_a = 52.89 \text{ KJ/mol}$$

Q.25. A first order reaction takes 69.3 min for 50% completion. Set up on equation for determining the time needed for 80% completion

$$k = \frac{0.693}{t1/2} = \frac{0.693}{69.3} \text{ min}$$

$$= 10^{-2} \text{ min}^{-1}$$

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

$$= \frac{2.303}{10^{-2}} \log 5$$

$$= 160.9 \text{ min}$$

Q.26. The activation energy of a reaction is 94.14 KJ/mol and the value of rate constant at 40° C is 1.8×10^{-5} sec^{-1}. Calculate the frequency factor A.

Ans. Given, $E_a = 94.14 \times 10^3$ Jmol^{-1}, T=40+273=313 K, K=1.8×10^{-1} Sec^{-1}

By using, $k = Ae^{-Ea/RT}$ $\quad$ $\ln k = \ln A - \frac{E_a}{RT}$

Or $\log k = \log A - \frac{Ea}{2.303RT}$

$$\text{Or} \quad \log(1.8 \times 10^{-1}) + \frac{94.19 \times 10^{3}}{2.303 \times 8.314 \times 313} = \log A$$

$$\text{Or} \quad A = \text{antilog}(10.9635) = 9.194 \times 10^{10}\ S^{-1}$$

Q.27. The rate constant of a reaction at 700 K and 760 k are 0.011 $M^{-1}S^{-1}$ and 0.105 $M^{-1}S^{-1}$ respectively. Calculate the value of arrhenius parameters

Ans. 2.824×10^{10}

Q.28. The initial concentration of N_2O_5 in the first order reaction $N_2O_5 \rightarrow 2NO_2 + \frac{1}{2}O_2$ was 1.24×10^{-2} mol L^{-1} at 318 K. The concentration of N_2O_5 after 60 minutes was 0.20×10^{-2} mol L^{-1}. Calculate the rate constant of the reaction at 318 K.

Ans.

$$k = \frac{2.303}{t}\log\frac{[A]_0}{[A]} = \frac{2.303}{t}\log\frac{[N_2O_5]_0}{[N_2O_5]_t} = \frac{2.303}{60}\log\frac{1.24 \times 10^{-2}}{0.2 \times 10^{-2}}$$

$$= \frac{2.303}{60}\log 6.2 = \frac{2.303}{60} \times 0.7924 \text{ min}^{-1}$$

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

LONG ANSWER TYPE QUESTIONS (5 Marks)

Q.1. (a) Define order or reaction

(b) Rates of reaction double with every 100 rise in temperature. If this generalization holds for a reaction in the temperature ranges 298 K to 308 K, What would be the value of activation energy for their reaction? R = 8.314 J k^{-1} mol^{-1}

Ans. (a) Order of Reaction: It is the sum of powers to which to conc. terms are raised in rate law expression.

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

Here, $T_1 = 298$ K, $T_2 = 308$ K, R = 8.314 JK^{-1} Mol^{-1}

$$\frac{k_2}{k_1} = 2$$

$$\log 2 = \frac{E_a}{2.303 \times 8.314}\left[\frac{1}{298} - \frac{1}{308}\right]$$

$$0.3010 = \frac{E_a}{2.303 \times 8.314}\left[\frac{10}{298 \times 308}\right]$$

$$E_a = \frac{0.3010 \times 2.303 \times 8.314 \times 298 \times 308}{10}$$

$$= 52898 \text{ Jmol}^{-1}$$

$$= 52.898 \text{ KJ mol}^{-1}$$

Q.2. (a) What are pseudo order reaction ? Give example.

(b) Rate constant K of a reaction varies with temperature 'T' according to the equation :

$$\log k = \log A - \frac{E_a}{2.303R}\left(\frac{1}{T}\right)$$

where E_a is the activation energy. When a graph is plotted for log k vs 1/T, a straight line with a slope of − 4250 K is obtained. Calculate E_a for the reaction.

Ans. (a) The chemical reaction which look like higher order reaction but in real they follow lower order kinetics.

For example,

$$CH_3COOC_2H_5 + \underset{\text{excess}}{H_2O} \xrightarrow{H^+} CH_3COOH + C_2H_5OH$$

$$\text{Rate} = k[CH_3COOC_2H_5]$$

$$\text{Order} = 1$$

(b) $$\text{Slope} = \frac{E_a}{2.303R} = -4250 \text{ K}$$

So, $$E_a = -2.303 \times R \times \text{Slope} = -2.303 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 4250$$

$$= 81375.3 \text{ J mol}^{-1} \quad = 81.375 \text{ kJ mol}^{-1}$$

Q.3. (a) Determine the units of rate constant for first and zero order reaction.

(b) Show that time required for the completion of 99% of the first order reaction is twice the 90% of completion of the reaction.

Ans. (a) $k = (\text{mol})^{1-n}\,L^{n-1}\,s^{-1}$

For zero order, $n = 0$

So, $k = (\text{mol})^{1-0}\,L^{0-1}\,s^{-1} = s^{-1}\ \text{mol}\,L^{-1}$

For first order, $n = 1$

$k = (\text{mol})^{1-n}\,L^{n-1}\,s^{-1}$

So, $k = (\text{mol})^{1-1}\,L^{1-1}\,s^{-1}$

$= s^{-1}$

(b) For a first order reaction,

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

$$[A]_0 = a,\ [A] = a - \frac{a \times 99}{100} = 0.01\,a$$

$$t_{99\%} = \frac{2.303}{k}\log\frac{a}{0.01a} \qquad = \frac{2.303}{k}\log 100 \qquad = \frac{2.303}{k}\times 2$$

...(i)

For 90% completion of reaction,

$$[A] = a - \frac{a \times 99}{100} = 0.1a$$

$$t_{90\%} = \frac{2.303}{k}\log\frac{a}{0.1a} \qquad = \frac{2.303}{k}\times 1$$

...(ii)

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

$$t_{99\%} = 2 \times t_{90\%}$$

Q.4. (a) Define rate constant of reaction.

(b) A first order reaction takes 40 mins for 30% decomposition. Calculate $t_{1/2}$.

Ans. (a) **Rate constant :** It is the rate of chemical reaction when the concentration of reactant taken as unity at a given temperature.

(b) Let initial conc. = a

$$\text{Conc. after 40 mins.} = a - \frac{a \times 30}{100}$$
$$= 0.70\,a$$

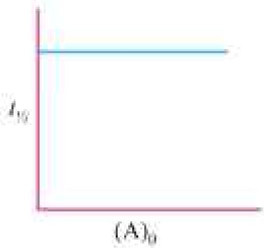
$$k = \frac{2.303}{t}\log\frac{[A]_0}{[A]}$$

$$= \frac{2.303}{40}\log\frac{a}{0.70a} \quad = \frac{2.303}{40}\log\frac{1}{0.70}$$

$$= \frac{2.303}{40} \times 0.1549 \quad = 8.92 \times 10^{-3}\ \text{min}^{-1}$$

$$t_{1/2} = \frac{0.693}{k} \quad = \frac{0.693}{8.92 \times 10^{-3}} = 77.7\ \text{min}$$

Q. 5. (a) Determine the order of reaction and also determine the units of rate constant.



(b) The following data were given for thermal decomposition of SO_2Cl_2 at a constant volume :

$$SO_2Cl_2\,(g) \rightarrow SO_2\,(g) + Cl_2\,(g)$$

Exp.	Time/s	Total p/atm
1	0	0.5
2	100	0.6

Calculate the rate of the reaction when total pressure is 0.65 atm.

Ans. (a) First order reaction

$$k = mol^{1-n}\,L^{n-1}\,s^{-1}$$

$$n = 1$$

$$k = (mol)^{1-1}\,L^{1-1}\,s^{-1}$$

$$= s^{-1}$$

(b)

$$k = \frac{2.303}{t}\log\frac{P_i}{(2P_i - P_t)}$$

$$= \frac{2.303}{100}\log\frac{0.5}{(2\times 0.5 - 0.6)}$$

$$= \frac{2.303}{100}\log\frac{0.5}{0..4}$$

$$= \frac{2.303}{100}\times 0.969 = 2.23\times 10^{-3}\,s^{-1}$$

Now, Rate = $P_{SO_2Cl_2}$

Pressure of SO_2Cl_2 when total pressure = 0.65 atm

$$P_{SO_2Cl_2} = 2P_i - P_t$$

$$= 2\times 0.5 - 0.65 \quad = 0.35\text{ atm}$$

$$\text{Rate} = 2.23\times 10^{-3}\times 0.35 \quad = 7.8\times 10^{-4}\text{ atm s}^{-1}$$

Q.6. **(a)The activation energy of a reaction is 100 kJ/mol. In the presence of catalyst the activation energy is decreased by 75%. What is the effect on rate constant of the reaction at 20°C ?**
(b) $A+2B \rightarrow 3C+2D$
The rate of disappearance of B is 1×10^{-2} mol L^{-1} sec^{-1}. What will be
(i) rate of reaction (ii) rate of change in the concentration of A and C ?

Ans. (a) 2.35×10^{10} times

(b) $(5\times10^{-3}, 5\times10^{-3}, 15\times10^{-3})$ mol L^{-1} s^{-1}

Q.7. **(a)A reaction is of first order in A and of second order in B. Write the differential rate equation for this reaction. How will its initial rate be affected if the concentration of both A and B are together doubled ?**
(b) The rate constant k of a reaction increases four fold when the temperature changes from 300 K to 320 K. Calculate the activation energy for the reaction. ($R=8.314$ J K^{-1} mol^{-1})

Ans. (a) $r=k[A]^1$ .... (1)
$r=k[B]^2$ .... (2)
Differential rate equation is
$r=k[A]^1 \quad [B]^2$ .... (3)
When conc. of both A and B is doubled
$r'=k[2A]^1 \quad [2B]^2$ .... (4)
Divide (4) by (3),
$r'/r=8$
Thus, rate becomes 8 times.

(b) $\dfrac{k_2}{k_1} = 4$, $T^1 = 300K$, $T_2 = 320$ K

$R=8.314J\ K^{-1}\ mol^{-1}$

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

$$\Rightarrow \quad \log 4 = \frac{E_a}{2.303\times8.314JK^{-1}\ mol^{-1}} \times \left[\frac{320-300}{300\times320}\right] K^{-1}$$

$$\Rightarrow \quad 0.6020 = \frac{E_a}{2.303\times8.314JK^{-1}\ mol^{-1}}\left[\frac{20\ K^{-1}}{96\times10^3}\right]$$

$E_a = 55327.6\ J\ mol^{-1} = 55.33\ kJ\ mol^{-1}$

Q.8. **(a) What are the factors on which rate of the reaction depends ? Discuss each factor in brief.**
(b) The following results have been obtained during the kinetics studies of the reaction:
$2A + B \rightarrow C + D$

Experiment	[A] mol L^{-1}	[B] mol L^{-1}	Initial rate of formation of D mol $L^{-1}min^{-1}$
I	0.1	0.1	6.0×10^{-3}
II	0.3	0.2	7.2×10^{-2}
III	0.3	0.4	2.88×10^{-1}
IV	0.4	0.1	2.40×10^{-1}

Ans. **Determine the rate law and the rate constant for the reaction.**
(a) Refer "Points to Remember"
(b) For the reaction $2A + B \rightarrow C + D$
Assume rate law expression as Rate $= k[A]^a [B]^b$
According to question,

$$6.0 \times 10^{-3} = k (0.1)^a (0.1)^b \quad .....(i)$$
$$7.2 \times 10^{-2} = k (0.3)^a (0.2)^b \quad .....(ii)$$
$$2.88 \times 10^{-1} = k (0.3)^a (0.4)^b \quad .....(iii)$$
$$2.40 \times 10^{-2} = k (0.4)^a (0.1)^b \quad .....(iv)$$

Divide eqn. (iv) by (i), we get

$$4 = (4)^a \quad \therefore a = 1$$

Divide eqn. (iii) by (ii), we get

$$4 = (2)^b$$
$$22 = (2)^b \quad \therefore b = 2$$

Order with respect to A = 1
Order with respect to B = 2
$\therefore$ Rate Law $= k[A][B]^2$

On putting the value of 'a' and 'b' into any equation say (i)

$$\therefore \quad 6.0 \times 10^{-3}\ M\ min^{-1} = k(0.1M)(0.1M)^2$$
$$k = 6\ M^{-2}\ min^{-1}$$

Q.9. **(a) Derive the general from of the expression for the half life of a first order reaction.**

(b) The decomposition of NH_3 on platinum surface is a zero order reaction. What are the rates of production of N_2 and H_2 if $k=2.5 \times 10^{-4}$ mol^{-1} Ls^{-1}?

Ans. **(a)** $t = \frac{2.303}{k} \log \frac{[R]_0}{[R]}$

When $[R] = \frac{[R]_0}{2}$, then $t = t_{1/2}$

$\therefore \quad t_{1/2} = \frac{2.303}{k} \log \frac{[R]_0}{[R]_{0/2}} = \frac{2.303}{k} \log 2$

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

or $\quad t_{1/2} = \frac{0.693}{k}$

(b)

$2NH_3 \longrightarrow N_2 + 3H_2$

$$-\frac{1}{2}\frac{d[NH_3]}{dt} = \frac{d[NH_2]}{dt} + \frac{1}{3}\frac{d[H_2]}{dt}$$

$$\frac{d[NH_3]}{dt} = \text{rate} = k \times [NH_3]^0 = 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ sec}^{-1}$$

$$\frac{d[N_2]}{dt} = -\frac{1}{2}\frac{d[NH_3]}{dt} \quad = \frac{1}{2} \times 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ sec}^{-1}$$

$$d[H_2] = -\frac{3}{2}\frac{d[NH_3]}{dt} = \frac{3}{2} \times 2.5 \times 10^{-4} = 3.75 \times 10^{-4} \text{ mol L}^{-1} \text{ sec}^{-1}$$

$$= -\frac{d[NH_3]}{dt} = k \times [NH_3]^0 = 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ sec}^{-1}$$

Rate of production of $N_2 = 2.5 \times 10^{-4}$ mol L^{-1} sec^{-1}

Q.10. **(i) What is rate constant ?**
(ii) On what factors it depends ?
(iii)In a pseudo first order reaction of hydrolysis of an ester in H_2O, the following results were obtained:

t/s	0	30	60	90
Ester (M/L)	0.55	0.31	0.17	0.085

(a) Calculate the average rate of reaction between the time interval 30 to 60 sec.

(b) Calculate the pseudo first order rate constant for the hydrolysis of ester.

Ans. **(i) rate constant(k) of a chemical reaction is rate of reaction when the concentration of the reactants is unity .**
(ii) Rate constant (k) depends upon (i) temperature (ii) order of reaction
(iii)

(a) Average rate during 30-60 sec. $= \frac{0.17-0.31}{60-30} = 4.67\times10^{-3}$ mol L^{-1} sec^{-1}

(b)
$$k_{30} = \frac{2.303}{t}\log\frac{[A]_0}{[A]} = \frac{2.303}{30}\log\frac{0.55}{0.31}$$
$$k_{60} = \frac{2.303}{60}\log\frac{0.55}{0.17}$$
$$k_{90} = \frac{2.303}{90}\log\frac{0.55}{0.085}$$

Average $k = 1.98\times10^{-2}$ sec^{-1}

CASE STUDY BASED QUESTIONS

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

The rate of reaction is the change of concentration of reactant or product with time. The rate law for the reaction $aA+bB \rightarrow cC+dD$ the rate law is rate=$k[A]^a[B]^b$. The rate of reaction is calculated by knowing k, a and b. The rate laws are determined experimentally. During the collisions among two A and two B molecules, doubling the number of either type of molecule increases the number of collisions to eight. The species temporarily formed by the reactant molecules as a result of the collision before they form the product is called the *activated complex*. The temperatare-dependent rate constant is given by the Arrhenius equation. In many cases, the sum of a series of simple reactions are called elementary steps or elementary reactions because they represent the progress of the overall reaction at the molecular level. The sequence of elementary steps that leads to product formation is called the reaction mechanism. The number of molecules reacting in an elementary step determines the molecularity of a reaction.

(A) **On which of the following quantities does the rate constant of a reaction depend?**

(a) Concentrations of reactants (b) Nature of reactant

(c) Temperature (d) All the above

(B) **Instantaneous rate of reaction is measured from the:**

(a) graph of time versus concentration (b) molecularity of reaction

(c) integration method (d) reaction mechanism of a reaction

(C) **The order of reaction is always defined in terms of:**

(a) product concentration (b) rate constant of a reaction

(c) reactant concentration (d) ratio of the product concentration to the reactant concentration

(D) **The number of molecules reacting in an elementary step of a reaction may be:**

(a) 1 (b) 1/2 (c) 12 (d) 5

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

The integrated rate equations can be fitted with kinetic data to determine the order of a reaction. The integrated rate equations for zero and first order reaction are:

Zero order : $[A] = -kt + [A]_o$

First order : $\log [A] = \frac{-kt}{2.303} + \log [A]_o$

These equations can also be used to calculate the half life periods of different reactions, which give the time during which the concentration of a reactant is reduced to half of its initial concentration i.e. at time $t_{1/2}$; $[A] = [A]_o$

In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

c) Assertion is correct statement but reason is wrong statement.

d) Assertion is wrong statement but reason is correct statement.

(A) **ASSERTION:** For the first order reaction the units of rate constant are $time^{-1}$.

REASON: The rate of first order reaction remains constant throughout.

(B) **ASSERTION:** In zero order reaction, the conc. versus time graph is a straight line.

REASON: The rate of change of concentration per unit time in zero order reaction remains constant.

(C) **ASSERTION:** Half-life period is always independent of initial concentration.

REASON: Half-life period is inversely proportional to rate constant.

(D) **ASSERTION**: The slowest step in the reaction is rate determining step.

REASON: Order of a reaction is given by rate law expression.

ANSWERS

I MULTIPLE CHOICE QUESTION:

1. (a) 2. (a) 3. (a) 4. (a) 5. (d) 6. (b) 7. (a) 8. (c) 9. (d) 10. (c) 11. (c)
12. (a,d) 13. (b) 14. (c) 15. (a) 16. (b) 17. (b) 18. (d) 19. (c) 20. (d) 21. (d)

II FILL IN THE BLANKS:

1.	Pseudo first	2.	Fast	3.	Slowest
4.	0.693/k	5.	Cannot	6.	First, two
7.	Activation energy	8.	min^{-1}	9.	0.1 min^{-1}
10.	Effective collisions				

III ASSERTION REASON TYPE QUESTIONS:

1. (a) 2. (c) 3. (c) 4. (d) 5. (a) 6. (d) 7. (a) 8. (d) 9. (c) 10. (c)

IV ONE WORD ANSWER TYPE QUESTIONS:

1.	Zero order	2.	Activation energy	3.	First order reaction
4.	Decrease	5.	First order	6.	No effect
7.	Elementary reaction	8.	Second order	9.	Increase
10.	Endothermic	11.	Two		
12.	Rate of Disappearence of $H_2 = -\frac{d[H_2]}{dt}$			13.	3
14.	Zero	15.	10 Kcal/mol		

CASE STUDY BASED QUESTIONS:

1: (A)	c	(B)	a	(C)	c	(D)	a
2: (A)	c	(B)	a	(C)	d	(D)	b

UNIT TEST-1
CHAPTER - 4
CHEMICAL KINETICS

TIME ALLOWED : 1 HR **M.M. : 20**

1. Which of the following statements is not correct for the catalyst? 1
   (a) It catalyses the forward and backward reaction to the same extent.
   (b) It alters ΔG of the reaction.
   (c) It is a substance that does not change the equilibrium constant of a reaction.
   (d) It provides an alternate mechanism by reducing activation energy between reactants and products.
2. For the reaction: $5Br^-(aq) + BrO_3^-(aq) + 6H^+(aq) \rightarrow 3Br_2(aq) + 3H_2O(l)$ 1
   Which of the following expression is correct for the rate of the reaction?
   (a) $\Delta[Br^-]/\Delta t = 5\Delta[H^+]/\Delta t$ (b) $\Delta[Br^-]/\Delta t = 6\Delta[H^+]/5\Delta t$
   (c) $\Delta[Br^-]/\Delta t = 5\Delta[H^+]/6\Delta t$ (d) $\Delta[Br^-]/\Delta t = 6\Delta[H^+]/\Delta t$
3. For a zero order reaction will the molecularity be equal to zero? Explain. 1

ASSERTION REASON TYPE QUESTIONS

(a) Both assertion and reason are correct statements, and reason is the correct explanation of the assertion.
(b) Both assertion and reason are correct statements, but reason is not the correct explanation of the assertion.
(c) Assertion is correct, but reason is wrong statement.
(d) Assertion is wrong, but reason is correct statement.

4. **ASSERTION:** The rate of reaction is the rate of change of concentration of a reaction or a product. 1
   REASON: Rate of reaction remains constant during the course of reaction.
5. **ASSERTION:** Rate constants determined from Arrhenius equation are fairly accurate for simple as well as complex reactions. 1
   REASON: Reactant molecules undergo chemical change irrespective of their orientation during collision.
6. (i) Why does the rate of a reaction increase with increase in temperature? 2
   (ii) Why is the probability of reaction with molecularity higher than three very rare?

8. After 24 hours, only 0.125 g out of the initial quantity of 1g of a radioactive isotope remains behind. What is its half-life period? 3

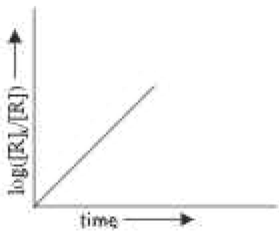
9. A first order reaction is 50% completed in 40 minutes at 300K and in 20 minutes at 320K. Calculate the activation energy of the reaction. 3
(Given: log2= 0.3010, log4=0.6021, R= 8.314$JK^{-1}mol^{-1}$)

10. (i) Define order of reaction. How does order of a reaction differ from molecularity for a complex reaction? 5
(ii) Define instantaneous rate of reaction
(iii) Why H_2 and O_2 do not react at room temperature?
(iv) For which type of reactions, order and molecularity have the same value?

UNIT TEST-2
CHAPTER - 4
CHEMICAL KINETICS

TIME ALLOWED : 1 HR **M.M. : 20**

1. Identify the order of reaction from the following unit for its rate constant: $Lmol^{-1}s^{-1}$ (1)
2. for the reaction, $4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$ If rate of formation of NO is $6X10^{-4}$ atm min^{-1}, calculate the rate of formation of H_2O (1)
3. Write the relationship between k and $t_{1/2}$ (half life period) for first order reaction. (1)
4. Explain with an example, what is a pseudo first order reaction? (1)
5. For the chemical reaction, what is the effect of a catalyst on the rate constant of the reaction? (1)
6. Differentiate between: Average rate and instantaneous rate of a chemical reaction. (2)
7. Observe the graph shown in figure and answer the following question. (2)
   (a) What is the order of the reaction ?
   (b) What is the slope of the curve ?



8. Show that in case of first order reaction, the time required for 99.9% of the reaction to take place is about ten times than that required for half the reaction. (3)
9. The rate constant of a reaction at 500K and 700 K are 0.02 s^{-1} and 0.07s^{-1} respectively. Calculate the value of Ea and A. (3)
10. (i) Answer the following questions (3)
    (a) The conversion of molecules A to B follow second order kinetics. If concentration of A is increased to three times, how will it affect the rate of formation of B ?
    (b) Write the expression of integrated rate equation for zero order reaction.
    (ii) A first order reaction is 20% complete in 20 minutes. Calculate the time taken for the reaction to go to 80% completion (5)

UNIT 8

d- and f- Block Elements

Points to Remember

Element having partially filled d-subshell in their elemental or common oxidation state.

Zn, Cd and Hg not considered as transition elements as not having partially filled d - subshell in their elemental or common oxidation state.

General Electronic configuration of the d-block elements is $(n-1)\,d^{1-10}ns^{1-2}$.

Outer Electronic Configurations of four d-block series elements.

First (3d) Transition Series										
	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Z	21	22	23	24	25	26	27	28	29	30
4s	2	2	2	1	2	2	2	2	1	2
3d	1	2	3	5	5	6	7	8	10	10

Second (4d) Transition Series										
	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
Z	39	40	41	42	43	44	45	46	47	48
5s	2	2	1	1	1	1	1	0	1	2
4d	1	2	4	5	6	7	8	10	10	10

Third (5d) Transition Series										
	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
Z	57	72	73	74	75	76	77	78	79	80
6s	2	2	2	2	2	2	2	1	1	2
5d	1	2	3	4	5	6	7	9	10	10

Fourth (6d) Transition Series										
	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub
Z	89	104	105	106	107	108	109	110	111	112
7s	2	2	2	2	2	2	2	2	1	2
6d	1	2	3	4	5	6	7	8	10	10

General Properties of the Transition Elements

Atomic and Ionic Radii : In a given transition series, from left to right net nuclear charge as well as screening effect increase. Due to this, the atomic and ionic radii for transition elements for a given series show a decreasing trend for first five elements and then screening effect counter balance nuclear charge due to which atomic size becomes almost constant for next five elements of the series. Size of 4d and 5d series elements is almost same due to lanthanoid contraction.

Enthalpies of Atomisation: Transition elements exhibit higher enthalpies of atomization because of large number of unpaired electrons in their atoms they have stronger interatomic interaction and hence stronger bonding between atoms.

Ionisation Enthalpies : • In a series from left to right, ionization enthalphy increases due to increase in nuclear charge.

• The irregular trend in the first ionization enthalphy of the 3d metals, though of little chemical significance, considering that the removal of one electron alters the relative energies of 4s and 3d orbitals.

Standard Electrode Potentials:

$$\begin{tikzcd} M(s) \arrow[rr, leftrightarrow, "E^\circ_{-}", "E^\circ_{\ldots}"'] \arrow[d, "\Delta H_{sub}"] & & M^{+}(aq) \arrow[d, "\Delta H_{hyd}"] \\ M(g) \arrow[rr, "I.E."] & & M^{+}(aq)+e \end{tikzcd}$$

Total energy change E°red. = ΔHsub + I.E. + ΔH_{hyd}. Thus, we can find the total energy change for a particular oxidation state of a metal in its aqueous solution.

The irregularity is due to irregular variation of ionisation energies and the sublimation energies of the atoms and the hydration energies of the divalent ions of the members of first transition series. Greater the value of negative electrode potential, greater will be the stability of M^{2+} state.

Oxidation States : Transition metals shows variable oxidation state due to two incomplete outermost shells. Only stable oxidation states of the first row transition metals are Sc(+3), Ti(+4), V(+5), Cr(+3,+6), Mn(+2,+7), Fe(+2,+3), Co(+2,+3), Ni(+2), Cu(+2), Zn(+2)

• The transition elements in their lower oxidation states (+2 and +3) usually forms ionic compounds. In higher oxidation state compounds are normally covalent. • Only Os and Ru show + 8 oxidation states in their compounds. • Ni and Fe in $Ni(CO)_4$ and $Fe(CO)_5$ show zero oxidation state.

General Properties of the Transition Elements

Magnetic Properties :

• When a magnetic field is applied to substances, mainly two types of magnetic behavior are observed : diamagnetism and paramagnetism. Paramagnetism due to presence of unpaired electrons, each such electron having a magnetic moments associated with its spin angular momentum.

• The magnetic moment is determined by the number of unpaired electrons.

Magnetic moment $=\sqrt{n(n+2)}$ BM

where, n=number of unpaired electron. If all electrons are paired, substance will be diamagnetic and magnetic moment will be zero.

Formation of Complex Compounds

• Transition metals have small size high nuclear charge which facilitates the acceptance of lone pair of elements from ligands.

• They have vacant d-orbitals of appropriate energy in order to accommodate the lone pair of electrons.

Formation of Coloured

• The d-orbitals are non-degenerated in presence of ligands. When an electron from a lower energy d-orbitals is excited to a higher energy d-orbital, the energy of required wavelenght is absorbed and rest light is transmitted out. Therefore, the colour observed corresponds to the complementary colour of the light absorbed.

• In V_2O_5, V is in + 5 oxidation state. It is coloured due to defects in crystal lattice.

General Properties of the Transition Elements

Catalytic Propeties

- Transition metals have two outermost shells incomplete and ability to adopt multiple oxidation states and to form complexes, therefore used as a catalyst.
- Transition metals also provide larger surface area for the reactant to be adsorbed.

Alloy Formation

Alloy is the homogeneous mixture of two or more metals. Transition metals have approximate same size therefore, in molten form they can fit to each other crystalline structure and form homogenous mixture and form the alloy. e.g., Brass (copper-zinc) and bronze (copper-tin) etc.

Formation of Interstitial Compounds

- Small size of non-metals (H, C, N) fit into the voids of crystalline solid of transition metals and form interstitial compounds.
- The principal physical and chemical characteristics of these compounds are as follow :

(i) They have high melting points, higher then those of pure metals.

(ii) They are very hard, some borides approach diamond in hardness.

(iii) They retain metallic conductivity.

(iv) They are chemically inert.

Some important Compounds of Transition Elements

Potassium Dichromate ($K_2Cr_2O_7$)

Preparation

Ore- Ferrochrome or chromite

($FeO.Cr_2O_3$) or ($FeCr_2O_4$)

$FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO$
(yellow)

$2Na_2CrO_4 + 2H^+ + Na_2Cr_2O_7 + 2Na^+ + H_2O$
(orange)

$Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$

Sodium dichromate is more soluble than potassium dichromate.

- Chromates and dichromates are interconvertible in aqueous solution depending upon pH of the solutions.

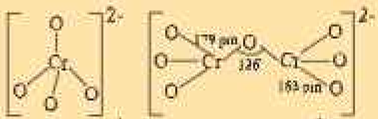
Propeties

Sodium and potassium dichromates are strong oxidizing agents, thus, acidified $K_2Cr_2O_7$ will oxidise iodides to iodine, sulphides to sulphur, tin (II) to tin (IV) and iron (II) salts to iron (III).

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

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

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



chromate ion sp^3 dichromate ion sp^3

Uses

(a) $K_2Cr_2O_7$ is used as oxidizing agent in volumetric analysis.

(b) It is used in mordant dyes, leather industry, photography (for hardening of film).

(c) It is used in chromyl chloride test.

(d) It is used in cleaning glassware.

Preparation

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

$3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^-$(green)$MnO_2 + 2H_2O$

Commercial preparation

$MnO_2 \xrightarrow[\text{with air or } KNO_3]{\text{Fused with KOH oxidised}} MnO_4^{2-}$ Manganate ion

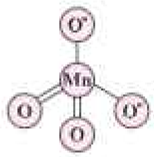
$MnO_4^{2-} \xrightarrow[\text{(alkaline medium)}]{\text{Electrolytic oxidation}} MnO_4^-$ Permanganate ion (purple)

Uses

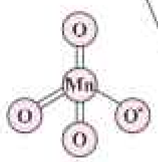
(a) In laboratory preparation of Cl_2.

(b) $KMnO_4$ is used as an oxidizing agent, disinfectant.

(c) In making Baeyer's reagent.



Tetrahendral manganate (green) ion



Tetrahendral permanganate (purple) ion

Potassium Permanganate $KMnO_4$

NOTE :

$K_2Cr_2O_7$ and $KMnO_4$ are coloured due to charge transfer complex formation.

PROPERTIES:

$KMnO_4$ acts as strong oxidizing agent.

(a) In presence of dilute H_2SO_4, $KMnO_4$ is reduces to manganous salt.

$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

Acidic $KMnO_4$ solution oxidizes oxalates to CO_2, iron (II) and iron (III), nitrites to nitrates and iodides to iodine. The half reactions of reductants are

$$C_2O_4^{2-} \rightarrow CO_2 + 2e^-$$
$$Fe^{2+} \rightarrow Fe^{3+} + e^-$$
$$NO_2^- \rightarrow NO_3^- + 2e^-$$
$$2I^- \rightarrow I_2 + 2e^-$$

To acidify $KMnO_4$, only H_2SO_4 is used and not HCl or HNO_3 because HCl reacts with $KMnO_4$ and produce Cl_2 while HNO_3, itself acts as oxidizing agent.

(b) in alkaline medium, $KMnO_4$ is reduced to insoluble MnO_2.

$MnO_4^- + 3e^- + 2H_2O \rightarrow MnO_2 + 4OH^-$

Alkaline or neutral $KMnO_4$ solution oxidizes I^- to IO_3^-, $S_2O_3^{2-}$ to SO_4^{2-}, Mn^{2+} to MnO_2 etc.

The Inner Transition Elements (f-Block)

The f-block consists of the two series, lanthanoids and actinoids. Lanthanoids are known as rare earth metals and actinoids are known as radioactive elements (Th to Lr).

LANTHANOIDS:

General electronic configuration [Xe] $4f^{1-14}$, $5d^{0-1}$, $6s^2$.

- Atomic and ionic size from left to right, decreases due to increase in nuclear charge. This is known as lanthanoid contraction.
- All the lanthanoids are silvery white soft metals and tarnish rapidly in air.
- Many trivalent lanthanoid ions are coloured both in the solid state and in aqueous solutions. Neither La^{3+} nor Lu^{3+} ion shows any colour but the rest do so.
- The lanthanoid ions other than the f^0 type (La^{3+} and Ce^{4+}) and the f^{14} type (Yb^{2+} and Lu^{3+}) are all paramagnetic. The paramagnetism arises to maximum in neodymium.
- Oxidation states→Ce^{4+}; (Some elements) is favoured by its noble gas configuration, but it is a strong oxidant reverting to the common+3 state. The E^ovalue for Ce^{4+}/Ce^{3+} is +1.47 V, the reaction rate is very slow and hence, Ce(IV) is a good analytical reagent. Pr, Nd, Tb and Dy also exhibit + 4 state but only in oxides. Eu^{2+} is formed by losing the two s-electrons and its f^7 configuration accounts for the formation of this ion. However, Eu^{2+} is a strong reducing agent changing to the common + 3 state. Similarly, Yb^{2+} which has f^{14} configuration is a reductant. Tb^{4+} has half-filled f-orbitals and is an oxidant.
- Misch metals, contain lanthanoids about 90-95% (Ce 40-5%, Lanthanum and neodymium 44%) iron 4.5%, calcium, carbon and silicon, used in cigrette and gas lighters, toys, tank and tracer bullets.

ACTINOIDS:

- General electronic configuration [Rn] $5f^{1-14}$,$6d^{0-1}$, $7s^2$.
- Actinoids exhibit a range of oxidation states due to comparable energies of 5f, 6d and 7s orbitals. The genral oxidation state of actinoids is + 3.
- All the actinoids are strong reducing agents and very reactive.
- Actinoids also react with oxygen, halogen, hydrogen and sulphur, etc. like lanthanoids.
- Actinoids are radioactive in nature and therefore, it is difficult to study their chemical nature.
- Actinoid contraction is greater than lanthanoid contraction from element to element because 5f electrons are more effectively shielded from nuclear charge.

OBJECTIVE TYPE QUESTIONS

I. MULTIPLE CHOICE QUESTIONS

1. The characteristics of transition metals which is not responsible for formation of the complex ion is:
   (a) Presence of unpaired electron in d-subshell
   (b) Presence of paired electrons in d-subshells
   (c) Providing vacant d-orbitals
   (d) Having high charge/size ratio

2. The correct electronic configuration of copper atom is:
   (a) $3d^{10}4s^{1}$ (b) $3d^{10}4s^{2}$
   (c) $3d^{9}4s^{2}$ (d) $3d^{5}4s^{2}4p^{4}$

3. Maximum number of unpaired electrons are in :
   (a) Cr (Z = 24) (b) Mn (Z = 25)
   (c) Fe^{2+} (Z = 26) (d) Co (Z = 27)

4. Manganese exhibits maximum oxidation state in:
   (a) K_2MnO_4 (b) $KMnO_4$
   (c) MnO_2 (d) Mn_3O_4

5. General electronic configuration of d-block elements is :
   (a) $(n-1)d^{1-10}ns^{0-2}$ (b) $(n-1)d^{1-10}ns^{1-2}$
   (c) $(n-1)d^{1-10}ns^{0}$ (d) $(n-1)d^{1-10}ns^{1}$

6. Electronic configuration of d-block element 'X' in +3 oxidation state in [Ar] $3d^5$. Atomic number of 'X' is :
   (a) 25 (b) 26
   (c) 27 (d) 24

7. $Cr_2O_7^{2-}$ dissolves in aqueous NaOH to give:
   (a) CrO_4^{2-} (b) $Cr(OH)_3$
   (c) $Cr_2O_7^{2-}$ (d) $Cr(OH)_2$

8. The electronic configuration of gadolinium (At. No. 64) is:
   (a) [Xe] $4f^{8}\,5d^{0}\,6s^{2}$ (b) [Xe] $4f^{7}\,5d^{1}\,6s^{2}$
   (c) [Xe] $4f^{3}\,5d^{5}\,6s^{2}$ (d) [Xe] $4f^{6}\,5d^{2}\,6s^{2}$

9. On addition of small amount of $KMnO_4$ to concentrated H_2SO_4, a green oily compound is obtained which is highly explosive in nature. Identify the compound from the following.

   (a) Mn_2O_7 (b) MnO_2

   (c) Mn_2O_4 (d) Mn_2O_3

10. Which of the following oxidation state is common for all lanthanoids?

    (a) +2 (b) +3

    (c) +4 (d) +5

11. When $KMnO_4$ solution is added to oxalic acid solution, the decolourisation is slow in the beginning but becomes instantaneous after same time because:

    (a) CO_2 is formed as the products

    (b) Reaction is exothermic

    (c) MnO_4^- catalysis the reaction

    (d) Mn^{2+} acts as autocatalyst

12. $KMnO_4$ acts as an oxidising agent in acidic medium. The number of moles of $KMnO_4$ that will be needed to react with one mole of sulphide ions in acidic solution is:

    (a) 2/5 (b) 3/5

    (c) 4/5 (d) 1/5

13. Which of the following are amphoteric oxides?

    (a) V_2O_5, Cr_2O_3

    (b) Mn_2O_7, CrO_3

    (c) CrO_3, V_2O_5

    (d) V_2O_5, V_2O_4

14. The magnetic moment is associated with its spin angular momentum. Spin only magnetic moment value of Cr^{3+} ion is............

    (a) 2.87 B.M.

    (b) 3.87 B.M.

    (c) 3.47 B.M.

    (d) 357 B.M.

15. Generally transition elements and their salts are coloured due to the presence of unpaired electrons in metal ions. Which of the following compound is coloured?

    (a) $KMnO_4$ (b) $ZnSO_4$

    (c) $TiCl_4$ (d) Cu_2Cl_2

16. Transition elements show magnetic moment due to spin and orbital motion of electrons. Which of the following metallic ions have almost same spin only magnetic moment?

    (a) Co^{2+}, Cr^{2+} (b) Cr^{2+}, Mn^{2+}

    (c) Mn^{2+}, Co^{2+} (d) Co^{2+}, Cr^{3+}

17. Which of the following actionoids show oxidation states upto + 7?

    (a) Am (b) Pu

    (c) U (d) Th

18. Which of the following ions show highest spin only magnetic moment value?

    (a) Ti^{3+} (b) Mn^{2+}

    (c) Fe^{2+} (d) Co^{3+}

II FILL IN THE BLANKS

1. Hybridisation of Cr in Chromate ion is.................
2. Maximum oxidation state exhibited by Mn is.....................
3. Electronic configuration of Cr is...............
4. Theoretical magnetic moment (spin - only) of Ti^{3+} ion is.................
5. The equivalent weight of $K_2Cr_2O_7$ in acidic medium is.................
6. Last element in the actinide series is.................
7. The general electronic configuration of d — block elements is.................
8. The colour of $KMnO_4$ is due to.................
9. Out of Sc^{2+} and Sc^{3+} ion, ... is paramagnetic in nature.
10. The oxidation state of Mn in K_2MnO_4 is ....

III ASSERTION REASON TYPE QUESTIONS

In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choice.

(a) Both assertion and reason are True, and reason is the correct explanation of the assertion.

(b) Both assertion and reason are True, but reson is not the correct explanation of the assertion.

(c) Assertion is true, but reason is false.

(d) Assertion is false, reason is true.

1. **ASSERTION** : Sc does not show variable oxidation states.
   REASON : Sc has only one electron in the 3d subshell.
2. **ASSERTION :** Separation of Zr and Hf is difficult.
   REASON: Because Zr and Hf lie in the same period of the periodic table.
3. **ASSERTION :** Actinoids form relatively less stable complexes as compared to lanthanoids.
   REASON: Actinoids can utilise their 5f orbitals along with 6d orbitals in bonding but lanthanoids do not use their 4f orbital for bonding.
4. **ASSERTION :** Cu cannot liberate hydrogen from acids.
   REASON: Because it has positive electrode potential.
5. **ASSERTION :** The highest oxidation state of osmium is + 8.
   REASON: Osmium is a 5d element.
6. **ASSERTION :** Highest oxidation state is exhibited by transition metal lying in the middle of the series.
   REASON: The highest oxidation state exhibited corresponds to number of (n-1)d electrons.
7. **ASSERTION :** Fe^{3+} is more stable than Fe^{2+}
   REASON: Fe^{3+} has $3d^5$ configuration while Fe^{2+} has $3d^6$ configuration.
8. **ASSERTION :** Vanadium has the ability to exhibit a wide range of oxidation states.
   REASON: The standard potentials Vanadium are rather small, making a switch between oxidation states relatively easy.
9. **ASSERTION :** Transition metals like Fe, Cr and Mn form oxyions.
   REASON: Oxygen is highly electronegative and has a tendency to form multiple bonds.
10. **ASSERTION :** The highest oxidation states of the 3d metals depends only on electronic configuration of the metal.
    REASON: The number of electrons in the (n-1)d and ns subshells determine the oxidation states exhibited by the metal.

IV ONE WORD ANSWER TYPE QUESTIONS

1. Which element in 3d series shows highest number of oxidation states?
2. Out of cuprous and cupric ions which is coloured?
3. Out of Zn and Cr which is having higher first ionisation enthalpy?
4. Give general Electronic configuration of actinoids.
5. Name the element of 3d series which does not exhibit variable oxidation state.

6. What is the equivalent mass of $KMnO_4$ in alkaline medium.

7. What is the maximum oxidation state shown by actinoids.

8. Out of $CuCl_2$ and Cu_2Cl_2 which is more stable?

9. What is the cause of similar size of Zr and Hf ?

VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)

Q.1. Explain $CuSO_4.5H_2O$ is blue while $CuSO_4$ is colourless ?

Ans. Because water molecules act as ligands and results in crystal field splitting of d-orbitals of Cu^{2+} ion.

Q. 2. Which transition element 3d series exhibit highest oxidation state ?

Ans. Os

Q.3. In 3d series (Sc to Zn), the enthalpy of atomization of Zn is low. Why ?

Ans. Due to absence of unpaired electrons.

Q.4. Which element among 3d series exhibit only one oxidation state ?

Ans. Sc

Q.5. Why is the 3rd ionization energy of Mn (Z=25) is unexpectedly high ?

Ans. Due to half-filled electronic configuration.

Q.6. Define alloy.

Ans. Alloys are homogeneous solid solutions of two or more metals.

Q.7. Transition metals show zero oxidation state with ligands like CO. Explain.

Ans. CO form synergic bonding with metal ion.

Q.8. Why HCl can not be used to acidify $KMnO_4$ solution ?

Ans. Because $KMnO_4$ oxidize HCl into Cl_2.

Q. 9. Name one ore of Mn and Cr.

Ans. Mn : MnO_2 Cr : $FeCr_2O_4$

Q.10. Why Mn^{2+} compounds are more stable than Fe^{2+} compounds towards oxidation to their +3 state ?

Ans. Mn^{2+} has half-filled electronic configuration (d^5).

Q.11. Why do transition elements show variable oxidation states ?

Ans. Due to presence of partially filled (n-1)d subshell in addition of ns subshell.

Q.12. Write any uses of pyrophoric alloy.

Ans. Making bullets, shells and ligher flints.

Q.13. Which is more basic - $La(OH)_3$ or $Lu(OH)_3$? Why ?

Ans. $La(OH)_3$, due to lanthanoid contraction, lower size, more covalent character, least basic.

Q.14. Find out number of Cr - O - Cr bond/bonds in $Cr_2O_7^{2-}$ ion.

Ans. 1

Q.15. Why is Ce^{4+} in aqueous solution a good oxidizing agent ?

Ans. Because Ce is most stable in Ce^{3+} state in aqueous solution.

Q.16. What is lanthanoid contraction ?

Ans. The regular steady decrease in the atomic or ionic radii of lanthanoids with increasing atomic number.

Q.17. Why is Cu (Z = 29) considered a transition metal ?

Ans. Due to its partially filled d-orbital in Cu^{2+} state.

Q.18. Arrange the given in increasing order of acidic character : CrO_3, CrO, Cr_2O_3.

Ans. $CrO_3 < CrO < Cr_2O_3$

SHORT ANSWER TYPE QUESTIONS (2 or 3 Marks)

Q. 1. Chromium is typical hard metal while mercury is a liquid. Explain why ?

Ans. Cr has five unpaired d-electrons. Hence metallic bonds are strong. In Hg, there is absence of 'unpaired electrons and size is larger.

Q.2. Why $KMnO_4$ is deep purple in colour?

Ans. $KMnO_4$ forms charge transfer complex.

Q.3. Most of the transition metals do not displace hydrogen from dilute acids, why ?

Ans. Due to their negative reduction potential.

Q.4. Explain why Cu^{+} is not stable in aqueous solution ?

Ans. Due to less negative $\Delta_{hyd}H$ of Cu^{+}/it cannot compensate 2nd ionization potential of Cu.

Q.5. Why is the highest oxidation state of a metal exhibited in its oxide or fluoride only ?

Ans. Oxygen and fluoride have small size and high electronegativity. They can oxidise the metal.

Q.6. Write electronic configuration of Cu^{2+} and Co^{2+}.

Ans. Cu^{2+} – [Ar] $3d^9 4s^0$ Co^{2+} - [Ar] $3d^7$

Q.7. Briefly explain why electronic configuration of lanthanoids are not known with certainty ?

Ans. 4f/5d subshells are very close in energy. So electrons can jump from 4f to 5d or vice-versa.

Q.8. Why Zn, Cd, Hg are soft and have low melting point ?

Ans. Due to weak interatomic attraction/absence of unpaired electrons.

Q.9. Which of the following is/are transition element and why ? Zn, Cd, Ag, Fe, Ni

Ans. Fe, Ni, Ag

Q.10. What are interstitial compounds ? Give example.

Ans. When small atoms like C, H, B and N occupy interstitial site in crystal lattice of metals.

Example : TiC.

Q.11. Why is first ionization enthalpy of 5d elements higher than those of 3d and 4d elements ?

Ans. Due to greater effective nuclear charge acting on outer most electrons because of poor shielding of 4*f* electrons.

Q.12. Explain 'Misch metal' and write its use.

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

Q.13. Write balanced chemical equations :

(a) $Cr_2O_7^{2-} + H^{+} + Fe^{2+} \rightarrow$

(b) $MnO_4^{-} + H^{+} + C_2O_4^{2-} \rightarrow$

Q.14. Out of Fe and Cu, which one would exhibit higher melting point ?

Ans. Fe, due to large number of unpaired d-electrons/more interatomic attraction.

Q.15. Sc does not exhibit variable oxidation state. Why ?

Ans. Due to noble gas electronic configuration in + 3 oxidation state no other oxidation state is stable.

Q.16. (a) Deduce the number of 3d electrons in the following ions : Cu^{2+}, Sc^{3+}

(b) Why do transition metals form alloy ?

(c) Why Zn^{2+} salts are white ?

Ans. (a) Cu^{+2} : 9 electrons : Sc^{3+} : 0 electron

(b) Transition metals have similar atomic radii.

(c) Absence of unpaired electron.

Q.17. (a) Why is separation of lanthanoid elements difficult ?

(b) Transition metal exhibit higher enthalpies of atomization. Explain.

(c) Why the transition metals have ability to form complexes?

Ans. (a) Due to lanthanide contraction, the size of these elements is nearly same.

(b) Transition metal contain large number of unpaired electrons, and they have strong interatomic attractions.

(c) Due to their small size and large nuclear charge.

Q.18. (a) Use Hund's rule to derive the electronic configuration of Ce^{3+} ions and calculate its magnetic moment.

(b) Is lanthanum a f-block element ?

Ans. (a) $Ce(58) = [Xe]\,4f^1 5d^1 6s^2$; $Ce^{3+} = 4f^1$, $\mu = 1.73$ BM $\mu = \sqrt{n(n+2)}$

(b) No, it is a d-block element.

Q.19. Account for the following :

(a) Silver chloride dissolves in excess of NH_3.

(b) Cuprous chloride is diamagnetic while cupric chloride is paramagnetic.

(c) In CrO_4^{2-} ion, all the Cr-O bond length are equal.

Ans. (a) AgCl forms a soluble complex with NH_3. ($AgCl + 2NH_3 \rightarrow [Ag(NH_3)_2]Cl$)

(b) Cu^+ : $3d^{10}\,4s^0$ - All electrons are paired. Cu^{2+} : $3d^9$ - Here, one unpaired electron is present.

(c) Due to resonance.

Q.20. The E^o values in respect of electrodes of Cr, Mn and Fe are : $Cr^{3+}/Cr^{2+} = -0.4$ V $Mn^{3+}/Mn^{2+} = +1.5$ V $Fe^{3+}/Fe^{2+} = +0.8$ V Compare the feasibilities of further oxidation of these ions.

Ans. Cr^{3+} is more stable than Cr^{2+}. Mn^{2+} is more stable than Mn^{3+}. Fe^{3+} is more stable than Fe^{2+}. Order of feasibility of + 2 oxidation state is : $Mn^{2+} > Fe^{2+} > Cr^{2+}$

Q.21. Write any four properties of interstitial compounds.

Ans. (a) They are chemically inert.

(b) They retain metallic conductivity.

(c) They have high melting point than their pure metals.

(d) These are harder and more corrosion resistant.

Q.22. Account for the following :

(a) All Scandium salts are white.

(b) The first ionization energy of the 5d series are higher than 3d and 4d transition elements in respective groups.

(c) Ce^{3+} can be easily oxidized to Ce^{4+}.

Ans. (a) Sc has only + 3 oxidation state, there is no unpaired electron.

(b) Due to lanthanoid contraction, effective nuclear charge increase.

(c) Due to attainment of noble gas electronic configuration.

LONG ANSWER TYPE QUESTIONS (5 Marks)

Q. 1. (a) What is meant by disproportionation of an oxidation state ? Give one example.

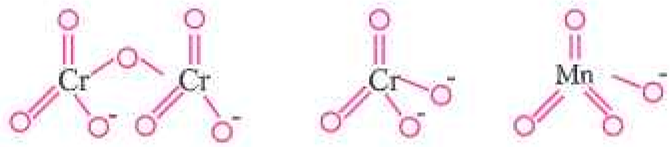
(b) Draw the structures of $Cr_2O_7^{2-}$, CrO_4^{2-}, MnO_4^-.

(c) What is the effect of lanthoid contraction beyond lanthanoid ?

Ans. (a) When any atom or ion undergo oxidation and reduction simultaneously it is called disproportionation.

$2Cu^+ \rightarrow Cu^{2+} + Cu$

(b)



(c) Size of respective 4d and 5d series elements becomes comparable (e.g., Zr and Hf).

2. 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.

Ans. (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.

3. (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 $M(CO)_5$

(ii) MO_3F

Ans. (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 [Hint : As above].

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

(b) (i) $Fe(CO)_5$

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

4. (i) How would you account for the following?

(a) The oxidising power of oxo-anions are in the order $VO^{2+} < Cr_2O_7^{2-} < MnO_4^-$

(b) The third ionisation enthalpy of manganese (Z = 25) is exceptionally high.

(c) Cr^{3+} is a stronger reducing agent than Fe^{2+}.

(ii) Give reasons for the following:

(a) Mn^{3+} is a good oxidising agent.

(b) $E^\circ(M^{2+}/M)$ values are not regular for first row transition metals (3d-series).

(c) Although 'F' is more electronegative than 'O' the highest Mn fluoride is MnF_4, where as the highest oxide is Mn_2O_7 reducing agent than Fe^{2+}.

Ans (i) (a) It is due to the fact that V in its lower oxidation state is less stable than Cr which in turn is less stable than Mn. Thus, MnO_4^- has a great tendency to get reduced and hence, behave as a good oxidising agent. Similary VO^{2+} has the least oxidising power.

(b) The third ionisation enthalpy of Mn is very high due to the fact that the third electron has to be removed from stable half-filled configuration, i.e., $3d^5$.

(c) Cr^{2+} is stronger reducing agent than Fe^{2+} because $d^4 \rightarrow d^3$ transition occurs in case of Cr^{2+} to Cr^{3+} while $d^6 \rightarrow d^5$ transition occurs in case of Fe^{2+} to Fe^{3+}. In a medium like water d^3 is more stable as compared to d^5.

(ii) (a) Mn^{3+} $(3d^4)$ is a good electron acceptor as the resulting species is more stable $(3d^5)$.

(b) The $E^\circ(M^{2+}/M)$ values are not regular which can be explained from the irregular variation of ionisation enthalpies $(\Delta_iH_1 + \Delta_iH_2)$ and also the sublimation enthalpies which are relatively much less for Mn and V.

(c) Due to multiple bond formation ability of oxygen. Mn can form Mn_2O_7.

5. The elements of 3d-transition series are given as:

SC, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn

Answer the following :

(i) Name the element which shows maximum number of oxidation states. Give reason.

(ii) Which element has the highest melting point?

(iii) Name the element which shows only + 3 oxidation state?

(iv) Which element is a strong oxidizing agent in + 3 oxidation state and why?

Ans (I) Mn. It has maximum unpaired electrons.
(ii) Cr
(iii) Sc
(iv) Manganese. Mn^{3+} to Mn^{2+} results in the stable half filled (d^5) configuration.

6. On the basis of the figure given below, answer the following questions:

(i) Why Manganese has lower melting point than Chromium.
(ii) Why do transition metals of 3d series have lower melting points as compared to 4d series ?
(iii) In the third transition series, identify and name the metal with the highest melting point.
(iv) Which element is a strong oxidizing agent in + 3 oxidation state and why?

Ans. (i) Managnese is having lower m.p. as compared to Chromium, as it has highest number of unpaired electrons, strong interatomic metallic bonding, hence no delocalization of electrons.
(ii) Due to more frequent metal-metal bonding in compounds of heavy transition metals i.e. 4d and 5d series.
(iii) tungsten

CASE STUDY BASED QUESTIONS

1. Read the passage and answer the following questions.

Potassium dichromate is one of the crystalline inorganic chemical reagents. Hexavalent chromium compounds are harmful to health. $K_2Cr_2O_7$ is widely used in laboratories and industry as an oxidizing agent because it is not deliquescent. Potassium dichromate looks very bright and red-orange color. In this work different amount of acidic (HCl) and alkaline (NaOH) solutions were added to stoke solutions of K_2CrO_4 and $K_2Cr_2O_7$ to show the effect of pH values on their spectra.

The results of UV-Visible spectroscopy shows that, the changing of solution pH value when drops of HCl were added led to shift wavelength of K_2CrO_4 spectrum while no change has been occurred in $K_2Cr_2O_7$ spectrum. However, Changing pH values solution by adding drops of NaOH led to change in wavelength red shift for $K_2Cr_2O_7$ while no changes has been occurred in spectrum of K_2CrO_4.

Reference: Effect of the Acidic and Alkaline Solutions on K_2CrO_4 and $K_2Cr_2O_7$ by Ultraviolet and Visible Measurement Mohammad Radi Mohammad, Hasanain Saad Azeez* Al-Mustansiriyah Journal of Sience ISSN: 1814-635X (print), ISSN:2521-3520 (online) Volume 30, Issue 1, 2019, 221-224

(A) The hybridization of Cr in dichromate ion is :

(a) d^3sp^3 (b) sp^3

(c) dsp^2 (d) sp^3d

(B) Colour of potassium dichromate is :

(a) purple (b) green

(c) yellow (d) orange

(C) Chemical formula of ferrochrome is :

(a) $FeCrO_2$ (b) $FeO.Cr_2O_3$

(c) Fe_2CrO_4 (d) None of these

(D) On increasing pH of dichromate, it converts in :

(a) CrO_4^{2-} (b) $Cr_2O_4^{2-}$

(c) CrO_4^{-1} (d) CrO_3

2. **Read the passage and answer the following questions.**

Heavy rare earth elements crystallize into hexagonally close packed (h.c.p.) structures and share a common outer electronic configuration, differing only in the number of 4*f* electrons they have. These chemically inert 4f electrons set up localized magnetic moments, which are coupled via an indirect exchange interaction involving the conduction electrons. This leads to the formation of a wide variety of magnetic structures, the periodicities of which are often incommensurate with the underlying crystal lattice. Such incommensurate ordering is associated with a 'webbed' topology of the momentum space surface separating the occupied and unoccupied electron states (the Fermi surface). The shape of this surface—and hence the magnetic structure—for the heavy rare earth elements is known to depend on the ratio of the interplanar spacing c and the interatomic, intraplanar spacing a of the h.c.p. lattice. A theoretical understanding of this problem is, however, far from complete. Here, using gadolinium as a prototype for all the heavy rare earth elements, we generate a unified magnetic phase diagram, which unequivocally links the magnetic structures of the heavy rare earths to their lattice parameters. In addition to verifying the importance of the c/o ratio, we find that the atomic unit cell volume plays a separate, distinct role in determining the magnetic properties: we show that the trend from ferromagnetism to incommensurate ordering as atomic number increases is connected to the concomitant decrease in unit cell volume. This volume decrease occurs because of the so-called lanthanide contraction, where the addition of electrons to the poorly shielding 4f orbitals leads to an increase in effective nuclear charge and, correspondingly, a decrease in ionic radii.

Reference:

Lanthanide contraction and magnetism in the heavy rare earth elements.

Hughes, I., Dane, M., Ernst, A. et al. Nature 446,650-653 (2007). https://doi.org/10.1038/nature05668

(A) Rare earth elements are also called :

(a)	Actinoids	(d)	Lanthanoids
(c)	Alkali metals	(d)	None of these

(B) Radioactive lanthanoids is :

(a)	Pm	(b)	Ce
(c)	Nd	(d)	Er

(C) Cause of lanthanoid contraction is :

(a)	poor shielding of 5f orbitals	(b)	poor shielding of 4f orbitals
(c)	poor shielding of 6f orbitals	(d)	All of these

(D) The common oxidation state of lanthanoides is :

(a)	+4	(b)	+3
(c)	+2	(d)	+1

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

The d block elements are the 40 elements contained in the four rows of ten columns (3-12) in the periodic table. As all the d block elements are metallic, the term d-block metals is synonymous. This set of d-block elements is also often identified as the transition metals, but sometimes the group 12 elements (zinc, cadmium, mercury) are excluded from the transition metals as the transition elements are defined as those with partly filled d or f shells in their compounds. Inclusion of the elements zinc, cadmium and mercury is necessary as some properties of the group 12 elements are appropriate logically to include with a discussion of transition metal chemistry.

The term transition element or transition metal appeared to derive from early studies of periodicity such as the Mendeleev periodic table of the elements. His horizontal table of the elements was an attempt to group the elements together so that the chemistry of elements might be explained and predicted. In this table there are eight groups labeled 1-VIII with each subdivided into A and B subgroups. Mendeleev recognized that certain properties of elements in. Group VIII are related to those of some of the elements in Group VII and those at the start of the next row Group I. In that sense, these elements might be described as possessing properties transitional from one row of the table to the next.

Reference: Winter, M. J. **d-Block Chemistry** *(Vol. 27)*. Oxford University Press, USA.)

In the following questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices on the basis of the above passage.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

(c) Assertion is correct statement but reason is wrong statement.

(d) Assertion is wrong statement but reason is correct statement.

(A) Assertion: Group 12 elements are not considered as transition metals.
Reason: Transition metals are those which have incompletely filled d sub-shell in their compounds.

(B) Assertion: All d block elements are metallic in nature.
Reason: The d—block elements belong to Group 3 -12 of the periodic table.

(C) Assertion: Nickel is a transition element that belongs to group 10 and period 4 of the modern periodic table.
Reason: Electronic configuration of nickel is [Ar] $3d^8 4s^2$

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

The transition metals when exposed to oxygen at low and intermediate temperatures form thin, protective oxide films of up to some thousands of Angstroms in thickness. Transition metal oxides lie between the extremes of ionic and covalent binary compounds formed by elements from the left or right side of the periodic table. They range from metallic to semiconducting and deviate by both large and small degrees from stoichiometry. Since d-electron bonding levels are involved, the cations exist in various valence states and hence give rise to a large number of oxides. The crystal structures are often classified by considering a cubic or hexagonal close-packed lattice of one set of ions with the other set of ions filling the octahedral or tetrahedral interstices. The actual oxide structures, however, generally show departures from such regular arrays due in part to distortions caused by packing of ions of different size and to ligand field effects. These distortions depend not only on the number of d-electrons but also on the valence and the position of the transition metal in a period or group.

Reference: Smeltzer, W.W., & Young, D. J. (1975). Oxidation properties of transition metals. Progress in Solid State Chemistry, 10,17-54.)

In the following questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices on the basis of the above passage.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

(c) Assertion is correct statement but reason is wrong statement.

(d) Assertion is wrong statement but reason is correct statement.

(A) Assertion: Cations of transition elements occur in various oxidation states
Reason: Transition metals are those which have incompletely filled d subshell in their compounds.

(B) Assertion: Crystal structure of oxides of transition metals often show defects.
Reason: Ligand field effect cause distortions in crystal structures.

(C) Assertion : Transition metals form protective oxide films.
Reason: Oxides of transition metals are always stoichiometric.

(D) Assertion: CrO crystallises in a hexagonal close-packed array of oxide ions with two out of every three octahedral holes occupied by chromium ions
Reason: Transition metal oxide may be hexagonal close-packed lattice of oxide ions with metal ions filling the octahedral voids.

ANSWERS

I. MULTIPLE CHOICE TYPE QUESTIONS

1. b 2. a 3. b 4. b 5. b 6. b 7. a 8. b 9. a
10. b 11. d 12. a 13. a 14. b 15. a 16. d 17. b 18. b

II FILL IN THE BLANKS

1.	sp^3	2.	+7
3.	$[Ar]3d^5 4s^1$	4.	1.732
5.	49g	6.	lawrencium
7.	$(n-1)d^{1-10} ns^{1-2}$	8.	charge transfer complex
9.	Sc^{2+}	10.	6

III ASSERTION REASON TYPE QUESTIONS

1.(b) 2.(b) 3.(c) 4.(a) 5.(b) 6.(c) 7.(a) 8.(a) 9.(b) 10.(d)

IV ONE WORD TYPE QUESTIONS

1. Mn 2. Cupric 3. Zn 4. $5f^{1-14} 6d^{0-1} 7s^2$ 5. Sc
6. 158g 7. 7 8. $CuCl_2$ 9. Lanthanoid Contraction

CASE STUDY BASED QUESTIONS

1.	(A) b	(B) d
	(C) b	(D) a
2.	(A) b	(B) a
	(C) b	(D) b
3.	(A) a	(B) b
	© a	
4.	(A) b	(B) a
	(C) c	(D) d

UNIT TEST-1

d- and f- block Elements

Time Allowed: 1 Hour **Maximum marks: 20**

1. Which element among 3d-transition elements, exhibit the highest oxidation state? 1
2. Name the transition element which has highest $E^{\circ}(M^{2+}/M)$ value 1
3. Calculate the magnetic moment of Cu^{2+} (Z = 29) on the basis of "spin-only" formula. 1
4. Name a transition element which does not exhibit variable oxidation state in 3d series. 1
5. Write the general electronic configuration of d-block elements. 1
6. Write balanced chemical equations for:
   (a) Oxidation of Fe^{2+} by $Cr_2O_7^{2-}$ in acidic medium
   (b) Oxidation of Mn^{2+} by MnO_4^- in neutral or faintly alkaline medium. 2
7. Account for the following:
   (a) Copper shows its inability to liberate hydrogen gas from the dilute acids.
   (b) Scandium (Z = 21) does not exhibit variable oxidation states. 2
8. Explain lanthanoid contraction with its consequences. 2
9. Assign reasons for the following: 3
   (a) Majority of transition metals form complexes.
   (b) Ce^{3+} can be easily oxidised to Ce^{4+}.
   (c) Actinoids exhibits a variety of oxidation states.
10. Describe the preparation of potassium permanganate ($KMnO_4$), from MnO_2. Write the chemicalequations involved in the synthesis. 3
11. Explain giving reasons: 3
    (a) Zn, Cd and Hg are not considered as transition metals.
    (b) Elements in the middle of transition series have higher melting points.
    (c) The decrease in atomic size of transition elements in a series is very small.

UNIT TEST-2

d- and f- block Elements

Time Allowed: 1 Hour **Maximum marks: 20**

1. Explain- zinc is not regarded is transition element. 1
2. Name a lanthanoid well known to exhibit +4 oxidation state. 1
3. Out of Sc^{3+}, Co^{2+} and Cr^{3+} ions, which ion will be colourless in aqueous solutions? (Atomic no. : Co=27, Sc=21 and Cr=24) 1
4. Write general electronic configuration of lanthonoid series. 1
5. Why Zr(Z=40) and Hf(Z=72) shows similar properties? 1
6. Name the 3d element which: 2
   a) Does not exhibit variable oxidation state
   b) Exhibits highest oxidation state
   c) Has highest spin-only magnetic moment in +2 oxidation state
   d) Has highest E° (M^{2+} | M) value.
7. Write any two differences between lanthanoids and actinoids.
8. Explain disproportionation reaction giving one example of a compound/ion containing transition element. 2
9. Explain following in context of transition elements:
   a) High enthalpy of atomisation
   b) Catalytic activity
   c) Coloured complexes
10. Write balanced chemical equations for the following reactions: 3
    a) $MnO_4^- + S_2O_3^{2-} + H_2O \rightarrow$
    b) $Cr_2O_7^{2-} + Sn^{2+} + 4H^+ \rightarrow$
    c) $Fe^{2+} + MnO_4^- + 8H^+ \rightarrow$
11. When MnO_2 is fused with KOH and KNO_3 (oxidising agent) it gives a dark compound (A). Compound (A) disproportionates in acidic solution to give purple coloured compound (B). An alkaline solution of compound (B) oxidises KI to compound (C), whereas an acidified solution of compound (B) oxidises KI to (D). Identify A, B, C and D and write reactions involved. 3

UNIT 9

Coordination Compounds

Points to Remember

Introduction : Coordination compounds are those molecular compounds which retain their identify in solid as well as in solution

Example,

$$K_4[Fe(CN)_6] + H_2O \rightarrow 4K^+ (aq) + [Fe(CN)_6]^{4-} (aq)$$

Types of Complex

(I) Anionic complex

$K_3[Fe(C_2O_4)_3] \rightarrow 3K^+ + [Fe(C_2O_4)_3]^{3-}$

Anionic complex

(ii) Cationic complex

$[CoCl_2(en)_2]\,Cl \rightarrow [CoCl_2(en)_2]^+ + Cl^-$

Cationic complex

(iii) Neutral complex

$[Ni(CO)_4]$

Neutral complex

Ligands

The ions or molecules bound to the central atom/ion in the coordination entity are called ligands.

Types of Ligands

Unidentate :
A ligand which is bound to a metal ion through a single donor atom.
e.g., H_2O, NH_3, CO, Cl^-, NH_2^- etc

Bidentate :
A ligand which is bound to a metal ion through two donor atoms.
Example:

COO^- | COO^-	CH_2-NH_2 | CH_2-NH_2
Oxalate ion	Ethane-1,2-diamine

Polydentate :
A ligand which is bound to a metal ion through several donor atoms.
e.g., ethylenediamine tetraacetate ion $[EDTA]^{4-}$.

Ambidentate ligands,
which can bind through two different donor sites but binds through one site only
e.g., - NO_2 & -ONO
SCN & SNC
CN & NC

Chelate ligands: These may be a di- or polydentate ligand which form closed ring with central metal ion. Complex such formed are known as chelate complex. More the number of chelate ring in complex, complex will be more stable. The number of such ligating groups is called the denticity.

Homoleptic Complexes	Heteroleptic Complexes
Complexes in which a metal is bound to only one kind of donor groups are known as homoleptic.	Complexes in which a metal is bound to more than one kind of donor groups are known as heteroleptic.
e.g., $[Co(NH_3)_6]^{3+}$	e.g., $[Co(NH_3)_4Cl_2]^{+}$

Nomenclature of Coordination Compounds

Neutral Complex

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

Diamminechloridonitrito - N - platinum (II)

(I) Name of ligands in alphabetical order

(II) Central metal atom and oxidation state

Anionic Complex

$K_3[Fe(CN)_6]$

Postassium hexacyanatoferrate (III)

(I) Name of ionisable metal

(II)Name of ligand in alphabetical order

(III) Central metal atom + ate and oxidation state

Cationic Complex

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

Triamminetriaquachromium(III) chloride

1. Prefixes mono, di, tri, etc. are used to indicate the number of the individual ligands and ligands are named in an alphabetical order.
2. Central metal atom and oxidation state indicated by Roman numerals in parenthesis.
3. Name of ionisable anion.

Isomerism in Coordination Compounds

Note: Stereo isomerism and structural isomerism are the two principal types of isomerisms which are known among coordination compounds.

Stereo Isomerism

It occurs due to different arrangements of ligands around central metal atom. It is of two types :

Geometrical Isomerism

Optical Isomerism.

Optical Isomerism

● It arises when mirror images cannot be superimposed on one another. These mirror images are called as enantiomers. The two forms are called dextro (d) and laevo (l).

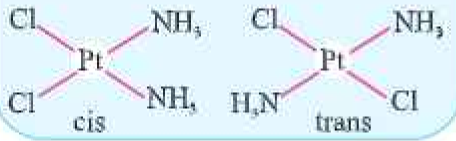
● Optical isomerism is common in octahedral complexes but at least one didentate ligand must be present.

e.g., $[Co(en)_3]^{3+}$, $[PtCl_2(en)_2]^{2+}$etc.

Geometrical Isomerism

It arises in heteroleptic complexes due to different possible geometric arrangements of the ligands. Important examples of this behavior are found in square planar and octahedral complexes.

Square planar complex of formula $[MX_2L_2]$ (X and L are unidentate), The two ligands X may be arranged adjacent to each other in a cis isomer, or opposite to each other in a trans isomer.
e.g., $[Pt(NH_3)_2Cl_2]$



cis trans

Square planar complex of the type [MABXL](where A, B, X, L are unidentates) shows three isomers - two cis and one trans. **Such isomerism is not possible for terahedral complexes.**
e.g., $[Pt(NH_3)(Br)(Cl)(Py)]$

Octahedral complexes of formula $[MX_2A_2]$ where X are unidentates and A are didentate and form cis and trans isomers.
e.g., $[CoCl_2(en)_2]$

Octahedral complexes of formula $[MX_2L_4]$ in which the two ligands X may be oriented cis or trans to each other.
e.g., $[Co(NH_3)_4Cl_2]^+$

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

Structural Isomerism

Linkage isomerism: arises in a coordination compound containing ambidentate ligand.
e.g., $[Co(NH_3)_5(NO_2)]Cl_2$
$[Co(NH_3)_5(ONO)]Cl_2$

Coordination isomerism: arises from the interchange of ligands between cationic and anionic entities of different metal ions present in a complex. e.g.,
$[Co(NH_3)_6][Cr(CN)_6]$,
$[Cr(NH_3)_6][Co(CN)_6]$

Ionisation isomerism: when the ionisable anion exhange with anion ligand.
e.g., $[Co(NH_3)_5SO_4]Br$ and $[Co(NH_3)_5Br]SO_4$

Solvate isomerism: is also known as 'hydrate isomerism'. In this case water is involved as a solvent.
e.g., $[Cr(H_2O)_6]Cl_3$,
$[Cr(H_2O)_4Cl_2]Cl.2H_2O$

Bonding in Coordination Compounds

Werner's Theory

(i) In complex compounds, metal atom exhibit two types of valencies - primary valency and secondary valency.

(ii) Primary valencies are satisfied by anions only while secondary valencies are satisfied by ligands. Primary valency depends upon oxidation number of central metal atom while secondary valency represents coordination number of central metal atom.

(iii) Primary valencies are ionisable and are non-directional while secondary valencies are non- ionisable and directional. Therefore, geometry of complex is decided by secondary valencies.

Valence Bond Theory

According to this theory, the metal atom or ion under the influence of ligands from inner orbital and outer orbital complex. These hybridized orbitals are allowed to overlap with ligand orbitals that can donate electron pairs for bonding.

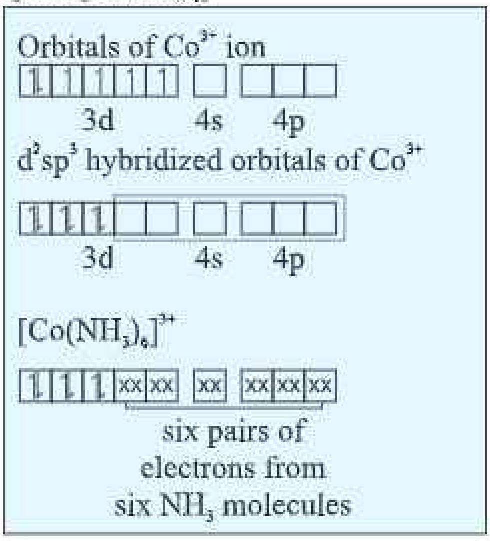
(i) **Six ligands (unidentate) (octahedral entity)** Generally central atom belongs 3d series and ligands can be monodentate or didentate but coordination number should be six and shape of complexes will be octahedral and form two types of complexes.

Inner orbital complexes, Which are formed due to participation of (n-1)d orbitals in hybridisation is (d^2sp^3) and shape of complex will be octahedral.

Outer orbital complexes, Which are formed due to participation of nd orbitals in hybridisation is (sp^3d^2).

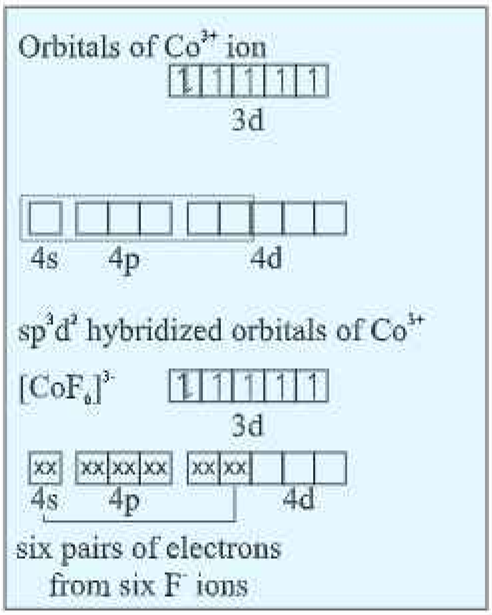
Generally halides (F^- Cl^- Br^- I^-), SCN^-,S^{2-} From outer orbital complexes and other ligands from inner orbital complexes.

e.g., Inner orbital complex, $[Co(NH_3)_6]^{3+}$



All electrons are paired therefore, complex will be diamagnetic in nature.

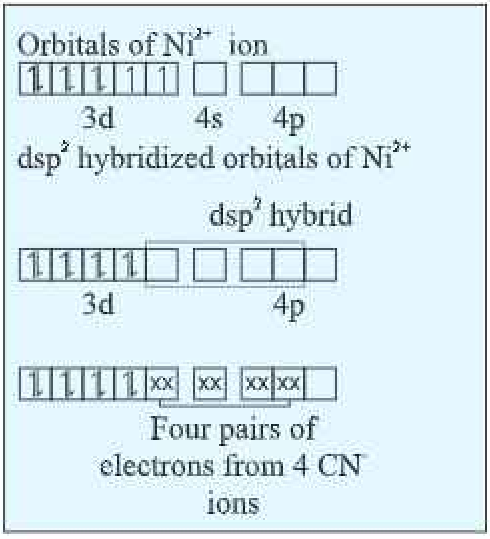
e.g., Outer orbital complex, $[CoF_6]^{3-}$



Complex has unpaired electrons, therefore, complex will be paramagnetic in nature.

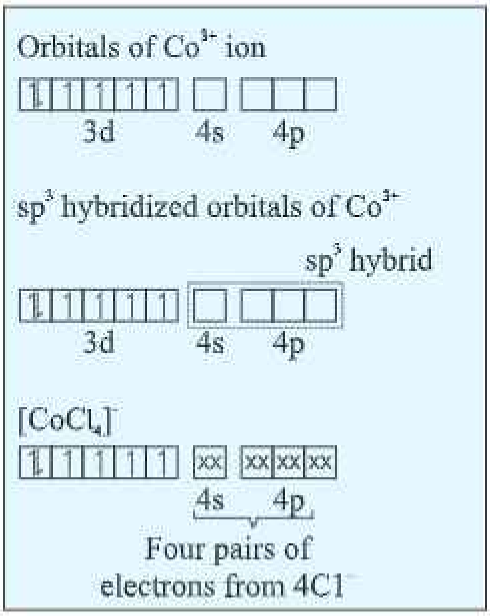
Complexes with coordination number: 4

1. **$[Ni(CN)_4]^{2-}$**



All electrons are paired. Complex will be diamagnetic in nature.

2. **$[CoCl_4]^-$**

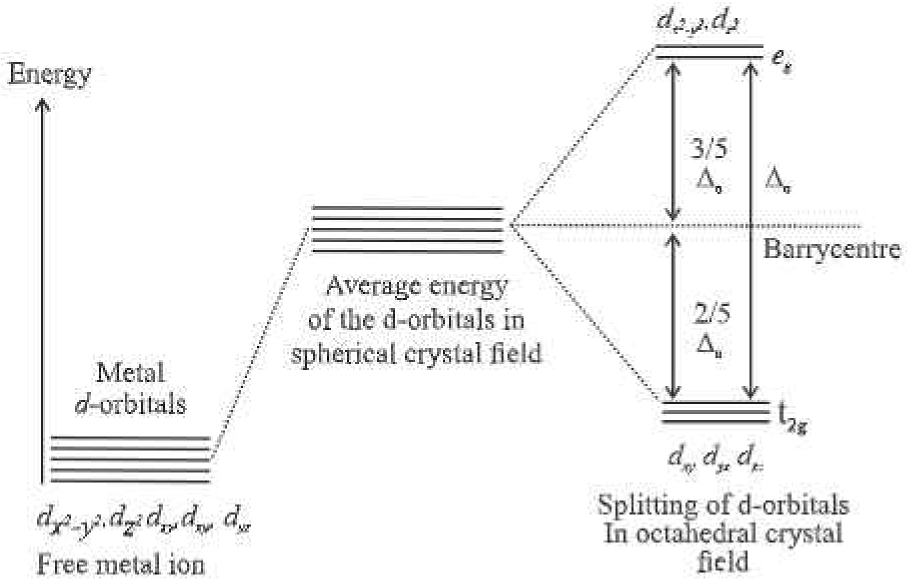


Complex has unpaired electrons. Complex will be paramagnetic in nature.

Crystal Field Theory

The five d-orbitals are split into lower and higher energy level due to approach of ligands is known as crystal field splitting. The five d-orbitals in a gaseous metal atom/ion have same energy.

(i) **Crystal field splitting in octahedral coordination entities**

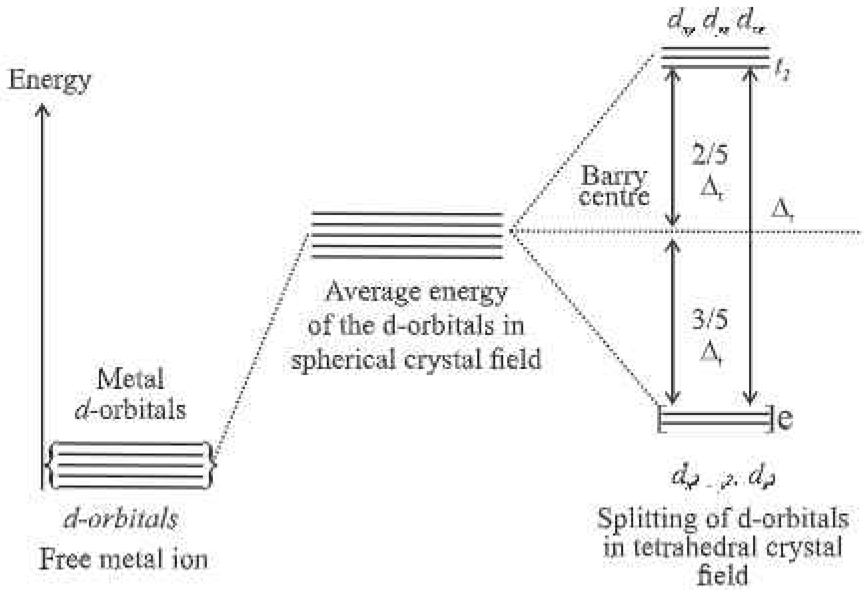


- Energy separation is denoted by Δ_o (the subscript o is for octahedral).
- The energy of the two e_g orbitals (higher energy orbitals) will increase by $(3/5)\Delta_o$. and that of the three t_{2g} (lower energy orbitals) will decrease by $(2/5)\Delta_o$.
- If $\Delta_o < P$, the fourth electron enters one of the e_g, orbitals giving the configuration $t^3_{2g}\,e_g^1$. Ligands for which $\Delta_o < P$ are known as weak field ligands and form high spin complexes.

• If $\Delta_o > P$, it becomes more energetically favourable for the fourth electron to occupy t_{2g} orbital with configuration $t_{2g}^4 e_g^0$.

Ligands which produce this effect are known as strong field ligands and form low spin complexes, where P represents the energy required for electron pairing in a single orbital.

(ii) **Crystal field splitting in tetrahedral coordination entities.**



• In tetrahedral coordination entities, $\Delta_t = (4/9)\Delta_o$.

Consequently the orbital splitting energies are not sufficiently large for forcing pairing, therefore, low spin configurations are rarely observed.

• Due to less crystal field stabilization energy, it is not possible to pair electrons and so all the tetrahedral complexes are high spin.

8. Colour in Coordination Compounds

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

Importance and Applications of Coordination Compounds.

- Hardness of water is estimated by simple titration with Na_2EDTA. The Ca^{2+} and Mg^{2+} ions form stable complexes with $EDTA^{2-}$.
- Some important extraction processes of metals, like those of silver and gold make use of complex formation.
- Similarly, purification of metals can be achieved through formation and subsequent decomposition of their coordination compounds. For example, impure nickel is converted to $[Ni(CO)_4]$, which is decomposed to yield pure nickel.
- Coordination compounds are used as catalysts for many industrial processes. Examples include rhodium.

Supplementary List of Ligands

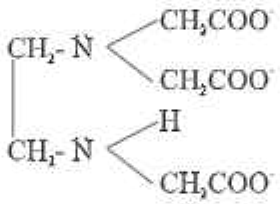
Ligand	F^-	Cl^-	Br^-	I^-	OH^-	CN^-	O^{2-}	O_2^{2-}	O_2^-	CO_3^{2-}	PH_3
Name	fluoro	chloro	bromo	iodo	hy droxo	cyano	oxo	per oxo	super oxo	carbonato	phos phine
Ligand	SO_4^{2-}	NO_2	ONO	SCN^-	NCS	CH_3COO	C_5H_5N	S^{2-}	$S_2O_3^{2-}$	NO_3	SO_3^{2-}
Name	supha-to	nitro	nitrito	thiocy-anato	isothio-cyana-to	acetate	pyridine (Py)	sul-phido	thiosul-phato	nitrato	sulphi-to
Ligand	NC	$(C_6H_5)_3P$	CS	NH_2^-	NH^{2-}	H_2NCSNH_2	$C_2O_4^{2-}$	H_2O	NH_3	CO	NO
Name	isocy-ano	triphenyl phos-phine	thio-carbo-nyl	amido	imido	thiourea (tu)	oxalate (ox)	aqua	ammine	carbo-nyl	nitro-syl

$H_2N\text{-}CH_2\text{-}NH_2$

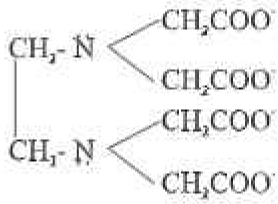
ethane-1, 2- diamine (en)

$H_2NCH_2CH_2NHCH_2CH_2NH_2$

Diethylenetriamine(diene)



Ethylenediaminetriacetate ion ($EDTA^{3-}$)



Ethylenediaminetetracetate ion ($EDTA^{4-}$)

OBJECTIVE TYPE QUESTIONS

I. MULTIPLE CHOICE QUESTIONS

1. Which of the following compounds formed by Cu^{2+} ions is most stable?
   (a) $Cu^{2+}+4NH_3 \rightarrow [Cu(NH_3)_4]^{2+}; \log K=11.6$
   (b) $Cu^{2+}+4CN^- \rightarrow [Cu(CN_4]^{2-}; \log K=27.3$
   (c) $Cu^{2+}+2en \rightarrow [Cu(en)_2]^{2+}; \log K=15.4$
   (d) $Cu^{2+}+4H_2O \rightarrow [Cu(H_2O)_4]^{2+}; \log K=8.9$
2. The colour of the coordination compounds depends on the crystals field splitting. What will be the correct order of absorption of wavelength of light in the visible region for the complexes $[Co(NH_3)_6]^{3+}$; $[Co(CN)_6]^{3-}$; $[Co(H_2O)_6]^{3+}$.
   (a) $[Co(CN)_6]^{3-}>[Co(NH_3)_6]^{3+}>[Co(H_2O)_6]^{3+}$
   (b) $[Co(NH_3)_6]^{3+}>[Co(H_2O)_6]^{3+}>[Co(CN)_6]^{3+}$
   (c) $[Co(H_2O)_6]^{3+}>[Co(NH_3)_6]^{3+}>[Co(CN)_6]^{3-}$
   (d) $[Co(CN)_6]^{3-}>[Co(NH_3)_6]^{3+}>[Co(H_2O)_6]^{3-}$
3. When 0.1 mol $CoCl_3 \cdot NH_3$ is treated with excess of $AgNO_3$, 0.2 mol of AgCl are obtained. The conductivity of solution will correspond to-
   (a) 1 : 3 electrolyte (b) 1 : 2 electrolyte
   (c) 1 : 1 electrolyte (d) 3 : 1 electrolyte
4. The correct IUPAC name of $[Pt(NH_3)_2 Cl_2]$ is-
   (a) Diamminedichloridoplatinum (II)
   (b) Diamminedichloridoplatinum (IV)
   (c) Diamminedichloridoplatinum (0)
   (d) Diamminedichloridoplatinum (IV)
5. Out of the following the most stable complex species is
   (a) $[Fe(CO)_5]$ (b) $[Fe(CN)_6]^{3-}$
   (c) $[Fe(C_2O_4)_3]^{3+}$ (d) $[Fe(H_2O)_6]^{3+}$
6. The CFSE for octahedral $[CoCl_6]^{4-}$ is 18,000 cm^{-1}. The CFSE for tetrahedral $[CoCl_4]^{2-}$ will be:
   (a) 18,000 cm^{-1} (b) 16,000 cm^{-1}
   (c) 8,000 cm^{-1} (d) 20,000 cm^{-1}

7. Which of the following species is not likely to be a ligand?
   (a) NH_3^- (b) NH_4^+
   (c) $NH_2CH_2NH_2$ (d) CO
8. IUPAC name of $[Pt(NH_3)_2Cl(NO_2)]$ is:
   (a) Platinum diaminechloritrite
   (b) Chloronitrito-N-ammine platinum(II)
   (c) Diamminechloridonitrito-N-platinum (II)
   (d) Diamminechlornitrite-N-platinate(II)
9. Atomic number of Mn, Fe and Co are 25, 26 and 27 respectively. Which of the following inner orbital octahedral complex is diamagnetic?
   (a) $[Co(NH_3)_6]^{3+}$ (b) $[Mn(CN)_6]^{5-}$
   (c) $[Fe(CN)_6]^{4-}$ (d) $[Fe(CN)_6]^{3-}$
10. $[Fe(CN)_6]^{3-}$ complex is ....
   (a) sp^3 hybridised (b) sp^3d^2 hybridised
   (c) paramagnetic (d) diamagnetic
11. The denticity of 'PPh_3' and 'en' are respectively-
   (a) 1,1 (b) 2,1
   (c) 3,2 (d) 1,2
12. The type of isomerism exhibited by complex $[Co(NH_3)_4Br_2]Cl$?
   (a) Geometrical and Ionization (b) Geometrical and Optical
   (c) Optical and Ionization (d) Geometrial only
13. Complex which will be colourless is -
   (a) $[Ti(H_2O)_6]^{3+}$ (b) $[Ti(NO_3)_4]$
   (c) $[Cr(NH_3)_6]^+$ (d) $[Fe(CN)_6]^{4-}$
14. $K_3[CoF_6]$ is a high spin complex. The hybridisation of Co in complex will be-
   (a) sp^3d (b) sp^3d^2
   (c) d^2sp^3 (d) dsp^2
15. Complex which is paramagnetic as well as tetrahedral is-
   (a) $[Ni(CO)_4]$ (b) $[NiCl_4]^{2-}$
   (c) $[Ni(CN)_4]^{2-}$ (d) None of these
16. On dissolving $K_4[Fe(CN)_6]$ in water, presence of .... ions are detected.
   (a) K^+ only (b) Fe^{2+} only
   (c) CN^- only (d) Both K^+ and CN^-

17. The complex ion, which does not have any 'd' electron in central metal atom is-
    (a) $[MnO_4]^-$ (b) $[Co(NH_3)_6]^{3+}$
    (c) $[Fe(CN)_6]^{3-}$ (d) $[Cr(H_2O)_6]^{3+}$
18. Two isomers of a complex are **A** and **B**. If **A** gives white precipitate on reacting with $BaCl_2$, while **B** gives precipitate of AgCl on reaction with $AgNO_3$. The complex **B** and type of isomerism exhibited by it are–
    (a) $[Co(NH_3)_5Cl]SO_4$, Ionization (b) $[Co(NH_3)_5Cl]SO_4$, coordination
    (c) $[Co(NH_3)_5SO_4]Cl$, Ionization (d) $[Co(NH_3)_5SO_4]Cl$, Coordination
19. The complex which shows optical isomerism is-
    (a) trans-$[Co(en)_2Cl_2]Cl$ (b) $[Co(NH_3)_4Cl_2]Cl$
    (c) $[Co(NH_3)_3Cl_3]$ (d) cis-$[Co(en)_2Cl_2]Cl$

II FILL IN THE BLANKS

1. The IUPAC name of linkage isomer of $[Co(NH_3)_5NO_2]Cl_2$ is................................
2. The oxidation state of Ni in $K_2[Ni(CN)_4]$ is............................
3. The metal present in vitamin B_{12} is.....................
4. NO is named as........................
5. Octahedral crystal field splitting of d-orbitals give the three d orbitals having lower energy are collectively called....................
6. The number of isomers of $[Pt(NH_3)_2Cl_2]$ are..........................
7. In complex $[Fe(H_2O)_6]^{3+}$ number of unpaired electrons are.......................
8. Number of ions produced per mole of the complex $[Co(NH_3)_5Cl]Cl_2$ are ....
9. Out of *cis* and *trans* isomer of $[RhCl(en)_2]^+$, ...isomer shows optical activity.
10. Dentisity of $EDTA^{4-}$ ligand is ....

III ASSERTION REASON TYPE QUESTIONS

Note: In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choice.

(a) Both assertion and reason are True, and reason is the correct explanation of the assertion.
(b) Both assertion and reason are True, but reason is not the correct explanation of the assertion.

(c) Assertion is True, but reason is False.

(d) Both assertion and reason are False.

1. **ASSERTION:** Toxic metal ions are removed by the chelating ligands.

   REASON: Chelate complex tend to be more stable.

2. **ASSERTION:** $[(Fe(CN)_6]^{4-}$ ion shows magnetic moment corresponding to two unpaired electrons.

   REASON: Because it has d^2sp^3 type hybridisation.

3. **ASSERTION:** Carbon monoxide forms low spin complexes with metals.

   REASON: Carbon monoxide is neutral oxide.

4. **ASSERTION:** Carbon monoxide is a deadly poison.

   REASON: CO can form strong complexes with haemoglobin.

5. **ASSERTION :** Tetrahedral complexes cannot exhibit geometrical isomerism.

   REASON: Tetrahedral complexes are chiral in nature.

6. **ASSERTION:** An octahedral complex with two didentate ligands is always optically active.

   REASON: The cis - isomer of the octahedral complex is chiral.

7. **ASSERTION:** Ionisation isomerism is shown by complexes having ambidentate ligands.

   REASON: Ambidentate ligands have two possible ligating centres.

8. **ASSERTION:** $[Fe(CN)_6]^{3-}$ is more paramagnetic than $[FeF_6]^{3-}$.

   REASON: $[FeF_6]^{3-}$ has more number of unpaired electrons.

9. **ASSERTION:** $[Co(NH_3)_6]^{3+}$ is an inner orbital complex.

   REASON: $[Co(NH_3)_6]^{3+}$ forms an octahedral complex.

10. **ASSERTION:** $[Fe(ox)_3]^{3-}$ is more stable than $[Fe(H_2O)_6]^{3+}$

    REASON: $[Fe(ox)_3]^{3-}$ is a chelate complex.

IV ONE WORD TYPE QUESTIONS

1. What is the oxidation state of Ni in $[Ni(CO)_4]$?
2. Write IUPAC name of $[Ni(CN)_4]^{2-}$.
3. What is the hybridisation of Co in the complex $[CoF_6]^{3-}$?
4. Write the chemical formula of potassiumtrioxalatochromate(III).
5. Name the transition element present in haemoglobin.

6. What is density of triphenylphosphine?
7. Out of NH_3 and H_2O which is strong field ligand?
8. Write electronic configuration of Fe in complex $[Fe(CN)_6]^{4-}$.
9. What is the coordination number of Cr in $[Cr(en)_2Cl_2]Cl$?
10. How many geometrical isomers are possible for $[Cr(ox)_3]^{3-}$?
11. Give the linkage isomer of $[Pd(PPh_3)_2(NCS)_2]$?
12. How many unpaired electrons are present in $[Fe(NH_3)_6]Cl_3$?
13. Name the imperfect complex compound which ionizes completely in solutions.
14. Give an example of hexadentate ligand.
15. Write the coordination number of 'Fe' in $K[Fe(CN)_2(en)_2]$

VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)

Q.1. What is ambidentate ligand ? Give one example.

Ans. Monodentate ligands contain more than one coordinating atoms. Example, CN^-.

Q.2 Write the IUPAC name of $[PtCl_2(en)_2(NO_3)_2]$.

Ans. Dichloridobis(ethane-1, 2-diamine)nitratoplatinum (IV)

Q.3. What is a chelate ligand ? Give one example.

Ans. The complex in which ligand binds through two or more donor sites simutaneously to form cyclic complexes. Example: ethane-1-2 diamine.

Q.4. How many geometrical isomers are possible for the $[Ni(NH_3)_4]^{2+}$?

Ans. Not possible, because all 4 ligands are same.

Q.5. Define coordination polyhedron.

Ans. The spatial arrangement of the ligand with the central metal ion.

Q.6. Give the chemical formula of potassium hexacyanoferrate (II).

Ans. $K_4[Fe(CN)_6]$.

Q.7. Name the metal present in : (i) Chlorophyll (ii) cis platin

Ans. (i) Mg (ii) Pt

Q.8. Which of the two is more stable — $K_4[Fe(CN)_6]$ Or $K_3[Fe(CN)_6]$?

Ans. $K_4[Fe(CN)_6]$ because Fe has d^6 configuration in this case.

Q.9. Arrange the following complexes in order of increasing electrical conductivity : $[Co(NH_3)_3Cl_3]$, $[Co(NH_3)_5Cl]Cl_2$, $[Co(NH_3)_6]Cl_3$

Ans. $[Co(NH_3)_3Cl_3] < [Co(NH_3)_5Cl]Cl_2 < [Co(NH_3)_6]Cl_3$

More number of ions, more electrical conductivity

Q.10. Give an example of the role of coordination compounds in biological system.

Ans. Haemoglobin, the red pigment of blood acts as oxygen carrier. It is a coordination compound of iron.

Q.11. Why is CO a stronger ligand than Cl^-?

Ans. CO is a stronger ligand than Cl^- due to back bonding between its empty p-orbitals and filled d-orbitals of central metal ion which in turn increases Δ_o value.

Q.12. What do you understand by denticity of a ligand?

Ans. Denticity of a ligand is the number of coordinating or ligating groups sites present in a ligand.

Q.13. What is the coordination number of central metal ion in $[Fe(C_2O_4)_3]^{3-}$?

Ans. Coordination number = Number of ligands x Denticity = 3 x 2 = 6

Q.14 Name two properties of the central metal atom/ion which enable it to form stable complex entities.

Ans. (a) Small size of metal ion

(b) High charge on the metal ion.

Q.15 Write the IUPAC name of the complex $[Cr(en)_3][Co(CN)_6]$.

Ans. Tris (ethane- 1, 2-diamine)chromium(III) hexacyanidocobaltate(III)

Q.16. A blue coloured solution of $[CoCl_4]^{2-}$ ion changes to pink on reaction with $HgCl_2$. Why?

Ans. $CoCl_4^{2-} + HgCl_2 \longrightarrow Co[HgCl_4] + 2Cl^-$

[Blue] [Pink]

SHORT ANSWER TYPE QUESTIONS (2 or 3 Marks)

Q.1. Explain the following :

(i) NH_3 act as a ligand but NH_4^+ does not.

(ii) CN^- is a ambidentate ligand.

Ans. (i) NH_3 has one lone pair while NH_4^+ does not.

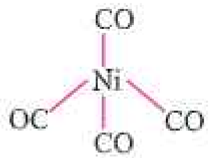
(ii) Because it has two donor atoms in a monodentate ligand, can bind through either C or N.

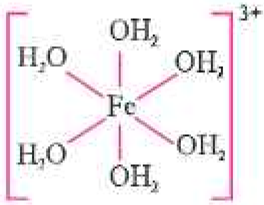
Q. 2. Mention the main postulates of Werner theory.

Ans. (i) Metal ion has two types of valency. (ii) Primary valency and secondary valency. (iii) Secondary valency is equal to coordination number.

Q. 3. Draw the structure of : (i) $[Ni(CO)_4]$ (ii) $[Fe(H_2O)_6]^{3+}$

Ans.





Q.4. How does EDTA help as a cure for lead poisoning ?

Ans. Calcium in Ca-EDTA complex is replaced by lead in the body. The more soluble complex Pb-EDTA is eliminated in urine.

Q.5. Define homoleptic and heteroleptic complexes.

Ans. Homoleptic : When metal atom/ion is linked with one type of ligands. Example, $[Ni(CO)_4]$.

Heteroleptic : When metal atom/ion is linked with the more than one kind of ligands. Example, $[Co(NH_3)_4Cl_2]^+$

Q.6. $[NiCl_4]^{2-}$ is paramagnetic while $[Ni(CO)_4]$ is diamagnetic though both are tetrahedral. Why ?

Ans. In $[NiCl_4]^{2-}$, Ni has $3d^8 4s^0$ configuration, Cl^- can not pair up while in $[Ni(CO)_4]$, Ni has $3d^8 4s^2$ configuration, CO pair up electrons

Q.7. The oxidation number of cobalt in the complex : (i) $K[Co(CO)_4]$ (ii) $[Co(C_2O_4)_3]^{3-}$

Ans. (i) - 1 (ii) + 3

Q.8. What are t_{2g} and e_g orbitals ?

Ans. In a free transition metal ion, the d-orbitals are degenerate. When it form complex, the degeneracy is split and d-orbitals split into t_{2g} and e_g orbitals.

Q.9. What is spectrochemical series ?

Ans. The arrangement of ligands in order of their increasing crystal field splitting field strength.

Q.10. What are the assumptions of Crystal Field theory.

Ans. (i) Ligand act as a point charge. (ii) Metal ion has electrostatic attraction force with the ligand. (Or any other)

Q.11. $CuSO_4$ is colourless while $CuSO_4.5H_2O$ is coloured. Why ?

Ans. $CuSO_4$ does not has any ligand, so no splitting of d-orbital take place while $CuSO_4$ $5H_2O$ has water at ligand.

Q.12. Differentiate between inner and outer orbital complexes.

Ans. Inner sphere complex : When d-orbital of inner shell take part in hybridisation. Outer sphere complex : When d-orbital of outermost shell take part in hybridisation.

Q.13. How is stability of coordination compound determined in aqueous solution ?

Ans. By using stability constant. Higher the value of stability constant, more stability.

Q.14. In a complex ion $[Co(NH_3)_5NO_2]Cl_2$,

(i) Identify the ligand. (ii) Oxidation number of metal ion.

Ans. (i) NH_3, NO_2^-. (ii) +3

Q.15. Explain how the nature of ligand affects the stability of complex ion.

Ans. Strong ligand : More stability Weak ligand : Less stability

LONG ANSWER TYPE QUESTIONS (5 Marks)

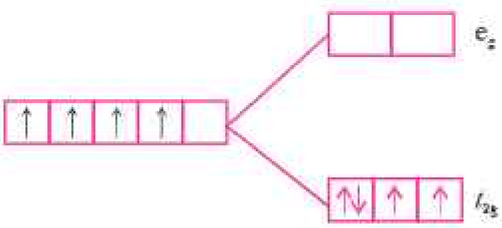
Q.1. A metal ion M^{n+} having d^4 valence electronic configuration combines with three didentate ligands to form a complex compound. Assuming $\Delta_o > P$:

(i) Draw the diagram showing d-orbital splitting during this complex formation.

(ii) What type of hybridisation will M^{n+} have?

(iii) Name the type of isomerism exhibited by this complex.

Ans. (i) If $\Delta_o > P$ then



(ii) d^2sp^3

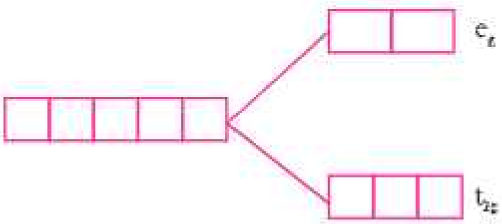
(iii) $[M(AA)_3]$ type complex show optical isomerism.

Q.2. (i) Discuss the nature of bonding in metal carbonyls.

(ii) Draw figure to show the splitting of d-orbitals in an octahedral crystal field and write electronic configuration of Mn^{2+} ion when : (a) $P > \Delta_o$ (b) $\Delta_o > P$

Ans. (i) The metal carbon bond in metal carbonyls possess both σ and π character. The M-C σ bond is formed by the M←C≡O while M-C π it bond is formed by the donation of a pair of electron from filled d-orbital of metal to antibonding π* orbital of CO.

(ii)



(a) $t_{2g}^{3}e_g^{2}$ (b) $t_{2g}^{5}e_g^{0}$

Q. 3. (i) $[Fe(CN)_6]^{4-}$ and $[Fe(H_2O)_6]^{2+}$ are of different colours in dilute solution. Why?

(ii) A complex is prepared by mixing $CoCl_3$ and NH_3 in the molar ratio of 1 : 4. A 0.1M solution of this complex was found to be freeze at - 0.372 °C. What is the formula of the complex ? (K_f = 1.86 °C/M)

Ans. (i) In both the cases Fe is in + 2 state, it has 4 unpaired electrons but CN^- and H_2O has different crystal field splitting energy.

(ii) $\Delta T_f = i.K_f.m$, $i = 2$ means complex dissociate into two ions. Hence the formula is $[Co(NH_3)_4Cl_2]Cl$.

Q.4. $CoSO_4Cl.5NH_3$ exists in two isomeric forms 'A' and 'B'. Isomer 'A' reacts with $AgNO_3$ to give white precipitate, but does not react with $BaCl_2$. Isomer 'B' gives white precipitate with $BaCl_2$ but does not react with $AgNO_3$.

(i) Identify 'A' and 'B' and write their structural formulae. (ii) Name the type of isomerism involved. (iii) Give the IUPAC name of 'A' and 'B'.

Ans. (i) A = $[Co(NH_3)_5SO_4]Cl$. B = $[Co(NH_3)_5Cl]SO_4$

(ii) Ionisation iosmerism

(iii) (A) = Pentaamminesulphatocobalt(III) chloride

(B) = Pentaamminechloridocobalt(III) sulphate

Q.5. For the complexes $[Fe(CN)_6]^{4-}$ and $[FeF_6]^{3-}$ write -

(i) Oxidation state of Fe

(ii) IUPAC names

(iii) Magnetic behaviour

(iv) Spin type

(v) Which complex has higher λ_{max} of absorption?

Ans.

S.No.	$[Fe(CN)_6]^{4-}$	$[FeF_6]^{3-}$
(i)	+2	+3
(ii)	Hexacyanoferrate (II)	Hexafluoridoferrate (III)
(iii)	Diamagnetic	Paramagnetic
(iv)	Low spin	High spin
(V)	lower λ_{max}	Higher λ_{max}

CASE STUDY BASED QUESTIONS

1. **Read the passage and answer the following question.**

According to the VBT , the metal atom or ion under the influence of ligands can use its (n-1) d, ns, np or ns, np, nd orbitals for hybridisation to yield a set of equivalent orbitals of definite geometry such as octahedral, tetrahedral, square planar and so on. These hybridised orbitals are allowed to overlap with ligand orbitals that can donate electron pairs for bonding. The geometry of a complex from the knowledge of its magnetic behaviour on the basis of the valence bond theory In the diamagnetic octahedral complex, $[Co(NH_3)_6]^{3+}$, the cobalt ion is in +3 oxidation state and has the electronic configuration $3d^6$. Six pairs of electrons, one from each NH_3 molecule, occupy the six hybrid orbitals. Thus, the complex has octahedral geometry and is diamagnetic because of the absence of unpaired electron. In the formation of this complex, since the inner d orbital (3d) is used in hybridisation, the complex, $[Co(NH_3)_6]^{3+}$ is called an inner orbital or low spin or spin paired complex. The paramagnetic octahedral complex, $[CoF_6]^{3-}$ uses outer orbital (4d) in hybridisation (sp^3d^2). It is thus called outer orbital or high spin or spin free complex.

Source : NCERT

(A) Number of unpaired electrons present in $[CoF_6]^{3-}$ are :

(a) 4 (b) 3

(c) 2 (d) 1

(B) Out of following, paramagnetic complex is :

(a) $[Ni(CN)_4]^{2-}$ (b) $[Ni(Cl)_4]^{2-}$

(c) $[Ni(CO)_4]$ (d) All of these

(C) Outer orbital complex is :

(a) $[CoF_6]^{3-}$ (b) $[Co(NH_3)_6]^{3+}$

(c) $[Ni(CN)_4]^{2-}$ (d) None of these

(D) Inner orbital complex involves :

(a) nd orbitals (b) (n-1)d orbitals

(c) ns orbitals (d) None of these

2. Read the passage and answer the following question.

The degeneracy of the d orbitals has been removed due to ligand electron-metal electron repulsions in the octahedral complex to yield three orbitals of lower energy, t_{2g} set and two orbitals of higher energy, e_g set. This splitting of the degenerate levels due to the presence of ligands in a definite geometry is termed as crystal field splitting and the energy separation is denoted by Δ_o (the subscript o is for octahedral) . Thus, the energy of the two e_g orbitals will increase by (3/5) Δ_o and that of the three t_{2g} will decrease by (2/5)Δ_o. The crystal field splitting, Δ_o, depends upon the field produced by the ligand and charge on the metal ion. Some ligands are able to produce strong fields in which case, the splitting will be large whereas others produce weak fields and consequently result in small splitting of d orbitals.

(A) The cause of removal of degeneracy of the d orbitals in coordination compunds is :

(a) higher nuclear charge

(b) ligand electron-metal electron repulsions

(c) Atomic size

(d) None of these

(B) The crystal field splitting is :

(a) The splitting of the degenerate levels due to the presence of ligands in a definite geometry.

(b) splitting of f- orbitals

(c) splitting of p- orbitals

(d) all of these

(C) Energy of two e_g orbitals in octahedral complexes increased by :

(a) $3/5\Delta_o$ (b) $2/5\Delta_o$

(c) $1/5\Delta_o$ (d) $5/3\Delta_o$

(D) The relationship between CFSE in tetrahedral field (Δ_t) and octahedral field (Δ_o) is

(a) $\Delta_t = 9/4\Delta_o$ (a) $\Delta_t = 4/9\Delta_o$

(c) $\Delta_t = 2\Delta_o$ (d) $\Delta_t = 5\Delta_o$

3. Read the passage and answer the following question.

The ions or molecules bound to the central atom/ion in the coordination entity are called ligands. These may be simple ions such as Cl^-, small molecules such as H_2O or NH_3, larger molecules such as $H_2NCH_2CH_2NH_2$ or $N(CH_2CH_2NH_2)_3$ or even macromolecules, such as proteins. When a ligand is bound to a metal ion through a single donor atom, as with Cl^- H_2O or NH_3, the ligand is said to be unidentate. When a ligand can bind through two donor atoms as in $H_2NCH_2CH_2NH_2$ (ethane-1,2-diamine) or $C_2O_4^{2-}$ (oxalate), the ligand is said to be didentate and when several donor atoms are present in a single ligand as in $N(CH_2CH_2NH_2)_3$, the ligand is said to be polydentate.

Ethylenediaminetetraacetate ion $(EDTA)^{4-}$ is an important hexadentate ligand. It can bind through two nitrogen and four oxygen atoms to a central metal ion. When a di- or polydentate ligand uses its two or more donor atoms to bind a single metal ion, it is said to be a chelate ligand. The number of such ligating groups is called the denticity of the ligand. Such complexes, called chelate complexes tend to be more stable than similar complexes containing unidentate ligands. Ligand which can ligate through two different atoms is called ambidentate ligand. Examples of such ligands are the NO_2^- and SCN^- ions. NO_2^- ion can coordinate either through nitrogen or through oxygen to a central metal atom/ion. Similarly, SCN^- ion can coordinate through the sulphur or nitrogen atom.

(A) Ambidentate ligand is :

(a) CN^- (b) CO

(c) NH_3 (d) H_2O

(B) Total number of donor sites in ethane–1,2 –diamine is/are :

(a) 1 (b) 2

(c) 3 (d) 4

(C) Ligand with maximum denticity is-

(a) NC^- (b) $C_2O_4^{2-}$

(c) NH_3 (d) H_2O

(D) Chelating ligand is :

(a) $EDTA^{4-}$ (b) NH_3

(c) CN^- (d) H_2O

ANSWERS

I MULTIPLE CHOICE QUESTIONS

1. (b) 2. (c) 3. (b) 4. (a) 5. (c) 6. (a) 7. (b) 8. (c) 9. (a) 10. (c) 11. (d) 12. (a) 13. (b) 14. (b) 15. (b) 16. (a) 17. (a) 18. (c) 19. (d)

II FILL IN THE BLANKS

1. pentaamminenitrito-O-cobalt(III) chloride 2. 2 3. Cobalt
4. Nitrosyl 5. t_{2g} 6. 4 7. 5 8. 3
9. cis 10. 6

III ASSERTION REASON TYPE QUESTIONS

1. (a) 2. (b) 3. (b) 4. (a) 5. (c) 6. (d) 7. (d) 8. (d) 9. (b) 10. (a)

IV ONE WORD QUESTION ANSWERS

1.	0	2.	tetracynatonickelate(II) ion
3.	$(CoF_6)^{3-}$, (sp^3d^2)	4.	$(K_3[Cr(C_2O_4)_3])$
5.	Iron	6.	1
7.	NH_3	8.	t_{2g}^6, e_g^0
9.	6	10.	0
11.	$[Pd(PPh_3)_2(NCS)_2]$	12.	1
13.	Double salt	14.	$[EDTA]^{4-}$
15.	6		

CASE STUDY BASED QUESTIONS

1.	(A) a		(B) b
	(C) a		(D) b
2.	(A) b		(B) a
	(C) a		(D) b
3.	(A) a		(B) b
	(C) b		(D) a

UNIT TEST-1

Coordination Compounds

Maximum Marks: 20 **Time Allowed : 1 hour**

1. Explain- $[Cr(en)_3]^{2+}$ is more stable than $[Cr(H_2O)_6]^{2+}$. 1
2. Give two examples of didentate ligands. 1
3. A metal ion M^{n+} having d^4 valence electronic configuration combines with three didentate ligands to form a complex compound. Assuming $\Delta_o > P$, write the electronic configuration of the valence electrons of the metal M^{n+} ion in terms of t_{2g} and e_g.
4. Predict the number of unpaired electrons in the square planar $[Pt(CN)_4]^{2-}$ ion. 1
5. For the complex $[CoBr_2(en)_2]^{2+}$, write coordination number and oxidation state of Co. 1
6. Name the isomerism exhibited by following coordination compounds: 2
   a) $[Co(NH_3)_5SO_4]Br$
   b) $[Fe(SCN)_6]^{3-}$
   c) $[Co(en)_3]^{2+}$
   d) $[Cr(en)_2(H_2O)_2]^{3+}$
7. Define following terms with suitable example. 2
   a) Spectrochemical Series
   b) Synergic Bonding
8. Write IUPAC names of following complexes: 2
   a) $[Fe(NH_3)_2(C_2O_4)_2]^{2-}$
   b) $[Cr(en)_2(H_2O)_2]^{2+}$
9. Explain hybridization, geometry, and magnetic behaviour of following complexes (Attempt any 2) 2
   a) $[Ni(CO)_4]$
   b) $[Mn(CN)_6]^{3-}$
   c) $[FeCl_6]^{3-}$
10. Arrange the following in increasing order of given properties: 3
    a) $[Co(NH_3)_3Cl_3]$, $[Co(NH_3)_5Cl]Cl_2$, $[Co(NH_3)_6]Cl_3$ (Electrical Conductivity)
    b) $[Co(NH_3)_6]^{3+}$, $[Co(CN)_6]^{3-}$, $[Co(H_2O)_6]^{3+}$ (Wavelength of absorption)
    c) $[Co(NH_3)_6]^{3+}$, $[Mn(CN)_6]^{3-}$, $[Fe(CN)_6]^{3-}$ (spin-only magnetic moment)
11. Explain following: 3
    a) $[Ni(H_2O)_6]^{2+}$ is green in colour while $[Ni(CN)_4]^{2-}$ is colourless.
    b) $[Fe(H_2O)_6]^{3+}$ is highly paramagnetic while $[Fe(CN)_6]^{3-}$ is weakly paramagnetic.
    c) $[NiCl_4]^{2-}$ is paramagnetic and $[Ni(CO)_4]$ is diamagnetic, even though both are tetrahedral

UNIT TEST-2

Coordination Compounds

Maximum Marks: 20 **Time Allowed : 1 hour**

1. Write coordination number and oxidation number of Cr in $[Cr(ox)_2Cl_2]^{3+}$. 1
2. Give two examples of ambidentate ligands. 1
3. Tetrahedral complexes does not exhibit geometrical isomerism. Explain.
4. Predict the hybridisation of $[FeCl_4]^-$ 1
5. Mention the denticity of $C_2O_4^{2-}$ & $EDTA^{4-}$ ligands. 1
6. Name the isomerism exhibited by following molecules: 2
   a) $[Fe(CN)_6]^{3-}$
   b) $[Co(NH_3)_5Cl]SO_4$
   c) $[Co(en)_3]^{3+}$
   d) $[Co(NH_3)_6][Cr(CN)_6]$
7. Define following terms giving examples: 2
   a) Ambidentate ligands
   b) Chelate effect
8. The molar conductivity of the complex $CrCl_3.4NH_3.\ 2H_2O$ is found to be same as that of 3:1 electrolyte. Write its structural formula, name and geometrical isomers of the complex. 2
9. Explain hybridization, geometry, and magnetic, behaviour of following Complexes (Attempt any 2) 3
   a) $[Ni(Cl)_4]^{2-}$
   b) $[Co(CN)_6]^{3-}$
   c) $[Cr(H_2O)_6]^{3+}$
10. a) Differentiate low spin and high spin complexes giving examples.
    b) How homoleptic complexes are different from heteroleptic complexes ?
    c) Write the chemical formula of potassium hexacyanatoferrate (II). 3
11. Explain following: 3
    a) CO is stronger ligand than NH_3 .
    b) Low spin octahedral complexes of nickel are not known.
    c) Aqueous solution of $[Ti(H_2O)_6]^{3+}$ is coloured.

UNIT 10

Haloalkanes and Haloarenes

Points to Remember

Classification

- No. of halogen atoms

C_2H_5X Monohaloakane

CH_2X-CH_2X Dihaloalkane

Monohaloarene Dihaloarene Trihaoarene

- Compounds containing sp^3 C-X bond

(a) Alkyl halides

(b) Allylic halides

(c) Benzylic halides

Compounds containing sp^2 C-X bond

(a) Vinylic halides

(b) Aryl halides

Nomenclature

Common name : Alkyl group followed by halides.

Dihalogen derivatves of arenes, prefix o-, p- are used

IUPAC name : Numerals are used for position of halogen.

Nature of C-X bond :

Carbon-halgoen bond is polarised due to more electronegativity of halogen

Properties and Reactions of Haloakanes and Haloarenses

Preperation

From alcohol:

- $R\text{-}OH + HCl \xrightarrow{ZnCl_2} R\text{-}Cl + H_2O$

$3R\text{-}OH + PX_3 \longrightarrow 3R\text{-}X + H_3PO_3$

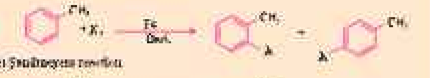
$R\text{-}OH + PCl_5 \longrightarrow R\text{-}Cl + POCl_3 + HCl$

- From hydrocarbons:

(a) By free radical halogenation

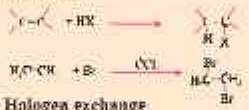
$CH_3CH_2CH_2CH_3 \longrightarrow CH_3CH_2CH_2CH_2Cl + CH_3CH_2CHClCH_3$

(b) By electrophilic substitution



(c) Sandmeyers reaction

(d) From alkenes



(e) Halogen exchange

$R\text{-}X + NaI \rightarrow R\text{-}I + NaX$

$R\text{-}X + AgF \rightarrow RF + AgX$

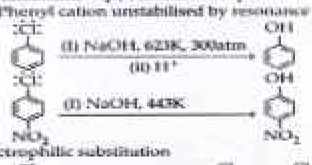
Reactions

(a) Nucleophilic substitution

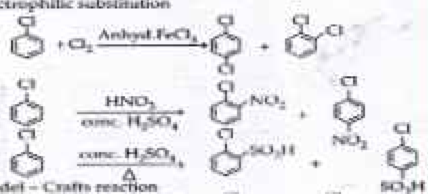
(i) Resonance effect

(ii) Hybridisation of C in C-X bond : Haloalkane $\rightarrow sp^3$ Haloarene $\rightarrow sp^2$

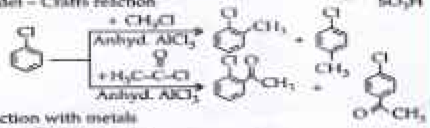
(iii) Phenyl cation unstabilised by resonance



(b) Electrophilic substitution



Friedel – Crafts reaction



(c) Reaction with metals

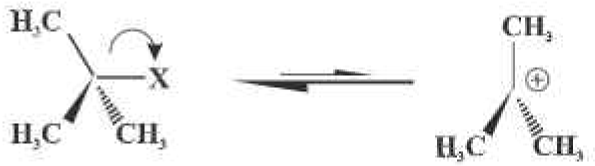
Wurtz – Fitting reaction

Fittig reaction

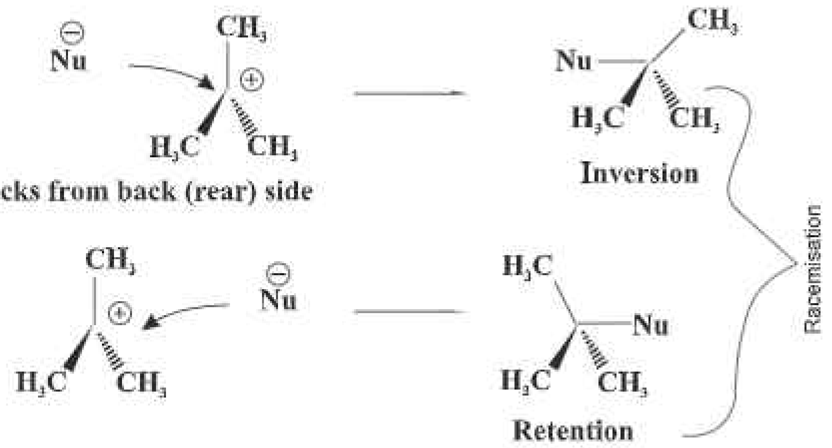
Mechanisms of S_N1 and S_N2:

S_N1 Mechanism

Step - 1



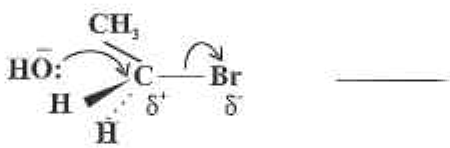
Step 2

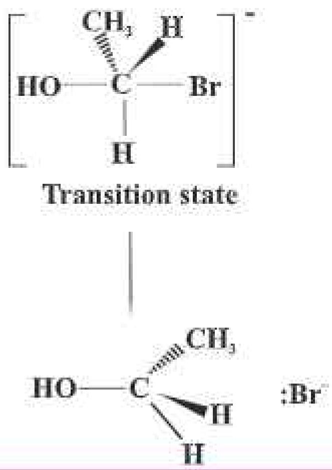


$\ominus$
Nu attacks from back (rear) side

$\ominus$
Nu attacks from same side as leaving group i.e. X

S_N2 Mechanism





Reaction occurs when bromoethane is added to a dilute NaOH solution.

	S_N1	S_N2
Carbon (sp^3) Electrophile	Favored by 3° alkyl halides or benzylic or allylic can also react by an S_N1 mechanism **(More stable carbocation)**	Favored by $-CH_3$ and 1° alkyl halides **(less sterically hindered)**
Nucleophile	Nature of the nucleophile has no affect on rate. In general, S_N1 use neutral, weak nucleophiles	Favored by more reactive nucleophiles $RS^- > NC^- > RO^- > HO^- > Cl^-$
Solvent Effect	Favored by polar, protic solvents.	Favored by polar, aprotic solvents.

IMPORTANT POINTS

- In haloarenes electrophilic substitution reaction occurs at *o*-& *p*-position.
- Haloarenes exhibit nucleophilic substitution reaction at extremely slow rate due to :

  (i) Partial double bond character of C-X bond.

  (ii) Benzene ring is electron rich.

  (iii) Phenyl carbocation is not stable.

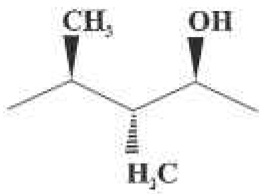
  (iv) More electronegativity of sp^2 hybridised carbon in haloarene as compared to sp^3 hybridisation in haloalkane

  (v) Steric hindrance due to benzene ring.

OBJECTIVE TYPE QUESTIONS

I. MULTIPLE CHOICE QUESTIONS

1. The Number of chiral carbons in given molecule is/are-



(a) 1 (b) 2

(c) 3 (d) 4

2. The correct increasing order for rate of reaction towards nucleophilic substitution for following is:

a b c

(a) a < b < c (b) a < c < b

(c) b < a < c (d) c < b < a

3. Which of the following molecule is chiral?

(a) 2-Bromobutane (b) 1-Bromobutane

(c) 2-Bromopropane (d) 2-Bromopropan-2-ol

4. Reaction of $C_6H_5CH_2Br$ with aqueous sodium hydroxide follows..................

(a) S_N1 mechanism

(b) S_N2 mechanism

(c) Either S_N1 or S_N2 mechanism depending on temperature

(d) E_1 mechanism

5. The correct IUPAC name for following molecule is-

(a) 1-Bromo-2-ethylpropane

(b) 1-Bromo-2-ethy1-2-methylethane

(c) 1-Bromo-2-methylbutane

(d) 2-Methyl-1-bromobutane

6. The correct increasing order of boiling points of the following compounds is-

(a) Bromobenzene < 1-Bromobutane < 1-Bromopropane < 1-Bromoethane

(b) Bromobenzene < 1-Bromoethane < 1-Bromopropane < 1-Bromobutane

(c) 1-Bromopropane < 1-Bromobutane < 1-Bromoethane < Bromobenzene

(d) 1-Bromoethane < 1-Bromopropane < 1-Bromobutane < Bromobenzene

7. Alkyl fluorides are synthesised by heating an alkyl chloride/bromide in presence of ______________ or ____________.

(a) CaF_2, CaF_2 (b) CoF_2, Hg_2F_2

(c) Hg_2F_2, CaF_2 (d) NaF, CaF_2

8. Which of the following haloalkanes reacts with aqueous KOH most easily?

(a) 1-Bromobutane (b) 2-Bromobutane

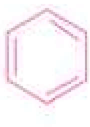
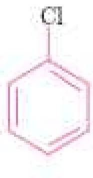
(c) 2-Bromo-2-methylpropane (d) 2-Chlorobutane

9. Toluene reacts with halogen in the presence of $FeCl_3$ giving *ortho* and *para* compounds. The reaction is :

(a) electrophilic elimination (b) electrophilic substitution

(c) free radical addition (d) nucleophilic substitution

10. Arrange the following compounds in the increasing order of their densities.

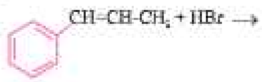
(A)  (B) 

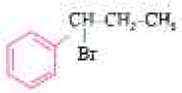
(C) 

(D) 

(a) (A) < (B) < (C) < (D) (b) (A) < (C) < (D) < (B)

(c) (D) < (C) < (B) < (A) (d) (B) < (D) < (C) < (A)

11. Chlorobezene is formed by reaction of chlorine with benzene in presence of $AlCl_3$. Which of the following species attacks the benzene ring in this reaction ?
    (a) Cl^- (b) Cl^+
    (c) $AlCl_3$ (d) $AlCl_4^-$
12. Which of the following statement is correct ?
    (a) Benzyl halides are more reactive than vinyl and aryl halides.
    (b) Vinyl halides are more reactive than alkyl halides.
    (c) Aryl halides are more reactive than alkyl halides.
    (d) Aryl halides are more reactive than benzyl halides
13. A new carbon-carbon bond is possible in the following reaction:
    (a) $C_6H_6 + CH_3Cl$ (anhyd. $AlCl_3$) $\rightarrow$
    (b) $CH_3CH_2Br + CH_3CH_2NH_2 \rightarrow$
    (c) CH_3-Br + CH_3CH_2-ONa$\rightarrow$
    (d) CH_3CH_2-Br + KOH (alc.) $\rightarrow$
14. Alcoholic $AgNO_3$ does not give precipitate with-
    (a) $C_6H_5CH_2Cl$ (b) CH_3CH_2Cl
    (c) C_6H_5Cl (d) CH_3-CHCl-CH_3
15. Reaction intermediate of E_1 reaction is-
    (a) Benzyne (b) Carbocation
    (c) Carbanion (d) Free radical
16. Best reagent for preparation of a chloroalkane from alcohol is -
    (a) $SOCl_2$ (b) $HCl/ZnCl_2$
    (c) PCl_5 (d) Cl_2/CCl_4
17. Highest nucleophilicity is shown by:-
    (a) F^- (b) OH^-
    (c) CH_3^- (d) NH_2^-
18. Cholroform on reaction with oxygen form poisonous gas
    (a) CO_2 (b) $COCl_2$
    (c) Cl_2 (d) HCl
19. The order of reactivity of alkyl halides for S_N2 reactions is-
    (a) RF > RCl > RBr > RI (b) RF > RBr > RCl > RI
    (c) RCl > RBr > RF > RI (d) RI > RBr > RCl > RF
20. An S_N2 reaction at an asymmetric carbon gives-
    (a) enantiomer of substrate (b) product with opposite optical rotation
    (c) mixture of diastereomers (d) single stereoisomer
21. The product in the following reaction is - 

(a) 

(b) 

(c) 

(d) 

II FILL IN THE BLANKS

1. Chlorobenzene may be converted into diphenyl by.......................reaction.
2. The mixture containing two enantiomers in equal amount, having zero optical rotation is called.......................
3. Reaction of haloalkanes with magnesium metal in dry ether forms the category of compounds called......................
4. The major product of Friedel-Crafts acetylation of chlorobenzene is....................
5. Polyhalogen compound having antiseptic property is........................
6. Alkyl halides are.................... in water but....................in organic solvents.
7. Bimolecular nucleophilic substitution of optically active haloalkanes leads to the ....of the configuration.
8. The molecules which rotates the plane-polarized light in clockwise direction are called....................
9. Halogens....................the aromatic ring towards electrophilic substitution due to -I effect of halogens.

III ASSERTION REASON TYPE QUESTIONS

In these questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices:

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
(c) Assertion is correct statement but reason is wrong statement.
(d) Assertion is wrong statement but reason is correct statement.

1. **ASSERTION :** S_N2 reaction is accompanied by the inversion of configuration.
   REASON: S_N2 reaction occurs in two step.
2. **ASSERTION :** Treatment of chloroethane with saturated solution of AgCN give ethylisocyanide as major product.
   REASON : Cyanide ion (CN^-) is an ambidentate nucleophile.
3. **ASSERTION :** The boiling points of alkyl halides decreases in the order : RI > RBr > RCl > RF
   REASON : The boiling points of alkyl chlorides, bromides and iodides are considerably higher than that of the hydrocarbon of comparable molecular mass.
4. **ASSERTION :** tert-Butyl bromide undergoes Wurtz reaction to give 2, 2, 3, 3-tetramethylbutane.
   REASON : In Wurtz reaction, alkyl halides react with sodium in dry ether to give hydrocarbon containing double the number of carbon atoms present in the halide.
5. **ASSERTION :** Presence of a nitro group at *ortho* or *para* position increases the reactivity of haloarenes towards nucleophilic substitution.
   REASON : Nitro group, being an electron withdrawing group decreases the electron density over the benzene ring.
6. **ASSERTION :** In monohaloarenes, further electrophilic substitution occurs at *ortho* and *para* positions.
   REASON : Halogens are deactivating towards electrophilic substitution reactions.

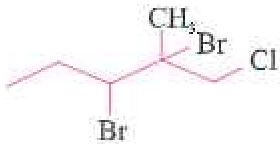
7. **ASSERTION :** Aryl iodides can be prepared by reaction of arenes with iodine in the presence of an oxidising agent.
   REASON : Oxidising agent oxidises HI into I_2.
8. **ASSERTION:** The nucleophilic substitution of vinyl chloride is difficult than ethyl chloride.
   REASON: Vinyl group is electron donating group.
9. **ASSERTION:** Silver nitrite gives nitro alkane when it reacts with an alkyl halide.
   REASON: Silver nitrite is an ionic compound.
10. **ASSERTION:** Chloroform is generally stored in completely filled bottles in dark.
    REASON : $CHCl_3$ get oxidised to phosgene in atmosphere.
11. **ASSERTION:** Neopentyl chloride undergoes S_N2 reaction easily.
    REASON: Neopentyl chloride is a tertiary halide.
12. **ASSERTION :** It is difficult to substitute chlorine by -OH in chlorobenzene in comparison to that in chloroethane.
    REASON : Chlorine-carbon (C-Cl) bond in chlorobenzene has a partial double bond character due to resonance.
13. **ASSERTION:** 2-Bromobutane reacts with aqueous KOH forming racemic mixture.
    REASON: 2-Bromobutane forms secondary carbocation which leads to bimolecular substitution reaction.

IV ONE WORD ANSWER TYPE QUESTIONS

1. Name the category of nucleophiles to which CN^-, NO_2^- belongs, which may attack through two different sites.
2. Name the reaction which converts aniline into chlorobenzene.
3. Which isomer of dichlorobenzene has highest boiling point?
4. If elimination takes place according to Zaitsev (Saytzeff) rule then from which carbon removal of -H takes place?
5. Which mechanism Ph_3C-Cl follows when it reacts with aqueous NaOH?
6. Name the instrument used to measure optical rotation.
7. Name the category of the molecules related by non-superimposable mirror images of each other.
8. Which gas is formed by the reaction of chloroform with oxygen in presence of light?
9. Name the first chlorinated organic insecticide used against mosquito during world war II?
10. Write name of major product formed by reaction of ethyl magnesium bromide with water.
11. What will be major product when 2-Bromopentane reacts with alcoholic KOH ?
12. What will be the sign of optical rotation for a laevorotatory molecule?

VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)

1. Give IUPAC name of:



Ans : 1-Chloro-2,3-dibromo-2-methylpentane

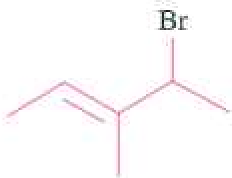
2. Identify A and B in each of the following process :

$CH_3CH_2Cl \xrightarrow{NaCN} A \xrightarrow{H_2/Ni} B$

Ans : A: CH_3-CH_2-CN; B: $CH_3CH_2CH_2NH_2$

3. Draw the structure of 4-bromo-3-methylpent-2-ene.

Ans:



4. Why Grignard reagent should be prepared under anhydrous condition?

Ans: It reacts with water and converts into corresponding hydrocarbon.

($RMgX + H_2O \rightarrow RH + MgX(OH)$)

5. Chloroform is stored in dark coloured and sealed bottles. Why ?

Ans: It is slowly oxidised by air in presence of light to form $COCl_2$(Phosgene) which is a poisonous gas. ($CHCl_3 + \frac{1}{2} O_2 \rightarrow COCl_2 + 2HCl$)

6. An alkyl halide having molecular formula C_4H_9Cl is optically active. Write its structure.

Ans: CH_3-CH-CH_2-CH_3
         |
        Cl

7. An organic compound 'A' on treatment with KCN gave 'B' which on hydrolysis with dil. HCl gave acetic acid. Identify A.

Ans: CH_3Cl

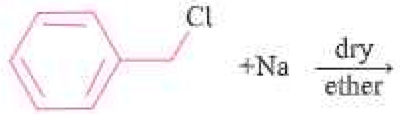
8. Arrange the following in order of their increasing reactivity in nucleophilic substitution reaction : CH_3F, CH_3I, CH_3Br, CH_3Cl

Ans: CH_3F, CH_3Cl, CH_3Br, CH_3I

9. Allyl chloride is more reactive than n-propyl chloride toward nucleophilic substitution reaction. Why?

Ans: Due to more stability of allyl carbocation than n-propyl carbocation.

10. Complete the reaction:



Ans: $PhCH_2CH_2Ph$ (Wurtz reaction)

11. Give one chemical test to distinguish between chlorobenzene and benzyl chloride?

Ans: $AgNO_3$ test: benzyl chloride gives white precipitate.

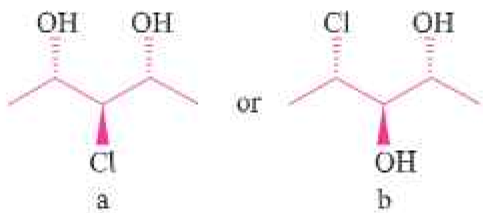
12. The presence of nitro group ($-NO_2$) at *ortho* or *para* position increases the reactivity of haloarenes towards nucleophilic substitution. Explain.

Ans: Nitro group withdraws electrons by -R, -I effect resulting in lesser election density on benzene ring.

13. For the preparation of alkyl chloride from alcohols, thionyl chloride ($SOCl_2$) is preferred. Give reason.

Ans: The by-products are gaseous SO_2 and HCl which can be easily removed to give pure haloalkane.

14. Which of the following molecule is optically active?



Ans: b is optically active

15. The dipole moment of chlorobenzene is lower than cyclohexyl chloride. Why?

Ans: Due to sp^2 hybridised carbon in chlorobenzene which is more electronegative and reduces polarity of C-Cl bond.

16. Name the compound which will be formed by reaction of (–)-1-chlorobutane with KOH?

Ans: (+)-Butan-1-ol

17. What happens when methylchloride is treated with KCN?

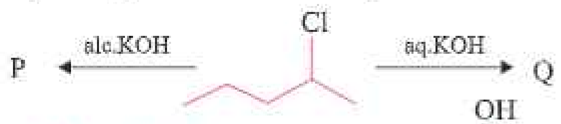
Ans: CH_3-CN will be formed

18. Identify X and Y :

$$R\text{-}Br + Mg \xrightarrow{\text{Dry Ether}} X \xrightarrow{D_2O} Y$$

Ans. X: R-MgBr Y: R-D

19. Complete by writing structures of P and Q:

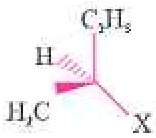


Ans. P:  Q: 

20. Name the product formed when 2,4,6- trinitrochlorobenzene reacts with warm water.

Ans. Picric acid(2,4,6-trinitrophenol)

21. Write structure of product formed when following undergoes S_N2 reaction taking OH^- as nucleophile:



Ans. 

22. Optical rotation of an enantiomer is +12.5°. Write optical rotation of :

(i) Its mirror image

(ii) mixture of enantiomer & mirror image (1:1)

Ans. (i)-12.5° (ii) Zero

23. Out of pentan-2-ol and pentan-3-ol, which is chiral molecule?

Ans. Pentan-2-ol

SHORT ANSWER TYPE QUESTIONS (2 or 3 Marks)

1. Why is sulphuric acid not used during the reaction of alcohols with KI?

Ans: H_2SO_4 cannot be used along with KI in the conversion of an alcohol to an alkyl iodide as it converts KI to corresponding acid, HI which is then oxidised by it to I_2.

2. Which compound in each of the following pairs will react faster in S_N2 reaction with OH^-?

(i) CH_3Br or CH_3I (ii) $(CH_3)_3CCl$ or CH_3Cl

Ans: (i) CH_3I will react faster than CH_3Br, as iodide is a better leaving group.

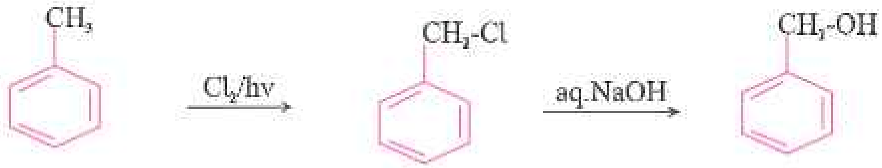
(ii) CH_3Cl as it is primary haloalkanes with less steric hindrance.

3. Carry out the following conversions in not more than two steps :

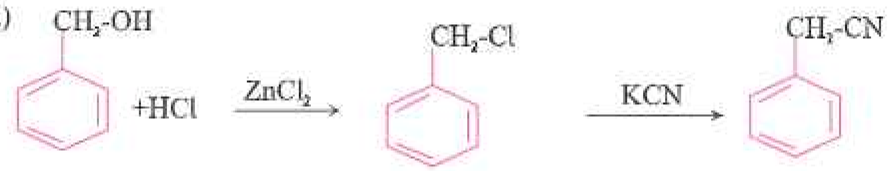
(i) Toluene to Benzyl alcohol

(ii) Benzyl alcohol to phenylethanenitrile

Ans: (i)



(ii)



4. Which of the following compounds would undergo S_N1 Reaction faster and why?

a **b**

Ans: a will be more reactive due to higher stability of benzyl carbocation.

6. Complete the following reaction :

(i) $C_6H_5N_2^+Cl^- + KI \rightarrow$

(ii) $CH_2{=}CH_2 + Br_2 \rightarrow$

(iii) $CH_3CH_2OH + SOCl_2 \rightarrow$

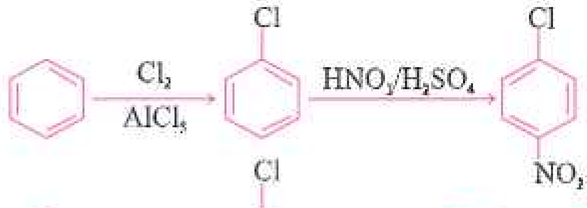
Ans: (i) C_6H_5I, (ii) $CH_2Br\text{-}CH_2Br$, (iii) CH_3CH_2Cl

7. Convert :

(i) Benzene to *p*- nitrochlorobenzene

(ii) Benzene to diphenyl

Ans:

(i) 

(ii) 

8. What happens when :

(i) Propene is treated with HBr in presence of peroxide.

(ii) Benzene is treated with methyl chloride in presence of $AlCl_3$.

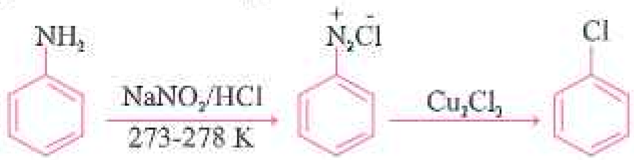
Ans: (i) 1-Bromopropane is formed (Anti-Markonikov addition)

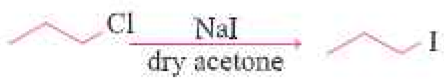
(ii) Toluene is formed (Friedel-Crafts Alkylation)

9. Write short note on :

(i) Sandmeyer reaction (ii) Finkelstein reaction

Ans:

(i) 

(ii) 

10. Name the reagent used to convert:

(i) 2-Chloropropane to 2- nitropropane

(ii) Chloroethane to butane

Ans: (i) $AgNO_2$ (ii) Na / dry ether

11. Give reasons :

    (i) Boiling point of alkyl bromide is higher than alkyl chloride.

    (ii) Alkyl halides are better solvents than aryl halides.

Ans: (i) High magnitude of van der Waals forces in alkyl bromides.

    (ii) C - X is more polar in alkyl halides.

12. Carry out the following conversion :

    (i) But-l-ene to n-Butyl iodide

    (ii) 2-Bromopropane to 1-Bromopropane

Ans:

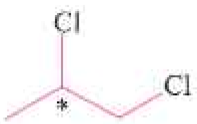
(i) 

(ii) 

13. Identify and indicate the presence of center of chirality (if any) in the following molecules. How many stereoisomers are possible for those containing chiral center?

    (i) 1,2- Dichloropropane   (ii) 3- Bromopent-1-ene

Ans:



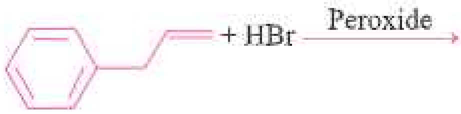
1,2-Dichloropropane

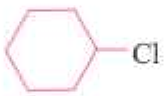
3-Bromopent-1-ene

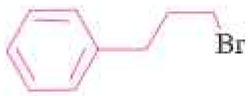
[*marked carbon are chiral centres]

14. Complete the reactions:

(a) 

(b) 

Ans : (a) 

(b) 

15. Haloalkanes react with KCN to form alkyl cyanides as main product while AgCN form isocyanide as the chief product. Explain

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

16. An organic compound **A** react with PCl_5 to give compound **B**, compound **B** react with Na /ether to give n-butane . What are compounds **A** and **B** ?

Ans : **A** = C_2H_5OH, **B** = C_2H_5Cl

17. The treatment of alkyl chlorides with aqueous KOH leads to the formation of alcohols but in presence of alcoholic KOH, alkenes are major products. Explain.

Ans: In aqueous medium i.e. water, KOH will produce strong nucleophile OH^- which will bring about the substitution of alkyl halides to form alcohols. At the same time, the OH^- ions will be highly hydrated also. They will not be able to abstract a proton (H^+) from the β-carbon atom to form alkenes.

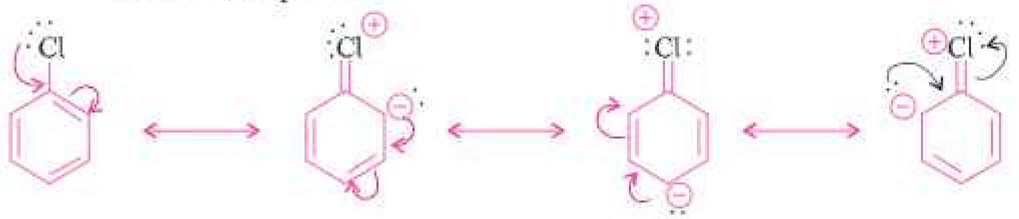
In alcoholic KOH, the solution will also contain ethoxide ions ($C_2H_5O^-$) in addition to OH^- ions. They being a stronger base than OH^- ions, will abstract a H^+ ion from the β-carbon atom giving alkene as the product as a result of dehydrohalogenation.

LONG ANSWER TYPE QUESTIONS (5 Marks)

1. Haloarenes are extremely less reactive towards nucleophilic substitution reactions. Explain.

Ans: Aryl halides are extremely less reactive towards nucleophilic substitution reactions due to the following reasons:

(i) Resonance effect : In haloarenes, the electron pairs on halogen atom are in conjugation with π-electrons of the ring and the following resonating structures are possible.



C-Cl bond acquires a partial double bond character due to resonance. As a result, the bond cleavage in haloarene is difficult than haloalkane and therefore, they are less reactive towards nucleophilic substitution reaction.

(ii) Difference in hybridisation of carbon atom in C-X bond: In haloalkane, the carbon atom attached to halogen is sp^3 hybridised while in case of haloarene, the carbon atom attached to halogen is sp^2-hybridised.

The sp^2 hybridised carbon with a greater s-character is more electronegative and can hold the electron pair of C-X bond more tightly than sp^3-hybridised carbon in haloalkane with less s-character. Since it is difficult to break a shorter bond than a longer bond therefore, haloarenes are less reactive than haloalkanes towards nucleophilic substitution reaction.

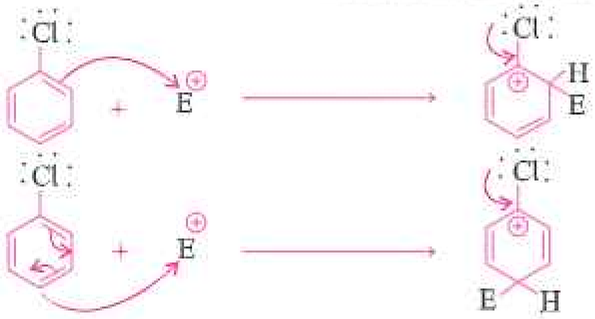
(iii) Instability of phenyl cation: In case of haloarenes, the phenyl cation formed as a result of self-ionisation will not be stabilised by resonance and therefore, S_N1 mechanism is ruled out.

(iv) Because of the possible repulsion, it is less likely for the electron rich nucleophile to approach electron rich arenes.

2. Although chlorine is an electron withdrawing group, yet it is *ortho-* and *para-*directing in electrophilic aromatic substitution reaction. Explain.

Ans: Chlorine withdraws electrons through inductive effect and releases electrons through resonance. Through inductive effect, chlorine destabilises the intermediate carbocation formed during the electrophilic substitution.

Inductive effect destabilises the intermediate carbocation



(attack at *ortho*-position)

(attack at *para*-position)

Resonance effect stabilises the intermediate carbocation

Through resonance, halogen tends to stabilise the carbocation and the effect is more pronounced at *ortho*- and *para*- positions. The inductive effect is stronger than resonance and causes net electron withdrawal and thus causes net deactivation. The resonance effect tends to oppose the inductive effect for the attack at *ortho*- and *para*-positions and hence makes the deactivation less for *ortho*- and *para*-attack. Reactivity is thus controlled by the stronger inductive effect and orientation is controlled by resonance effect.

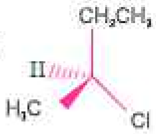
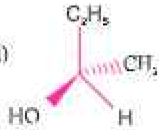
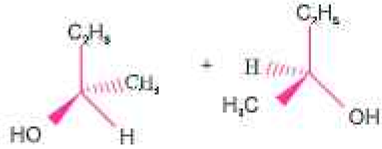
3. A primary alkyl halide (**A**), C_4H_9Br reacted with hot alcoholic KOH to give compound (**B**). Compound (**B**) reacted with HBr to give (**C**), which is an isomer of (A). When (**A**) was reacted with sodium metal, it gave a compound (**D**), C_8H_{18} which was different than the compound when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

Ans: (A) 1-Bromo-2-methylpropane
(B) 2-Methylprop-1-ene
(C) 2-Bromo-2-methylpropane
(D) 2,5-Dimethylhexane

3. Write wedge and dash representation of 2-Bromobutane then write structures of molecules when:

Ans: (i) It undergoes retention on reaction with HCl
(ii) It undergoes inversion on reaction with OH^-
(iii) It undergoes S_N1 reaction with H_2O

2-Bromobutane

(i)  (ii)  (iii) 

5. Predict A to E in following sequence of reactions:

$$\text{(i) A} \xrightarrow{HBr} CH_3\text{-}\underset{}{\overset{\displaystyle Br}{\overset{|}{C}H}}\text{-}CH_3 \xrightarrow{\text{alc.KOH}} \text{B} \xrightarrow[(C_6H_5CO)_2O_2]{HBr} \text{C}$$

$$\text{(ii) } CH_3Br \xrightarrow{KCN} \text{D} \xrightarrow{H_3O^+} \text{E}$$

Ans. A: $CH_3\text{-}CH{=}CH_2$ B: $CH_3\text{-}CH{=}CH_2$ C: $CH_3\text{-}CH_2\text{-}CH_2\text{-}Br$

D: $CH_3\text{-}CN$ E: $CH_3\text{-}COOH$

6. Give reasons:

(i) ($\pm$)- Butan-2-ol is optically inactive

(ii) Iodoethane is more reactive than chloroethane in S_N2 reaction

(iii) *p*-dichlorobenzene has higher metting point than *o*-& *m*-isomers.

(iv) Haloalkanes easily dissolves in organic solvents.

(v) Grignard's reagent is stored in moistue proof cotainers.

Ans. (i) Rotation due to one enantiomer cancelled out by another in racemic mixure.

(ii) Because I is better leaving group than Cl

(iii) Due to symmetry of *p*-isomer, it fits in lattice better

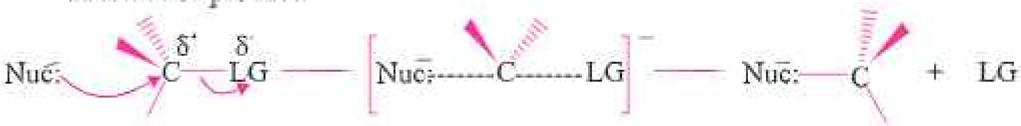
(iv) New intermolecular attractions between haloalkanes and solvent have much same strength as the ones being broken.

(v) Grignard's reagent reacts with water forming corresponding alkane.

CASE STUDY BASED QUESTIONS

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

The bimolecular nucleophilic substitution (S_N2) reactions are among the fundamental and most important organic reactions. Traditionally, the mechanism of the S_N2 reactions is studied using qualitative transition state theory. The functionalized sp^3 hybridized carbon in a substrate molecule functions as an electrophilic center. This electrophilicity is considered due to a partial positive charge created on carbon by the electronegative functional group. A nuelcophile (Nuc-) attacks the sp^3 hybridized carbon from the opposite side of the leaving group (-LG). This nucleophilic attack results in a transition state in which the carbon atom becomes sp^2 hybridized with the C-LG bond partially broken and the Nuc-C bond partially formed. Finally, the C-LG bond is broken completely coincident with formation of the Nuc-C bond, giving the nucleophilic substitution product.



sp^3 carbon sp^3 carbon sp^3 carbon

Reference : Xiaoping Sun, **Mechanistic Studies of Nucleophilic Substitution and β-Elimination Reactions**, *Symmetry* **2010**, 2(1), 201-212;https://doi.org/10.3390/sym2010201

(A) Which of the following undergoes S_N2 reaction at fastest rate?

(a)	Chloropropane	(b)	Bromopropane
(c)	Iodopropane	(d)	Chlorobenzene

(B) S_N2 reaction accompanied by.................of the configuration.

(a)	Retention	(b)	Inversion
(c)	Racemisation	(d)	Tautomerism

(C) Reaction of $(CH_3)_3$C-Cl with aq. NaOH gives:

(a)	$(CH_3)_3$ CH-OH	(b)	$(CH_3)_2$ CH-OH
(c)	(a) and (b)	(d)	But-2-ene

(D) The correct order of rate of reaction in S_N2 for following molecules are:

1 2 3

(a) $1>2>3$ (b) $2>1>3$

(c) $1>3>2$ (d) $3>2>1$

2. **Read the passage and answer the following questions:**

Halogenation of alcohols is a useful reaction as alcohol-starting materials are cheap and large varieties are commercially available. Many procedures are known that convert alcohols to halides however, they can involve harsh conditions and hazardous chemicals. For example, the chlorination of alcohols is traditionally performed using HCl gas or thionyl chloride, both of which are hazardous to human health and often produce many side reactions. Although improvements have been made upon these halogenation reactions, further green methodology is desired. On a laboratory scale, ammonium halide salts (NH_4X) are solid reagents, which means they are easy to handle and measure.

Discovering a mild, neutral, highly selective and environmentally friendly system for catalytic dehydroxyhalogenation is desirable but it is not a trivial task. Compromises in the journey towards an ideal sustainable process have to be made. This is exhibited by some of the trends found in the literature regarding chlorination of alcohols. Some reports involve the use of tripbenylphosphine (PPh_3) as a superstoichiometric additive in dehydroxychlorination reactions.

Reference : Petten, C.F., Kalviri, H.A. & Kelton, F.M. **Halodehydroxylation of alcohols to yield benzylic and alkyl halides in ionic liquids**. *Sustain Chem Process* 3, 16 (2015). https://doi.org/ 1 0.1186/s40508-015-0043-4

(A) Which of the following reaction may be used for the formation of 2-Fluorobutane?

(a) Finkelstein Reaction (b) Swarts Reaction

(c) Sandmeyer Reaction (d) S_N2 Reaction

(B) For the reaction, $R\text{-}OH + HX \rightarrow R\text{-}X + H_2O$ the rate of reaction will be highest with the-

(a) Ethanol (b) Propan-1-ol

(c) Propan-2-ol (d) 2-Methylbutan-2-ol

(C) When primary, secondary and tertiary alcohols reacts with Lucas' reagent ($HCl + Anhy.\ ZnCl_2$), the incorrect observation is-

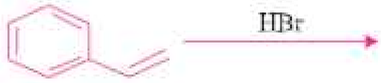
(a) Primary alcohol gives turbidity immediately.

(b) Secondary alcohols gives turbidity in 5-10 minutes.

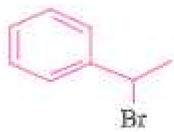
(c) Tertiary alcohols are most reactive.

(d) Reaction follows S_N1 pathway.

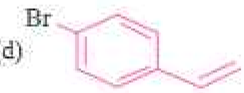
(D) The correct product of following reaction is-



(a) 

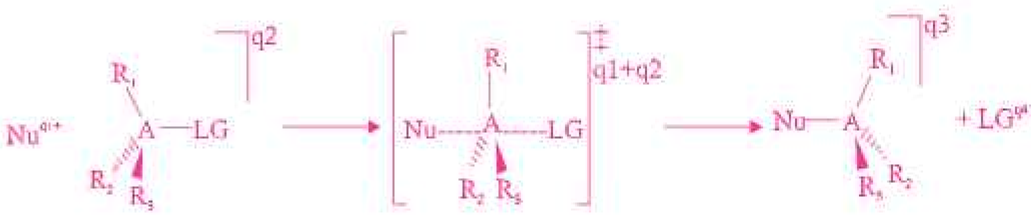
(b) 

(c) 

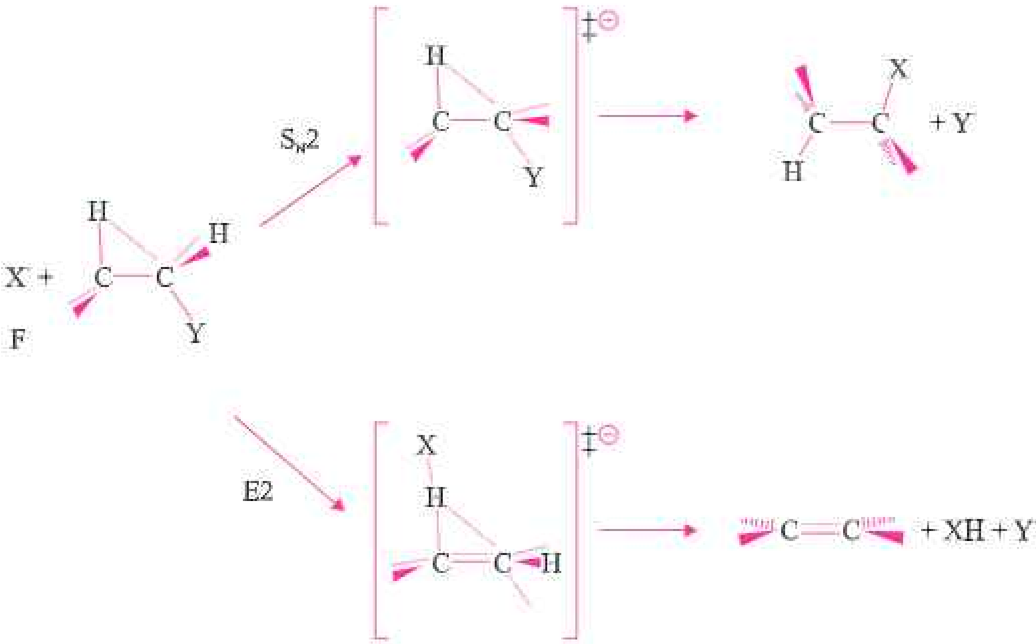
(d) 

3. **Read the passage and answer the following questions:**

Bimolecular nucleophilic substitution (S_N2) reactions constitute one of the most widely-used organic chemistry reactions, both in chemistry and biology. The general reaction scheme is summarized in Scheme I, where a nucleophile Nu^q attacks the central atom A and simultaneously a leaving group LG is displaced. The reaction can proceed for either anionic species (typically $q1=q4<0$), neutral (radical) species (typically $q1=q2=q3+q4=0$), or cationic species (typically $q2=q3>0$), together with a wide range of nucleophiles, leaving groups and central atoms. The number and nature of the substituents around the central atom play a major role in determining reactivity.



S_N2 substitution is, in principle, always in competition with base induced elimination (E2), and the two pathways may occur as unwanted side reactions of each other.



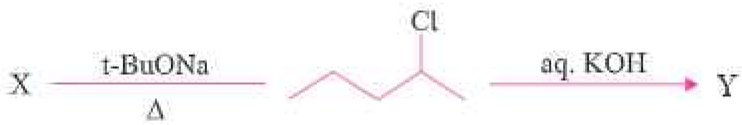
Reference : T.A. Hamlin, M. Swart, F. M. Bickelhaupt, **Nucleophilic Substitution (S_N2): Dependence on Nucleophile, Leaving Group, Central Atom, Substituents, and Solvent** *ChemPhysChem* **2018**, 19, 1315.

(A) Which of the following molecule leads to fastest reaction according to S_N2 mechanism?

(a) 2-Chloropropane (b) 1-Chloropropane

(c) Chlorophenylmethane (d) 2-Chlorotoluene

(B) In given reactions, X and Y are respectively-



(a) Pent-l-ene, Pent-2-ene

(b) Pent-2-ene, Pentan-2-ol

(c) Pentan-2-ol, Pent-2-ene

(d) Pent- 1 -ene, Pentan-2-ol

(C) Which of the following haloalkane reacts with nucleophile forming racemic mixture?

(a) 1-Chloropropane (b) Chlorobenzene

(c) 2-Chlorobutane (d) 1-Chlorobutane

(D) Which of the following statement is incorrect about S_N2 reaction?

(a) It takes place in single step.

(b) It is accompanied by the inversion of configuration.

(c) Stability of carbocation determines the rate of reaction.

(d) Iodopropane undergoes S_N2 faster than Chloropropane.

4. **Read the passage and answers the following questions:**

Nucleophilic substitution reaction of haloalkane can be conducted according to both S_N1 and S_N2 mechanisms. However, which mechanism it is based on is related to such factors as the structure of haloalkane, and properties of leaving group, ucleophilic reagent and solvent.

Influences of halogen : No matter which mechanism the nucleophilic substitution reaction is based on, the leaving group always leave the central carbon atom with electron pair. This is just the opposite of the situation that nucleophilic reagent attacks the central carbon atom with electron pair. Therefore, the weaker the alkalinity of leaving group is , the more stable the anion formed is and it will be more easier for the leaving group to leave the central carbon atom; that is to say, the reactant is more easier to be substituted. The alkalinity order of halogen ion is F < Br < CI < F and the order of their leaving tendency should be $I^- > Br^- > Cl^- > F^-$. Therefore, in four halides with the same alkyl and different halogens, the order of substitution reaction rate is RI> RBr > RCI > RF. In addition, if the leaving group is very easy to leave, many carbocation intermediates are generated in the reaction and the reaction is based on S_N1 mechanism. If the leaving group is not easy to leave, the reaction is based on S_N2 mechanism.

Influences of solvent polarity: In S_N1 reaction, the polarity of the system increases from the reactant to the transition state, because polar solvent has a greater stabilizing effect on the transition state than the reactant, thereby reduce activation energy and accelerate the reaction. In S_N2 reaction, the polarity, of the system generally does not change from the reactant to the transition state and only charge dispersion occurs. At this time, polar solvent has a great stabilizing effect on Nu than the transition state, thereby increasing activation energy and low down the reaction rate. For example, the decomposition rate (S_N1) of tertiary chlorobutane in 25°C water (dielectric constant 79) is 300000 times faster than in ethanol (dielectric constant 24). The reaction rate (S_N2) of 2-bromopropane and NaOH in ethanol containing 40% water is twice slower than in absolute ethanol. In a word, the level of solvent polarity has influence on both S_N1 and $S_N2$reactions, but with different results. Generally speaking, weak polar solvent is favorable for S_N2 reaction, while strong polar solvent is favorable for S_N1 reaction, because only under the action of polar solvent can halogenated hydrocarbon dissociate into carbocation and halogen ion and solvents with a strong polarity is favorable for solvation of carbocation, increasing its stability. Generally speaking, the substitution reaction of tertiary haloalkane is based on S_N1 mechanism in solvents with a strong polarity (for example, ethanol containing water).

Reference A Brief Discussion on Nucleophilic Substitution Reaction on **Saturated Carbon Atom**. In *Applied Mechanics and Materials* (Vol. 312, pp. 433-437). Trans. Tech Publications Ltd.) (Ding, Y. (2013).

(A) Solvent in which S_N1 mechanism is favoured is:
(a) benzene
(b) carbon tetrachloride
(c) acetic acid
(d) carbon disulphide

(B) Nucleophilic substitution will be fastest in case of:
(a) 1-Chloro-2,2-dimethyl propane
(b) 1-Iodo-2,2-dimethyl propane
(c) 1-Bromo-2,2-dimethyl propane
(d) 1-Fluoro-2,2-dimethyl propane

(C) S_N1 reaction will be fastest in which of the following solvents?
(a) Acetone (dielectric constant 21)
(b) Ethanol (dielectric constant 24)
(c) Methanol (dielectric constant 32)
(d) Chloroform (dielectric constant 5)

(D) Polar solvents make the reaction faster as they:
(a) destabilize transition state and decrease the activation energy
(b) destabilize transition state and increase the activation energy
(c) stabilize transition state and increase the activation energy
(d) stabilize transition state and decrease the activation energy

(E) S_N1 reaction will be fastest in case of:
(a) 1-Chloro-2-methylpropane
(b) 1-Iodo-2-methylpropane
(c) 1-Chlorobutane
(d) 1-Iodobutane

ANSWERS

I MULTIPLE CHOICE QUESTIONS

1. b	2. a	3. a	4. b	5. c	6. d	7. b	8. a	9. b
10. a	11. b	12. a	13. a	14. c	15. b	16. a	17. c	18. b
19. d	20. d	21. a						

II FILL IN THE BLANKS

1. Fittig
2. Racemic mixture.
3. Grignard reagent.
4. *p*-chloroacetophenone.
5. Iodoform.
6. Insoluble, soluble.
7. Inversion.
8. Dextrorotatory.
9. Deactivates

III ASSERTION REASON TYPE QUESTIONS

1. c	2. b	3. b
4. d	5. a	6. b
7. d	8. c	9. c
10. a	11. d	12. a
13. c		

IV ONE WORD TYPE QUESTIONS

1. Ambident nucleophile.
2. Sandmeyer reaction.
3. para-dichlorobenzene.
4. β-carbon.
5. S_N1.
6. Polarimeter.
7. Enantiomers.
8. Phosgene
9. DDT
10. Ethane
11. Pent-2-ene
12. Negative

CASE STUDY BASED QUESTIONS

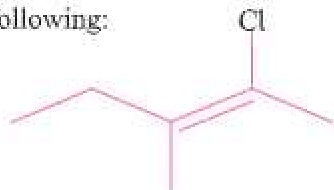
1.	(A) - (c)	(B) - (b)	(C) - (a)	(D) - (d)	
2.	(A) - (b)	(B) - (d)	(C) - (a)	(D) - (b)	
3.	(A) - (b)	(B) - (b)	(C) - (c)	(D) - (c)	
4.	(A)-(c)	(B)-(b)	(C)-(c)	(D)-(c)	(E)-(b)

UNIT TEST-1

HALOALKANES AND HALOARENES

Maximum Marks : 20 **Time Allowed : 1 Hr**

1. Write IUPAC name of following: 1



2. The correct ascending order of nucleophilic substitution reactions for following molecules is- 1
   (I) Chlorobenzene (II) 4-Nitrochlorobenzene
   (III) 4-Chlorotoluene
   (a) I, II, III (b) I, III, II
   (c) III, I, II d) III, II, I
3. How will you convert aniline into iodobenzene? 1
4. Chlorobenzene on reaction with chloromethane in presence of zinc chloride forms- 1
   (a) *o*-dichlorobenzene
   (b) *o*-chlorotoluene
   (c) *p*-chlorotoluene
   (d) *o*-chlorotoluene and *p*-chlorotoluene
5. A solution of a molecule (X) rotates plane polarised light 32° clockwise. Which of the following is incorrect? 1
   (a) X is optically active
   (b) X is dextrorotatory
   (c) X has all achiral carbons
   (d) X forms non-superimposable
6. Which of the following undergoes S_N2 reaction faster and Why? 2

7. How will you synthesize following from aniline? Write chemical equations. 2

   (i) Chlorobenzene (ii) Iodobenzene

8. Explain following giving examples: 2

   (i) racemic mixture (ii) enantiomers

9. What happens when: 3

   (i) Bromoethane reacts with sodium ethoxide

   (ii) Chloroethane reacts with AgCN.

   (iii) 2-Bromo-2-methylbutane is heated with ethanolic KOH.

10. Explain following: 3

    (i) Aryl chlorides and bromides can be easily prepared by electrophilic substitution of aromatic hydrocarbons with chlorine and bromine respectively in the presence of Lewis acid catalysts but for preparation of aryl iodides presence of an oxidising agent is required.

    (ii) Grignard reagent is kept under anhydrous conditions.

    (iii) Reactions through S_N2 mechanisms are accompanied by inversion of configuration.

11. Convert the following: 3

    (i) Ethanol to iodoethane

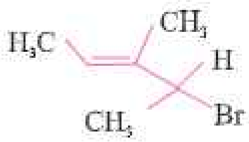
    (ii) Toluene to benzyl alcohol

    (iii) Benzene to diphenyl.

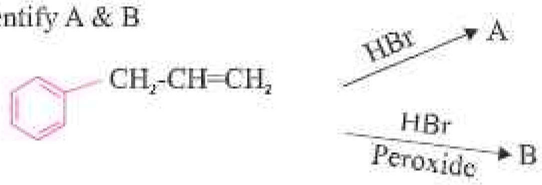
UNIT TEST-2

HALOALKANES AND HALOARENES

Maximum Marks : 20 **Time Allowed : 1 Hr**

1. Write the IUPAC name of  1

2. Identify A & B



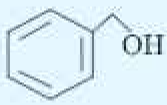
3. Define ambident nucleophile with suitable examples. 1
4. How will you convert chloroethane into butane? 1
5. Out of $C_6H_5CH_2Cl$ and $C_6H_5CHCl\ C_6H_5$, which is more easily hydrolysed by queous KOH ? 1
6. (i) Chloroform is kept in completely filled bottles in dark. Explain the reason.
   (ii) Mention one application of Iodoform 2
7. How Grignard's reagent is prepared using alkyl halides ? Why it is kept under anhydrous conditions ? 2
8. Explain following terms giving exmpales: 2
   (i) Chirality
   (ii) Inversion of configuration
9. Discuss mechanisms of S_N1 and S_N2 taking appropriate examples of optically active alkyl halides. 3
10. Which of the following undergoes S_N2 faster and why? 3
    (a)  Or 
    (b)  Or 
    (c)  Or 
11. Convert following: 3
    (i) Aniline to phenylisocyanide
    (ii) Benzene to 4-Bromonitrobenzene
    (iii) Propene to Propan-1-ol

UNIT 11

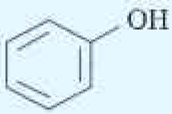
Alcohols, Phenols and Ethers

Points to Remember

Classification of Alcohols:
(a) Containg sp^3 C-OH bond (i)-CH_2-OH (1^0), (ii) > CH-OH(2^0), (iii)$-\overset{|}{\underset{|}{C}}-$ OH (3^0)
Allylic: CH_2=CH-CH_2OH

(iv)Benzylic: 

(b) Containg sp^2 C-OH bond - Vinylic (i) CH_2=CH-OH

(ii)Phenols: 

Classification of ethers:
Simple/Symmetric: Alkyl/aryl groups attached to oxygen are same e.g. $CH_3CH_2OCH_2CH_3$
Mixed/Unsymmetric: Two different alkyl/aryl groups attached to oxygen e.g. $CH_3OCH_2CH_3$

Classification and Nomenclature of Alcohols and ethers

Nomenclature:

Alcohols: Common names (Alkyl group + alcohol)

IUPAC (Alkan+ol, substituting -e by - ol e.g. ethanol)

Phenols: Common names (as derivatives of phenol with position like ortho-, meta-,para-)

IUPAC (Derivatives of phenols with numbers like 1,2-, 1,3-e.g.

2-Nitrophenol or o-nitrophenol)

Ethers: Common names (alkyl/aryl groups in alphabetical order followed by ether e.g. ethyl methyl ether) IUPAC (In alkyl/aryl group-e is replaced by oxy followed by parent hydrocarbon e.g. methoxyethane)

Preparation of Alcohols

1. From alkenes:

a) By acid catalyzed hydration Markonikov's addition)

b) By hydroboration-Oxidation(Anti-Markonikov)

$3CH_3\text{-}CH{=}CH_2 + (H\text{-}BH_2)_2 \rightarrow (CH_3\text{-}CH_2\text{-}CH_2)_3B$

$\downarrow H_2O \;\; H_2O_2, OH$

$3CH_3\text{-}CH_2\text{-}OH + B(OH)_3$

2. From carbonyl compounds

a) By reduction of aldehydes and ketones

$R\text{-}CHO + H_2 \xrightarrow{Pd} RCH_2OH$

b) By reduction of carboxylic acids and esters

$RCOOH \xrightarrow[H_2O]{i)\ LiAlH_4} RCH_2OH$

$RCOOH \xrightarrow[H^+]{R'\text{-}OH} RCOOR' \xrightarrow[Pd]{H_2} RCH_2OH + R'\text{-}OH$

3. From Grignard reagent

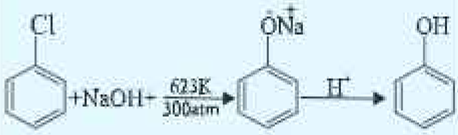
For Primary alcohol → methanal (formaldehyde)

Secondary → aldehydes other than methanal

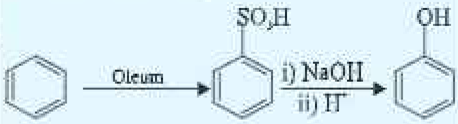
Tertiary → Ketones are used with appropriate Grignard reagent

Preparation of Phenol

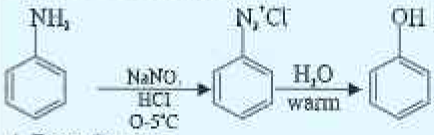
1. From Haloalkanes



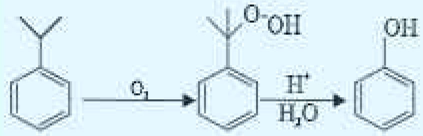
2. From Benzene sulphonic acid



3. From Diazonium salts



4. From Cumene



Preparation of Alcohols, Phenols and Ethers

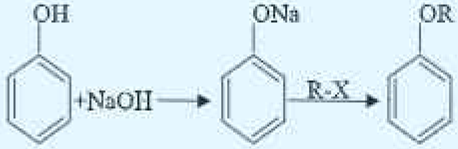
Preparation of Ethers

1. By dehydration of alcohols

$CH_3CH_2OH_1 \xrightarrow[413K]{H_2SO_4} CH_3CH_2OCH_2CH_3$

2. Williamsons Synthesis

$RX + R'\text{-}ONa \longrightarrow R\text{-}O\text{-}R'$



Physical Properties and Reactions of Alcohols and phenols

(a) Physical properties:

- Boiling point increases with increase of cabon chain
- Solubility decreases with increase in size of alkyl aryl group

(b) Chemical properties:

(i) $2R\text{-}O\text{-}H + 2Na \longrightarrow 2\ R\text{-}\overset{-}{O}\overset{+}{Na} + H_2$;
Acidity-primary>secondary>tertiary

(ii) $Ar/RO\text{-}H + R'\text{-}COOH \xrightleftharpoons{H^+} Ar/ROCOR' + H_2O$ (Esterification)

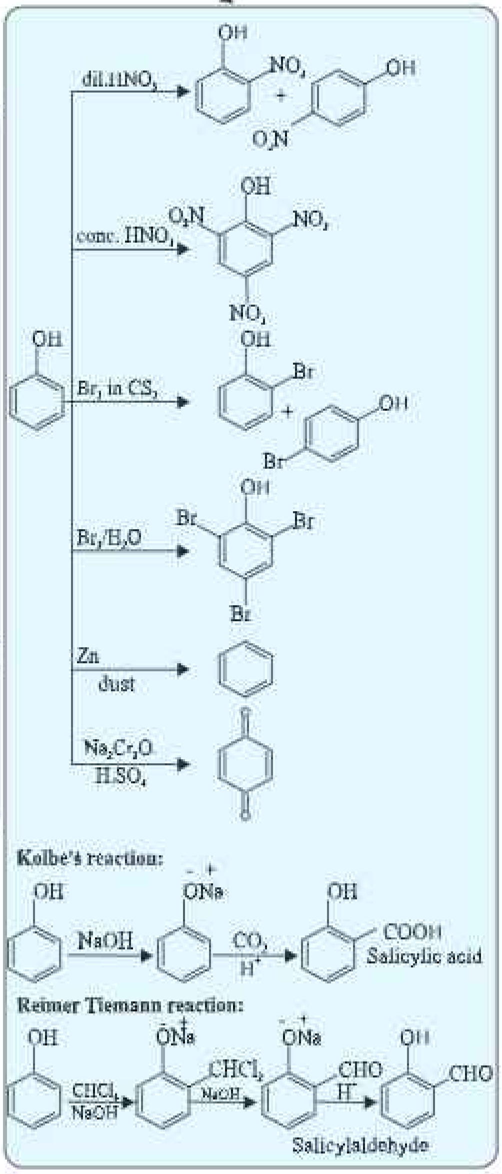
$ROH + HX \longrightarrow R\text{-}X + H_2O$ (withAnhydrous $ZnCl_2$+HCl, Lucas Test)

Order: Primary < Secondary < Tertiary

(iii) $C_2H_5OH \xrightarrow[443K]{H_2SO_4} CH_2{=}CH_2 + H_2O$:
Order: Primary<secondary<tertiary

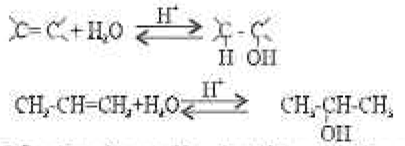
(iv) $RCH_2OH \xrightarrow[\text{or PCC}]{CrO_3} RCHO \longrightarrow R\text{- }COOH$

$RCH_2OH \xrightarrow{KMnO_4} R\text{- }COOH$



Mechanisms:

a) Hydration of Alkenes



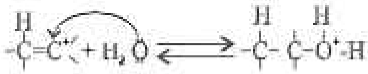
Mechanism of hydration of ethene

The mechanism of the reaction involves the following three steps:

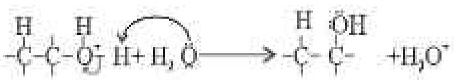
Step 1: Protonation of alkene to form carbocation by electrophilic attack of H_3O^+.

$H_2O + H^+ \longrightarrow H_3O^+$

Step 2: Nucleophilic attack of water on carbocation.

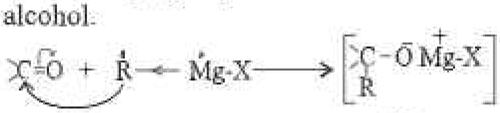


Step 3: Deprotonation to form an alcohol.

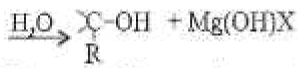


b) Reaction of Grignard reagent

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



Adduct ...(i)



...(ii)

The overall reactions using different aldehydes and ketones in dry ether medium are as follows:

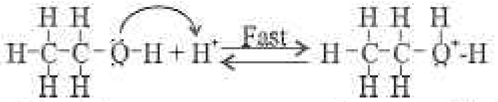
$$HCHO + RMgX \xrightarrow[\text{ether}]{\text{dry}} RCH_2\overset{-}{O}\overset{+}{M}gX \xrightarrow{H_2O} \underset{1^\circ \text{ alcohol}}{RCH_2OH} + Mg(OH)X$$

$$RCOR + R'MgX \longrightarrow R\text{-}\overset{R'}{\overset{|}{C}}H\text{-}\overset{-}{O}\overset{+}{M}gX \longrightarrow \underset{2^\circ \text{ alcohol}}{R\text{-}\overset{R'}{\overset{|}{C}}H\text{-}OH} + Mg(OH)X$$

$$RCOR + R'MgX \longrightarrow R\text{-}\underset{R}{\underset{|}{\overset{R'}{\overset{|}{C}}}}\text{-}\overset{-}{O}\overset{+}{M}gX \xrightarrow{H_2O} \underset{3^\circ \text{ alcohol}}{R\text{-}\underset{R}{\underset{|}{\overset{R'}{\overset{|}{C}}}}\text{-}OH} + Mg(OH)X$$

c) **Dehydration of Alcohols (Mechanism)**

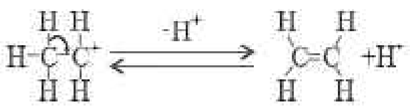
Step 1: Formation of protonated alcohol.



Ethanol — Protonated alcohol (Ethyl oxonium ion)

Step 2: Formation of carbocation: It is the slowest step and hence, the rate determining step of the reaction.

Step 3: Formation of ethene by elimination of a proton.



The acid used in step 1 is released in step 3. To drive the equilibrium to the right, ethene is removed as it is formed.

d) **Dehydration of alcohol at 413K to form Ether : Mechanism**

The formation of ether is a nucleophilic bimolecular reaction (S_N2) involving the attack of alcohol molecule on a protonated alcohol, as indicated below:

(i) $CH_3\text{-}CH_2\text{-}\ddot{O}\text{-}H + H^+ \rightarrow CH_3\text{-}CH_2\text{-}\underset{H}{\overset{+}{\ddot{O}}}\text{-}H$

(ii) $CH_3CH_2\text{-}\underset{H}{\ddot{O}}: + CH_3\text{-}CH_2\text{-}\overset{+}{O}{}^{H}_{H} \rightarrow CH_3CH_2\text{-}\underset{H}{\overset{+}{O}}\text{-}CH_2CH_3 + H_2O$

(iii) $CH_3CH_2\text{-}\underset{H}{\overset{+}{O}}\text{-}CH_2CH_3 \rightarrow CH_3CH_2\text{-}O\text{-}CH_2CH_3 + H^+$

Acidic dehydration of alcohols at 443 K to give an alkene is also associated with substitution reaction to give an ether.

c) Reaction of ethers with HI: (Mechanism)

The reaction of an ether with concentrated HI starts with with protonation of ether molecule.

Step 1:

$$CH_3-\ddot{O}-CH_2CH_3 + H-I \rightleftharpoons CH_3-\overset{\oplus}{\underset{|}{O}}-CH_2CH_3 \quad \underset{}{H}$$

Step 2:

Iodide is a good nucleophile. It attacks the least substituted carbon of the oxonium ion formed in step 1 and displaces an alcohol molecule by S_N2 mechanism.

Thus, in the cleavage of mixed ethers with two different alkyl groups. The alcohol and alkyl iodide formed, depend on the nature of alkyl groups. When primary or secondary alkyl groups are present, it is the lower alkyl group that forms alkyl iodide (S_N2 reaction).

$$I^- + CH_3-\overset{\oplus}{\underset{H}{O}}-CH_2CH_3 \rightarrow \left[I \cdots CH_3 \cdots \underset{\oplus}{\overset{H}{O}} — CH_2CH_3 \right] \rightarrow CH_3-I + CH_3CH_2-OH$$

When HI is in excess and the reaction is carried out at high temperature, ethanol reacts with another molecule of HI and is converted to ethyl iodide.

Step 3:

$$CH_3CH_2-\ddot{O}-H + H-I \rightleftharpoons CH_3CH_2-\overset{H}{\overset{|}{O}}H + I^-$$

$$I^- + \overset{CH_3}{\overset{|}{C}H_2}-\overset{}{\underset{+}{O}}H_2 \rightarrow CH_3CH_2I + H_2O$$

OBJECTIVE TYPE QUESTIONS

I. MULTIPLE CHOICE QUESTIONS

1. Arrange the following compound in decreasing order of boiling point?

(i) Propan-1-ol

(ii) Butan-2-ol

(iii) Butan-1-ol

(iv) Pentan-1-ol

(a) i>iii>ii>iv (b) i>ii>iii>iv

(c) iv>iii>ii>i (d) iv>ii>iii>i

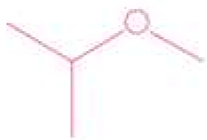
2. What is the correct order of reactivity of alcohols in the following reaction?

$$R-OH + HCl \xrightarrow{\text{Anhy. } ZnCl_2} R-Cl + H_2O$$

(a) 1°>2°>3° (b) 1°>3°>2°

(c) 3°>1°>2° (d) 3°>2°>1°

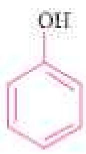
3. IUPAC name of the compound :



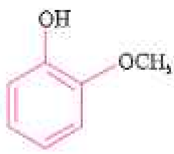
(a) 1-Methoxy-1-methylethane (b) 2-Methoxy-2-methylethane

(c) 2-Methoxypropane (d) Isopropylmethyl ether

4. The correct order of decreasing acid strength of the following compound is:

(i) 

(ii) 

(iii) 

(a) i>ii>iii (b) iii>ii>i

(c) ii>i>iii (d) ii>iii>i

5. The major product obtained on reaction of phenol with NaOH followed by CO_2 and acidification is:

(a) Benzoic acid (b) Salicylaldehyde

(c) Salicylic acid (d) Phthalic acid

6. Which of the following alcohol on dehydration with conc. H_2SO_4 gives but-2-ene?

(a) Butan- 1-ol (b) Butan-2-ol

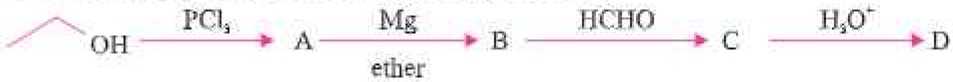
(c) 2-Methylpropan-l-ol (d) Both (a) and (b)

7. Which of the following alcohol give iodoform test?

(a) Butan-1-ol (b) Propan-1-ol

(c) Propan-2-ol (d) Pentan-3-one

8. In the following sequence of reaction. The product D is



(a) n-Butyl alcohol (b) n-Propyl alcohol

(c) Propanal (d) Butanal

9. Correct statement in case of n-butanol and t-Butanol is:

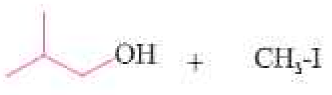
(a) both are having equal solubility in water

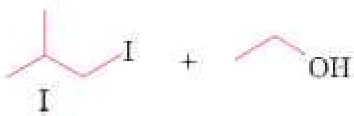
(b) 1-Butanol is more soluble in water

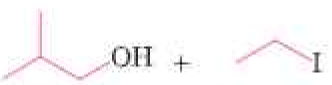
(c) boiling point of t-butanol is lower than n-butanol

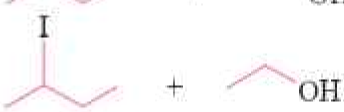
(d) boiling point of n-butanol is lower than t-butanol

10. The major products of following reaction are:

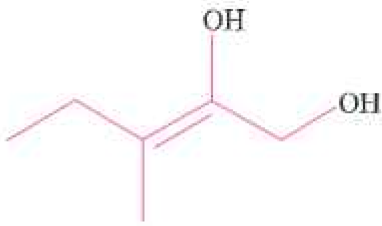
(a) 

(b) 

(c) 

(d) 

11. Write the IUPAC name of the compound given below.



(a) 3-Methylpent-2-ene-1,2-diol

(b) 2-Methylp ent-2-ene-1,2-diol

(c) 3-Methylpent-3-ene-2,3-diol

(d) 3-Methylpent-3-ene-4,5-diol

12. Which of the following are used to convert RCHO into RCH_2OH ?

(a) H_2/Pd (b) $LiAlH_4$

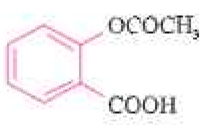
(c) $NaBH_4$ (d) All of the above

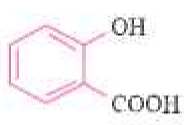
13. Monochlorination of toluene in sunlight followed by hydrolysis with aq. NaOH yields-

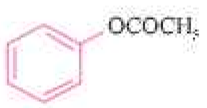
(a) *o*-cresol (b) *m*-cresol

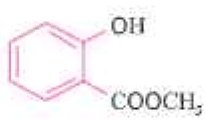
(c) 2,4-Dihydroxytoluene (d) Benzyl alcohol

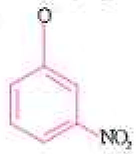
14. The product C in given reaction will be

(a) 

(b) 

(c) 

(d) 

15. Which of the following species can act as the strongest base?
   (a) ^{-}OH
   (b) ^{-}OR
   (c) $^{-}OC_6H_5$
   (d) 

16. CH_3CH_2OH can be converted into CH_3CHO by.........................
   (a) catalytic hydrogenation
   (b) treatment with $LiAlH_4$
   (c) treatment with pyridinium chlorochromate (PCC)
   (d) treatment with $KMnO_4$
17. Which of the following reactions will yield phenol?
   (a) Fusion of chlorobenzene with NaOH at 300 atm.
   (b) Diazotization of aniline followed by heating with water.
   (c) Sulphonation of benzene followed by treatment with NaOH then acidification.
   (d) All of the above
18. Williamson's synthesis is used to prepare
   (a) alcohol (b) ethers (c) Aldehydes (d) Amines
19. Which of the following compound will be most readily attacked by electrophile?
   (a) Chlorobenzene (b) Benzene (c) Phenol (d) Toluene

II FILL IN THE BLANKS

1. Phenol on reaction with bromine water gives white precipitate of........................
2. Ethanoic acid on reaction with $LiAlH_4$ forms........................
3. Reaction of........................with Grignard reagent gives primary alcohols.
4. Phenols are commercially manufactured by oxidation followed by acidification of........................
5. Reaction of alcohols/phenols with carboxylic acids is termed as........................
6. ....test is used to distinguish primary, secondary and tertiary alcohols.
7. Dehydration of tertiary alcohols is ....than primary alcohols.
8. Dehydration of alcohols to form ether is .... type reaction.
9. Benzyl alcohol on reaction with $KMnO_4$ followed by acidification forms...............
10. $SOCl_2$ converts Propan-1 -ol to ....

III ASSERTION REASON TYPE QUESTIONS

In the following questions a statement of Assertion followed by a statement of Reason is given. Choose the correct answer out of the following choices.

(A) Assertion and reason both are correct and reason is correct explation of assertion

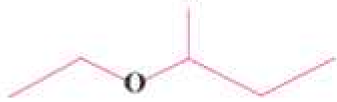
(B) Both assertion and reason are correct statement but reason is not correct explation of assertion.

(C) Assertion is correct statement but reason is wrong statement.

(D) Assertion is wrong statement but reason is correct statement.

1. **ASSERTION :** *p*-Nitrophenol is more acidic than phenol.
   REASON : Nitro group helps in the stabilization of the phenoxide ion by dispersal of negative charge due to resonance.

2. **ASSERTION :** IUPAC name of the compound is 2-Ethoxy-2-methylethane.

   REASON : In IUPAC nomenclature, ether is regarded as hydrocarbon derivative in which a hydrogen atom is replaced by -OR or -OAr group [where, R= alkyl group and Ar = aryl group].

3. **ASSERTION :** Bond angle in ethers is slightly less than the tetrahedral angle.
   REASON : There is a repulsion between the two bulky (-R) groups.

4. **ASSERTION :** *o*-Nitrophenol is less soluble in water than the –*m* and *p*-isomers.
   REASON: –*m* and *p*-Nitrophenols exist as associated molecule.

5. **ASSERTION :** Like bromination of benzene, bromination of phenol is also carried out in the presence of Lewis acid .
   REASON: Lewis acid polarises the bromine molecule.

6. **ASSERTION :** Ethanol is a weaker acid than phenol.
   REASON : Sodium ethoxide may be prepared by the reaction of ethanol with aqueous NaOH.

7. **ASSERTION :** Phenols give *o*-and *p*-Nitrophenol on nitration with dil. HNO_3.
   REASON : -OH group in phenol is o-, p- directing.

8. **ASSERTION :** $(CH_3)_3$ C- O-CH_3 gives $(CH_3)_3$ C-I and CH_3OH on treatment with HI.

   REASON : The reaction occur by SN' mechanism

9. **ASSERTION :** Protonation of phenol is difficult than ethanol.

   REASON : Ethyl group in ethanol is electron releasing.

10. **ASSERTION :** Tertiary alcohols gives turbidity almost immediately on treatment with $ZnCl_2$ /HCl.

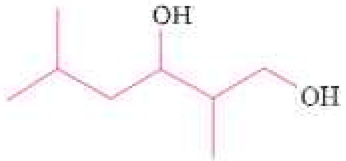
    REASON : Tertiary carbocation formed is very stable and undergoes substitution easily.

IV ONE WORD TYPE QUESTIONS

1. Which reagent used to convert primary alcohol to carboxylic acid?
2. Out of *ortho* and *para*- Nitrophenol which is more steam volatile?
3. Write the major product of bromination of anisole?
4. Give name reaction used to convert phenol to salicylaldehyde?
5. Out of picric acid and phenol, which is more acidic?
6. Which reagent could be used to reduce aldehyde selectively in presence of ester group?
7. Name the reagent(s) used to convert propene to propan-l-ol?
8. Out of primary, secondary and tertiary alcohols which is most acidic?
9. Write IUPAC of the product formed, when phenol is treated with conc. HNO_3 .
10. Draw structure of hex-1-en-3-ol.
11. Give a name of chemical test to distinguish between pentan-3-one and pentan-2-one.
12. _______ bonding is responsible for solubility of ethanol in water.
13. Name the product fromed when phenol is treated with $Na_2Cr_2O_7/H_2SO_4$
14. Write IUPAC name of aspirin.

VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)

1. Write IUPAC name of the following compound:



Ans: 2,5-Dimethylhexan-1,3-diol

2. How is phenol obtained from aniline ?

Ans:

3. Why phenol is acidic in nature ?

Ans: Due to stability of phenoxide ion by resonance

4. Among HI, HBr and HCl which is most reactive towards alcohols. Why?

Ans: Due to lowest bond dissociation enthalpy of HI, it is most reactive.

5. Name a compound which is used as antiseptic as well as disinfectant'.

Ans: Solution of phenol : 0.2% antiseptic, 2% disinfectant

6. What is nitrating mixture for monosubstitution of phenol?

Ans: Dilute HNO_3

7. Arrange the following in decreasing order of their acidic character:

(a) 

(b) 

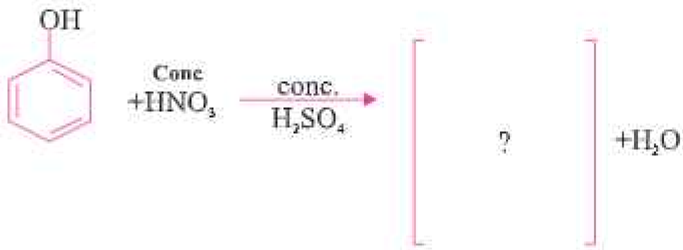
(c) 

Ans: (c) > (b) > (a)

8. Why lower alcohols are soluble in water while higher alcohols are not?

Ans: Due to formation of hydrogen bonds, lower alcohols are soluble but increase in hydrophobic chain decreases solubility.

9. Complete the following reaction :



Ans:

10. What happens when CH_3CH_2OH heated with red P and HI ?

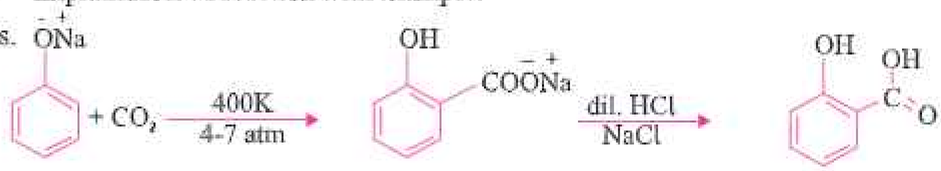
Ans:.

11. Ethanol has higher boiling point than Methoxymethane. Give reason.

Ans : Because of intermolecular H- bonding in ethanol.

12. Explain Kolbe's reaction with example.

Ans.

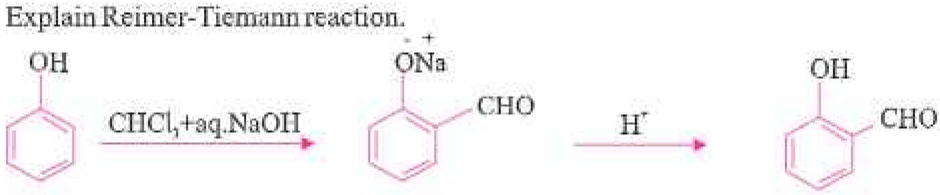


13. How could you convert ethanol to ethene ?

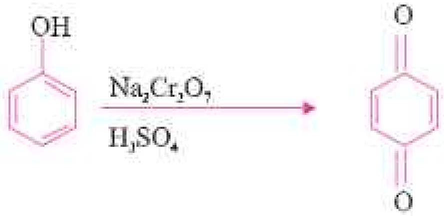
Ans .

14. Explain Reimer-Tiemann reaction.

Ans.



15. How will you get benzoquinone from phenol?

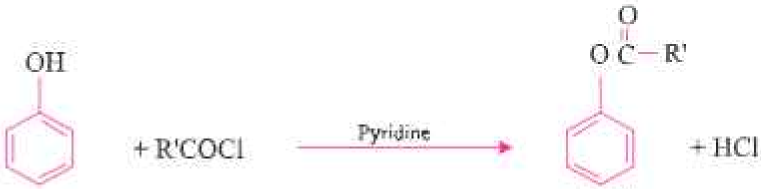
Ans. 

16. Predict the major product of acid catalysed dehydration of 1-Methylcyclohexanol

Ans. 

Major

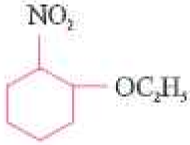
17. What is the significance of pyridine in following reaction.



Major

Ans. To remove HCl from product side and shift the reaction in forward direction.

18. Write the IUPAC name of



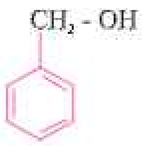
Ans: 1-Ethoxy-2-nitrocyclohexane.

19. How is acetone obtained from 2- bromopropane ?

Ans. $CH_3\text{-}\underset{\displaystyle Br}{\underset{|}{CH}}\text{-}CH_3 + KOH(aq) \longrightarrow CH_3\text{-}\underset{\displaystyle OH}{\underset{|}{CH}}\text{-}CH_3 \xrightarrow[573K]{Cu} CH_3\text{-}\overset{\displaystyle O}{\overset{||}{C}}\text{-}CH_3$

20. Which alcohol contain the -OH group attach to a sp^3 hybridised carbon atom next to an aromatic ring.

Ans. Benzyl alcohol



21. Which chemical is used as wood spirit ?

Ans. Methanol CH_3OH

22. Why boiling point of ethers are much lower than those of alcohols of comparable molecular masses.

Ans. There is no H-bonding in ethers which is present in alcohol.

23. Which test is used to distinguish between phenol and benzyl Alcohol.

Ans. Neutral $FeCl_3$

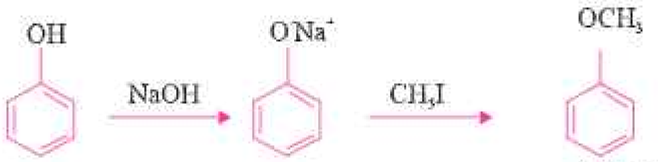
Phenol gives violet colour with aq. $FeCl_3$ while benzyl alcohol does not.

24. Why does phenol not undergo protonation easily.

Ans. In phenol, there is positive charge, in its resonation structure, therefore does not undego protonation.

25. Write the steps involved in conversion of phenol to anisole.

Ans.



Anisole

SHORT ANSWER TYPE QUESTIONS (2 or 3 Marks)

1. Out of t-Butyl alcohol and n-Butanol, which one will undergo acid catalysed dehydration faster and why?

Ans: t-Butyl alcohol will undergo dehydration faster due to formation of stable tertiary carbocation intermediate.

2. Carry out the following conversions:
   (a) Phenol to salicaldehyde
   (b) t-Butylchloride to t-butyl ethyl ether
   (c) Propene to propan-l-ol

3. Write the steps involved in the mechanism for the formation of ethanol from ethene.

Ans. Refer Points to remember

4. Predict the reagent for carrying out the following conversions:

   (a) Phenol to benzoquinone

   (b) Anisole to *p*-bromoanisole

   (c) Phenol to 2,4,6-tribromophenol

Ans. (a) $Na_2Cr_2O_7/H^+$ (b) Br_2/CH_3COOH (c) Br_2/H_2O

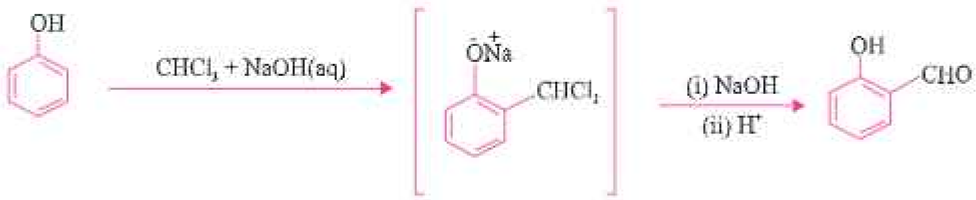
5. Write one chemical reaction to illustrate the following:

   (a) Reimer-Tiemann reaction

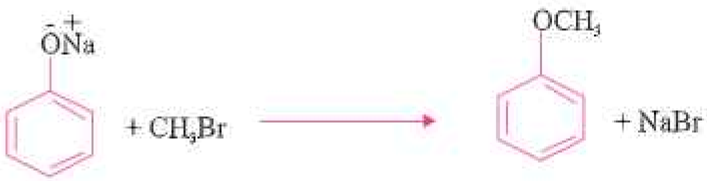
   (b) Williamson synthesis

Ans:

(a)

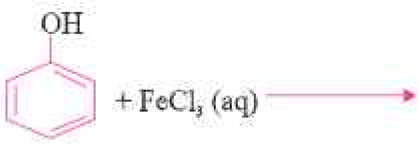


(b)

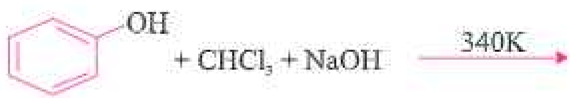


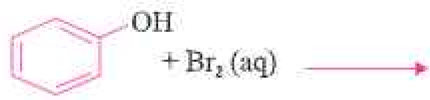
6. Complete the following the equations and name the products:

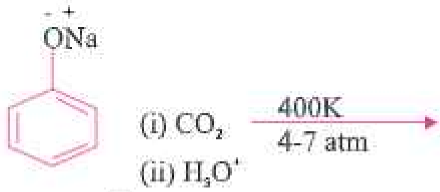
(i)



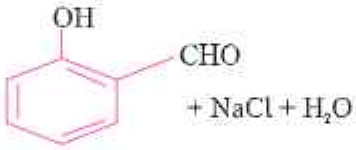
(ii)

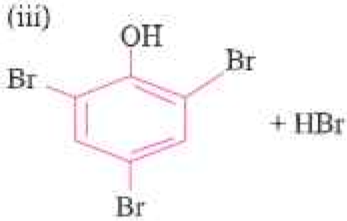


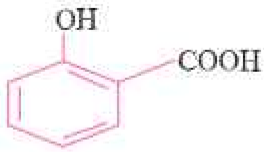
(iii) 

(iv) 

Ans: (i) $[Fe(C_6H_5O)_6]^{3-} + HCl$

(ii) 

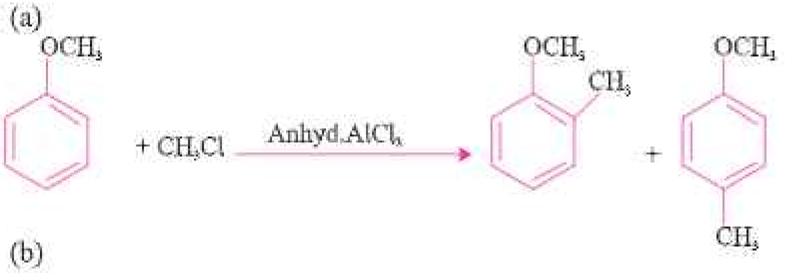
(iii) 

(iv) 

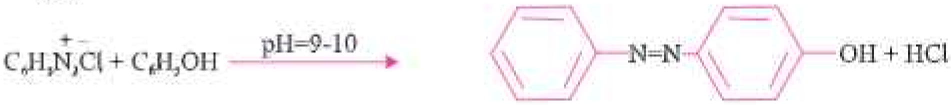
7. Write an example for the following name reactions :

(a) Friedel-Crafts alkylation of anisole (b) Coupling reaction

Ans: (a)



(b)



8. Account for the following:

   (a) Phenol has a smaller dipole moment than methanol.

   (b) Phenol undergoes electrophilic substitution reactions faster than benzene.

Ans: (a) Due to delocalization of electrons of oxygen in phenol.

   (b) Due to +R effect of -OH group in phenol which activates phenyl nucleus by increasing electron density as compared to benzene.

9. Give one reaction of alcohol involving cleavage of :

   (a) C-O bond (b) O-H bond

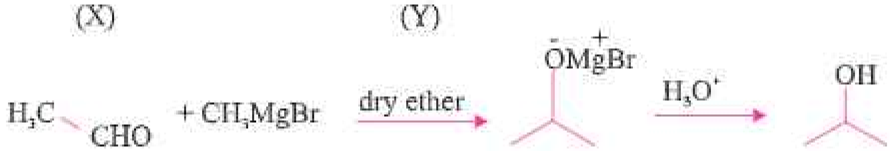
Ans: (a)

(b)

10. Ethereal solution of an organic compound 'X' when heated with Mg gave 'Y' which on treatment with CH_3CHO followed by acid hydrolysis gave 2-Propanol. Identify the compound 'X'. What is 'Y' known as ?

Ans:

$$\underset{(X)}{CH_3Br + Mg} \xrightarrow{\text{dry ether}} \underset{(Y)}{CH_3MgBr}$$



11. Phenol is more acidic than alcohol: Give reason.

Ans: Due to resonance stabilised phenoxide ion.

12. While separating a mixture of *o*- and *p*-nitrophenols by steam distillation, name the isomer which is steam volatile? Give reasons.

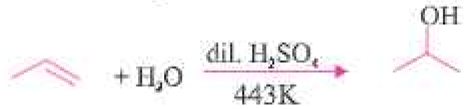
Ans: *o*-Nitrophenol is steam volatile because it is not stabilized by intermolecular hydrogen bonding.

13. Write the reactions and conditions involved in the conversion of:

(a) Propene to propan-2-ol

(b) Phenol to salicylic acid

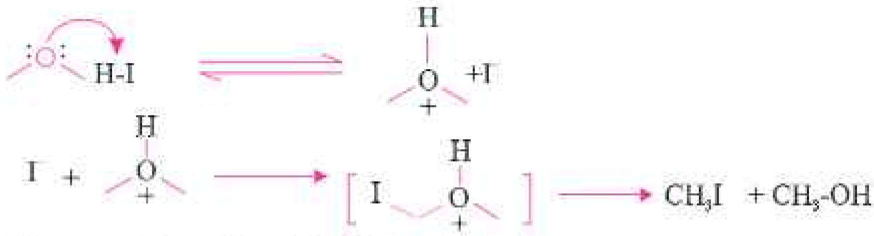
Ans:

(a) 

(b) 

14. Write the chemical reaction of HI with Methoxymethane.

Ans:



15. Ethers are relatively inert. Justify

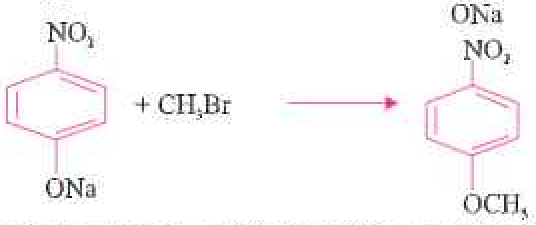
Ans: Due to absence of any active site in their molecules, divalent oxygen is linked to carbon atoms on both sides (C-O-C).

16. How will you distinguish between CH_3OH and C_2H_5OH?

Ans: $C_2H_5OH + 4I_2 + 3Na_2CO_3 \xrightarrow{heat} CH_3I + HCOONa + 5NaI + 2H_2O + 3CO_2$

17. Which of the following is an appropriate set of reactants for the preparation of 1-Methoxy-4-nitrobenzene and why?

Ans: (i)  (ii) 

(ii) 

Haloarene undergoes nucleophilic substitution reactions in drastic conditions hence correct option is (i).

18. Arrange in order of boiling points :

(a) C_2H_5-O-C_2H_5, C_4H_9COOH, C_4H_9OH

(b) C_3H_7CHO, $CH_3COC_2H_5$, $C_2H_5COOCH_3$, $(CH_3CO)_2O$

Ans: (a) $C_4H_9COOH > C_4H_9OH > C_2H_5$-O-$C_2H_5$

(b) $(CH_3CO)_2O > C_2H_5COOCH_3 > CH_3COC_2H_5 > C_3H_7CHO$

19. Describe the following reactions with examples :

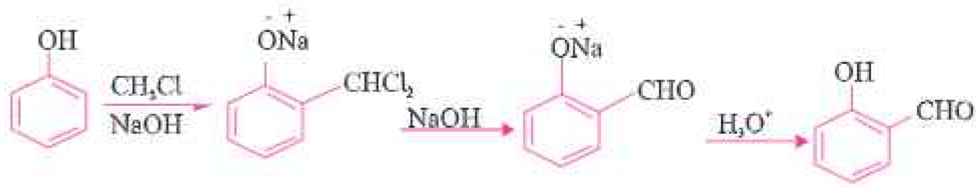
(a) Reimer-Tiemann reaction

(b) Kolbe's reaction

(c) Friedel Crafts acylation of anisole

Ans:

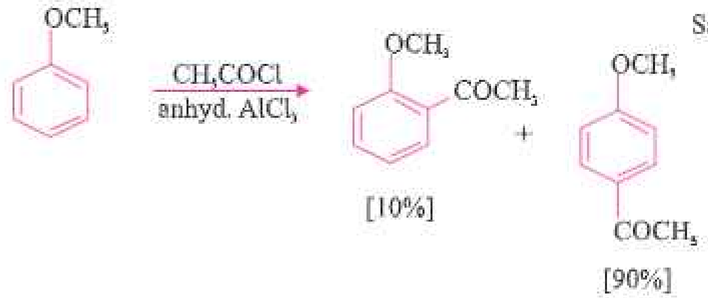
(a)



(b)

Salicylic acid

(c)

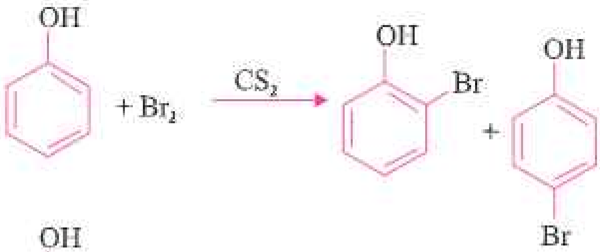


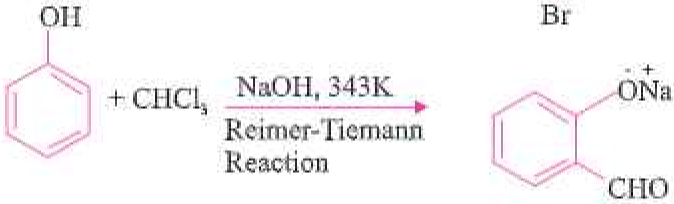
20. Give equations of the following reactions:

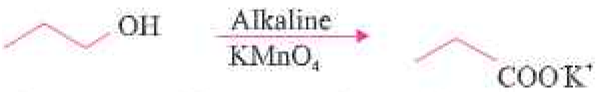
(a) Bromine in CS_2 with phenol

(b) Treating phenol with chloroform in presence of aqueous NaOH

(c) Oxidation of propan-1-ol with alkaline $KMnO_4$ solution.

(a) 

(b) 

(c) 

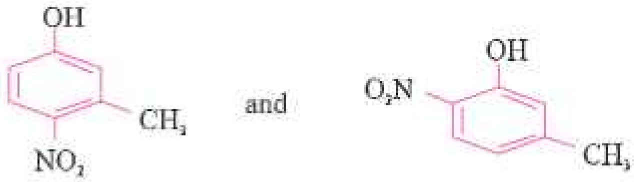
21. Write the structure of the major products of the following:

(a) Mononitration of 3-Methylphenol

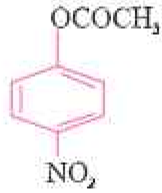
(b) Dinitration of 3-Methylphenol

(c) Mononitration of phenyl ethanoate

Ans : -OH and $-CH_3$ are *o*-and *p*-directing groups. The products are:

(a) 

(b) 

(c) 

22. Dehydration of alcohols to form an alkene is always carried out with conc. H_2SO_4 and not with conc. HCl or HNO_3. Explain.

Ans: In acidic medium alcohols are protonated then loses H_2O to form a carbocation. If HCl is used which is strong nucleophile causes nucleophilic substitution and HNO_3 causes oxidation.

23. Name the reagents which arc used in the following conversions:

(a) Primary alcohol to an aldehyde

(b) Butan-2-one to Butan-2-ol

(c) Phenol to 2,4,6-Trinitrophenol

Ans: (i) PCC, a complex of chromium trioxide with pyridine and HCl.

(ii) $NaBH_4$, sodium borohydride

(iii) Conc $HNO_3 + H_2SO_4$

24. Write major products of following reactions:

(i)  CHO $\xrightarrow{H_2/Pd}$

(ii)  OH $\xrightarrow{PCC}$

(iii)  $\xrightarrow[\text{(ii) } H_2O_2/OH^-]{\text{(i) } B_2H_6}$

(iv) $C_6H_5OH \xrightarrow[\text{(ii) } CO_2,\ H^+]{\text{(i) aq. NaOH}}$

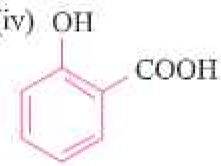
(v) $CH_2Br\text{-}CH_2Br \xrightarrow{\text{KOH (aq)}}$

(vi) $C_6H_5NH_2 \xrightarrow[\text{(ii) 0-5°C}]{\text{(i) } NaNO_2/HCl}$

Ans: (i) $CH_3CH_2CH_2CH_2OH$

(ii) $CH_3CH=CHCHO$

(iii) $CH_3CH_2CH_2OH$

(iv) 

(v) CH_2OH-CH_2OH

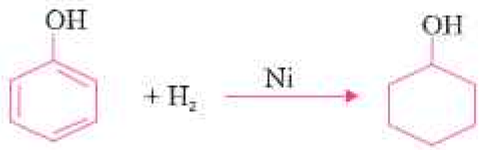
(vi) CH_3CH_2OH

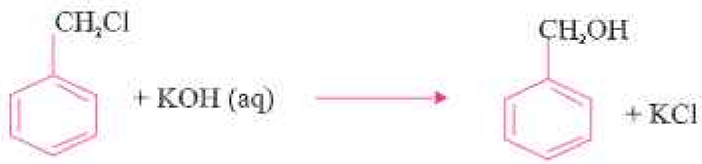
25. How will you carry out following conversion :

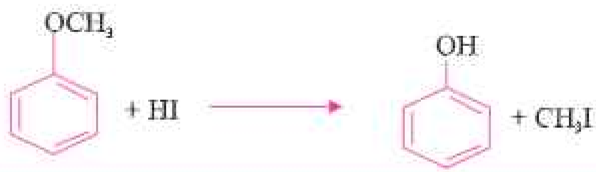
(a) Phenol to Cyclohexanol

(b) Benzyl chloride to Benzyl alcohol

(c) Anisole to phenol

Ans: (a) 

(b) 

(c) 

LONG ANSWER TYPE QUESTIONS (5 Marks)

1. An alcohol 'A' ($C_4H_{10}O$) on oxidation with acidified $K_2Cr_2O_7$ gives carboxylic acid 'B' ($C_4H_8O_2$). Compound 'A' when dehydrated with conc. H_2SO_4 at 443K gives compound 'C' with aqueous H_2SO_4. 'C' gives compound 'D' ($C_4H_{10}O$) which is an isomer of 'A'. Compound 'D' is resistant to oxidation but compound 'A' can be easily oxidised. Identify A, B, C and D and write their structure.

Ans: A: $(CH_3)_2CHCH_2OH$ C: $(CH_3)_2C{=}CH_2$

B: $CH_3CH(CH_3)COOH$ D: $(CH_3)_3C\text{-}OH$

2. An ether 'A' ($C_5H_{12}O$) when heated with excess of hot conc. HI produced two alkyl halides which on hydrolysis form compound 'B' and 'C'. Oxidation of B gives an acid 'D' whereas oxidation of 'C' gave a ketone 'E'. Deduce the structure of A, B, C, D and E.

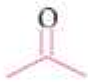
Ans:

A. 

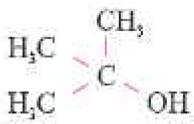
B. 

C. 

D. $CH_3\text{-}COOH$

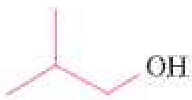
E. 

3. a) Which of the following compounds gives fastest reaction with HBr and why?

(i) 

(ii) 

(iii) 

(iv) 

Ans: (i) $(CH_3)_3C\text{-}OH$

Due to formation more stable of carbocation

b) Convert the following:

(i) Toluene from Phenol

(ii) Phenol from Aniline.

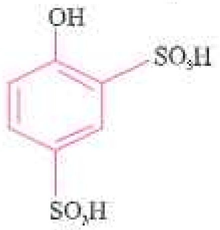
Ans. (i)

(i) 

(ii) 

4. Phenol, C_6H_5OH when reacts with concentrated sulphuric acid, forms 'Y'. The compound, 'Y' is reacted with concentrated nitric acid to form 'Z'. Identify 'Y' and 'Z' Explain why phenol is not converted commercially to 'Z' by reacting it with conc. HNO_3

Ans:



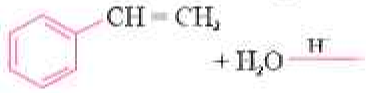
(Y)

(Picric acid)

(Z)

Reason: Picric acid yield is very poor.

5. Write the strucutre of the main product in the following reactions:

(i) 

(ii) 

(iii) 

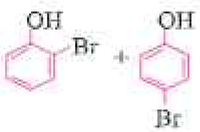
(iv) 

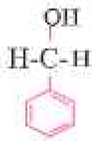
(v) 

Ans. (i) $C_6H_5\text{-}\underset{}{\overset{OH}{\overset{|}{C}}}H\text{-}CH_3$

(ii) 

(iii) 

(iv) 

(v) 

6. An organic compound 'A' (C_2H_6O) reacts with sodium to form a compound 'B' with the evolution of H_2. 'A' gives a yellow compound 'C' on reacting with Iodine and NaOH. When heated with conc. H_2SO_4 form 'D' which on reaction with conc. HI at 373 K gives compound 'E'. The compound 'D' is also obtained when 'B' is heated with 'E'. Identify A, B, C, D, E. Write the equation for the reactions involved.

Ans. A-CH_3CH_2OH

$$\underset{\text{'A'}}{CH_3CH_2OH} \xrightarrow{Na} \underset{(B)}{CH_3CH_2O^-Na^+ + H_2}$$

$$\underset{\text{'A'}}{CH_3CH_2OH} \xrightarrow[413\ K]{Conc\ H_2SO_4} \underset{(D)}{CH_3CH_2\text{-}O\text{-}CH_2\text{-}CH_3} \xrightarrow{HI} \underset{(E)}{CH_3CH_2I}$$

$$\underset{\text{'A'}}{CH_3CH_2OH} \xrightarrow{I_2/NaOH} \underset{(C)}{CHI_3}$$

7. Two compounds [A] and [B] have molecular formula C_2H_6O on reacting with HI, [A] gives alkyl iodide and water while [B] give alkyl iodide and alcohol. Identify compounds [A] and [B] write the reaction involved.

Ans. A-$C_2H_5OH + HI \longrightarrow C_2H_5I$

B- $CH_3OCH_3 + HI \longrightarrow CH_3I + CH_3OH$

8. A compound [A]$C_4H_{10}O$ is found to be soluble in sulpheric acid. [A] does not react with Na or $KMnO_4$. On heating with excess of HI, it is converted into single alkyl halide. Identify compound [A]

Ans. [A]- $CH_3CH_2O\text{-}CH_2CH_3 + HI \longrightarrow 2\ CH_3CH_2I$

9. (a) Write the chemical equation for the following reaction

(i) Friedel-Craft alkylation in anisole

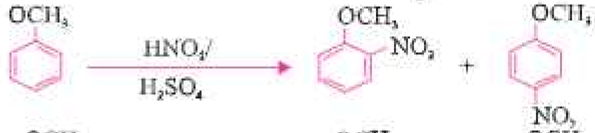
(ii) Nitration of anisole

(iii) Bromination of anisole in ethanolic medium

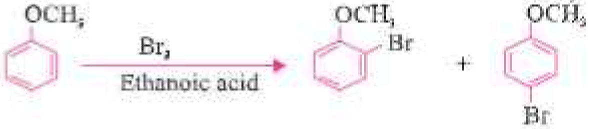
(b) Explain alkyl aryl ether directs the incoming substituents towards ortho and para position in the ring

Ans. (a) (i)

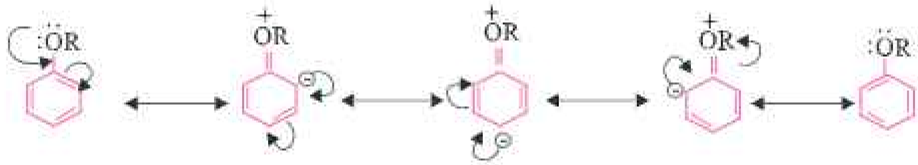
(ii)



(iii)



(b) Due to resonane



10. (i) Write the chemical test to distinguish between following pairs of compounds

(a)Ethanol and Propan-2-ol

(b) Butan-1-ol and Phenol

(c) Propan-2-ol and pentan-3-ol

(d)Phenol and Anisole

(ii) Write reagent(s) to carry out following conversions:

(a) Dehydrogeration of ethanol to ethanal

(b) Phenol to Benzene

Ans. (i) (a) Lucas Test (anhy $ZnCl_2$ + HCl)

(b) aq. $FeCl_3$ solution

(c) Iodoform test

(c) Neutral $FeCl_3$ solution

(d) Neutral $FeCl_3$ test

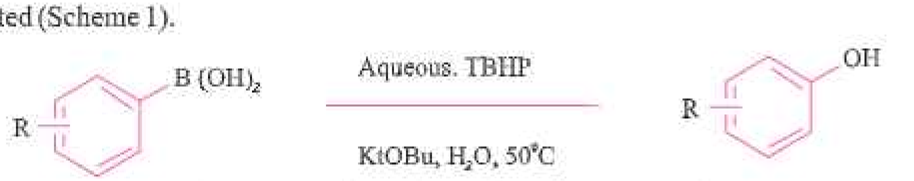
(ii) (a) Cu/573K

(b) zinc dust

CASE-STUDY BASED QUESTIONS

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

In the past few decades, phenols have received great attention in modern synthetic chemistry since ever Runge and Laurent made the first discovery in 1834 and 1841, respectively with regard to this motif, which is frequently found in natural products, flavonoids and pharmaceutically important compounds associated with certain bioactivities, such as antibacterial, antifungal, antibiotic, anti-inflammatory, antiviral, anxiolytic and antioxidant activities. Conventional methods for the large-scale synthesis of phenols include the Hock process, diazotization of aromatic amines and nucleophilic substitution reactions. Academicians have focused on the development of alternative approaches, for example, C-H activation of arenes and oxidation of C-Si bonds and C-halo bonds. Recently, the direct hydroxylation of aryl boronic acids to phenols has gained a lot of attention. In this context, a variety of oxidative methods employing metal catalysts, $Cu(OAc)_2$-H_2O_2, $CuSO_4$-phenanthroline, $CuCl_2$-miceller systems, Cu_2O-NH_3, $[Ru(bpy)_3Cl_2]$-$6H_2O$, Al_2O_3-H_2O_2, and H_3BO_3-H_2O_2 has been developed. On the other hand, the metal-free oxidative process are also competitive, Oxone, nBu_4NHSO_5, NH_2OH, H_2O_2-poly(N-vinylpyrrolidone), I_2-H_2O_2, Amberlite IR-120-H_2O_2, N-oxides, MCPBA, $NaClO_2$, photoredox catalysis, electrochemical oxidation, $(NH_4)_2S_2O_8$, PEG-400-H_2O_2, WERSA-H_2O_2, WEBPA-H_2O_2, nanoparticles of Ag, Cu_2O, and Fe_2O_3/silica gel and TBHP/Cl_3CCN. Despite these efficient oxidative processes, developing a new methodology free from metal oxidants and organic solvents is highly desirable. As part of our research interest involving metal-free oxidation reactions herein, a new protocol for the direct hydroxylation of aryl boronic acids with TBHP in the aqueous medium is reported (Scheme 1).



Scheme 1: Hydroxylation of aryl boronic acids.

Reference : Tanveer MahmadAlli Shaikh, **Synthesis of Phenols via Metal-Free Hydroxylation of Aryl Boronic Acids with Aqueous TBHP**, *Journal of Chemistry*, vol. **2020**, Article ID 1543081, 7 pages, 2020. https://doi.org/10.1155/2020/1543081

(A) Which of the following method of preparation of phenols is least likely to take place at 298K?

(i) Nucleophilic substitution in chlorobenzene

(ii) Reaction of diazonium salt with water.

(iii) Oxidation followed by acidification of cumene

(iv) Reaction of benzene sulphonic acid with NaOH followed by acidification

(B) In which of the following haloarene, nucleophilic substitution will be fastest to yield corresponding phenol?

(i) Chlorobenzene

(ii) *p*-Chloronitrobenzene

(iii) *p*-Cholrotoluene

(iv) *p*-Chloroanisole

(C) Aniline on reaction with $NaNO_2$ + HCl forms (X). (X) converts to (Y) on reaction with KI. (X) and (Y) are respectively-

(i) Benzene diazonium chloride, iodobenzene

(ii) Iodobenzene, Ethoxybenzene

(iii) Iodobenzene, Benzene

(iv) Benzene diazonium chloride, Phenol

(D) Phenols on reaction with bromine water forms-

(i) Colourless, 2-Bromophenol

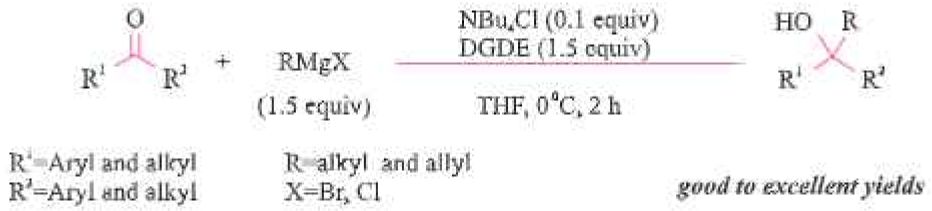
(ii) Dark coloured mixture of 2-Bromophenol and 4-Bromophenol

(iii) White precipitate of 2,4,6-Tribromophenol

(iv) Yellow colouration of 2,4-Dibromophenol

2. **Read the passage and answer the following questions:**

On the basis of the investigation of the combinational effect of quaternary ammonium salts and organic bases, an added-metal-free catalytic system for nucleophilic addition reactions of a variety of Grignard reagents to diverse ketones in the solvent has been developed to produce tertiary alcohols in good to excellent yields. By using tetrabutylammonium chloride (NBu_4Cl) as a catalyst and diglyme (DGDE) as an additive, this system strongly enhances the efficiency of



addition at the expense of enolization and reduction. NBu_4Cl should help to shift the Schlenk equilibrium of Grignard reagents to the side of dimeric Grignard reagents to favor the additions of Grignard reagents to ketones via a favored six-membered transition state to form the desired tertiary alcohols, and DGDE should increase the nucleophilic reactivities of Grignard reagents by coordination. This catalytic system has been applied in the efficient synthesis of Citalopram, an effective U.S. FDA-approved antidepressant, and a recyclable version of this catalytic synthesis has also been devised.

Reference : Hua Zong, Huayin Huang, Junfeng Liu, Guangling Bian, and Ling Song **Added-Metal-Free Catalytic Nucleophilic Addition of Grignard Reagents to Ketones** *J. Org. Chem.* **2012**, 77, 10, 4645-4652

(A) Which ketone and Grignard reagent can be used to form 2-methylbutan-2-ol ?

(B) Write structure and IUPAC name of product formed reaction of allyl magnesium bromide with acetophenone?

(C) Which reaction will take place at faster rate and why?

(i) Benzaldehyde + Propyl magnesium bromide

(ii) Propanal + Benzyl magnesium bromide

(D) Why Grignard reagent is stored under anhydrous conditions?

3. **Read the passage and answer the following questions:**

Phenols are compounds that possess a hydroxyl group directly attached to an aromatic, carbocyclic nucleus. Phenol is the trivial name for monohydroxybenzene. The *o*-, *m*-, and *p*-cresols are monohydroxytoluenes ($CH_3.C_6H_4OH$) and are distinct in their properties and reactions from the isomeric side-chain hydroxy compound, benzyl alcohol ($C_6H_5.CH_2OH$), which is a typical aromatic alcohol. Simple monohydric phenols are either corrosive liquids or low melting solids. The dihydric and trihydric phenols are solids. The mono-hydroxy compounds are only slightly soluble in water but are miscible with organic solvents. Water solubility increases and solubility in organic solvents decreases with the introduction of additional hydroxyl groups. They are all characterized by, and distinguished from, the aliphatic or aromatic alcohols by their ready solubility in aqueous alkali. Phenols and the cresols are widely used as antiseptics and disinfectants; the cresols are contained in the wood preserving fluid, creosote. Many phenols have wide application in the industrial production of plastics, dyestuffs, insectides, selective weedkillers, and germicides.

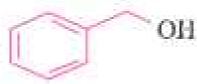
Reference : P.W.G. Smith, A.R. Tatchell, **Phenols**, *Aromatic Chemistry*, 1969

(A) Which of the following is not a phenol?

(a) 

(b) 

(c) 

(d) 

(B) Which of the following phenol has highest pK_a value?

(a) Phenol (b) p-Nitrophenol

(c) o-Nitrophenol (d) o-cresol

(C) Phenols may be characterized by the reaction with-

(a) $FeCl_3$ (b) Br_2 water

(c) $NaHCO_3$ (d) Both $FeCl_3$ and $NaHCO_3$

(D) Write IUPAC name of following phenol.

ANSWERS

I MULTIPLE CHOICE QUESTIONS

1. (c) 2. (d) 3. (c) 4. (c) 5. (c) 6. (d) 7. (d) 8. (b) 9. (c) 10. (c)
11. (a) 12. (d) 13. (d) 14. (a) 15. (b) 16. (c) 17. (d) 18. (b) 19. (c)

II FILL IN THE BLANKS

1. 2.4.6-Tribromophenol
2. Ethanol
3. Methanal
4. Cumene
5. Esterification
6. Lucas
7. Easier
8. S_N2
9. Benzoic acid
10. 1-Chloropropane

III ASSERTION REASON TYPE QUESTIONS

1. (A) 2. (D) 3. (D). 4. (C) 5. (D) 6. (C) 7. (A) 8. (A) 9. (B) 10. (A)

IV ONE WORD TYPE QUESTIONS

1. PCC
2. *ortho*-Nitrophenol
3. *para*-bromoanisole
4. Reimer-Tiemann reaction
5. Picric acid
6. $NaBH_4$
7. $B_2H_6/H_2O_2, OH^-$
8. Primary
9. 2,4,6-Trinitrophenol (Picric Acid)
10. $H_2\overset{1}{C}=\overset{2}{C}H-\underset{OH}{\overset{3}{C}H}-\overset{4}{C}H_2-\overset{5}{C}H_2-\overset{6}{C}H_3$
11. Iodoform Test
12. Intermolecular H-bond
13. Benzoquinone
14. 2-Acetoxybenzoic acid

CASE STUDY BASED QUESTIONS

1: (A) b (B) b (C) a (D) c

2: (A) CH_3COCH_3, C_2H_5MgCl

(B) $C_6H_5-\underset{CH_3}{\overset{OH}{\underset{|}{\overset{|}{C}}}}-CH_2-CH=CH_2$ IUPAC (i) 1-Methyl-1-phenyl but -3-ene-1-ol

(D) It react with water to form alkane R-Mgx+H-OH→R-H+Mg-X-OH

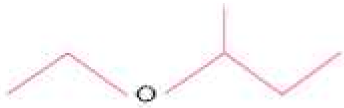
3: (A) d (B) d (C) a (D) 3-Ethyl-5-chlorophenol

UNIT TEST

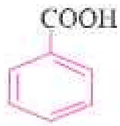
Alcohols, phenols and ethers

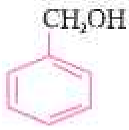
Maximum Marks : 20 **Time : 1 Hour**

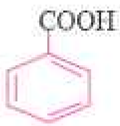
1. Write the IUPAC name of:



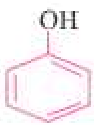
2. A and B in the following reaction are :

(a) A. 

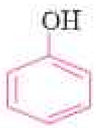
B. 

(b) A. 

B. 

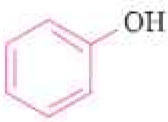
(c) A. 

B. 

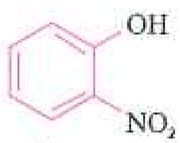
(d) A. 

B. 

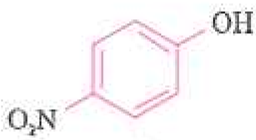
3. The correct order of acidic strength of following phenols is–



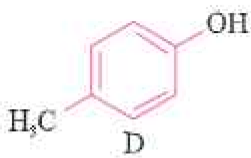
A



B



C



D

(a) A<B<C<D

(b) B<A<C<D

(c) D<A<B<C

(d) D<C<B<A

4. Identity the product: a

5. $(CH_3)_3C\text{-}OCH_3 + HI \rightarrow ?$

6. Give an example of following name reactions:

   (I) Kolbe's reaction

   (ii) Williamsons synthesis

7. Write the products formed by nitration of phenol . Which of the product has higher boiling point and why ?

8. Identify the product formed when ethanol is heated at 413 K. Write the mechanism of the reaction.

9. How will you convert ?

   (i) Ethanol into propan-2-ol

   (ii) Aniline into phenol

   (iii) Methanol into methoxyethane

10. Explain the following:

    (i) Alcohols are more soluble in water than ethers of comparable molar masses.

    (ii) t-Butyl chloride on heating with sodium methoxide gives 2- Methylpropene instead of t-Butylmethly ether.

    (iii) Reaction of phenol with bromine leads to formation of 2,4,6- tribromophenol

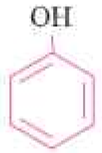
11. An Ether 'A' ($C_5H_{12}O$) when treated with excess of hot conc HI, produced two alkyl halides which on hydrolysis form 'B' and 'C'. Oxidation of 'B' forms an acid 'D', whereas oxidation of 'C' give a ketone 'E'. Identify A, B and C and reactions involved.

UNIT TEST-2

Alcohols, phenols and ethers

Maximum Marks : 20 **Time : 1 Hour**

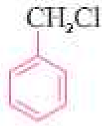
1. Write the IUPAC name of C_6H_5-CH_2-CH_2-OH
2. Out of t-Butyl alcohol and n-Butanol, which undergoes acid catalysed dehydration faster and why?
3. Write 'A' and 'B' in following reaction.



$\xrightarrow{Zn}$ 'A' $\xrightarrow[\text{Anhy } AlCl_3]{CH_3\text{-}Cl}$ 'B'

4. Name the reagent used for conversion of primary alcohol to an aldehyde.
5. Out of phenol and methanol, which one has smaller dipole moment
6. Write the mechanism of conversion of propan-1-ol into propene.
7. Explain Williamson synthesis and Riemerr – Tiemann Reaction
8. Complete the reaction.

(a)



+ KOH (aq) $\longrightarrow$

(b) C_6H_5-OH $\xrightarrow[\text{(ii) } CO_2,\ H^+]{\text{(i) aq.NaOH}}$

9. Convert the following
   (i) Phenol to picric acid
   (ii) Propan -2-ol to 2-methyl propan-2-ol
   (iii) Phenol to aspirin
10. Write the reason of following observations:
   (a) alcohols are generally soluble in water but alkyl halides are not.
   (b) Phenol exhibi acidic character.
   (c) *o*-nitrophenol is more steam volatile than *p*-nitrophenol
11. An ether 'A' ($C_5H_{12}O$) when heated with excess of hot conc HI produces two alkyl halides which on hydrolysis form compound 'B' and 'C'. Oxidation of 'B' gives an acid 'D' whereas oxidation of 'C' gives ketone 'E'. Write structures of A, B, C, D, E .

UNIT 12
Aldehydes, Ketones and Carboxylic Acids

Points to Remember

Nomenclature

Aldehydes and Ketones

Common names: replace -e from alkyl group by aldehyde or ketone e.g. CH_3-CHO is acetaldehyde

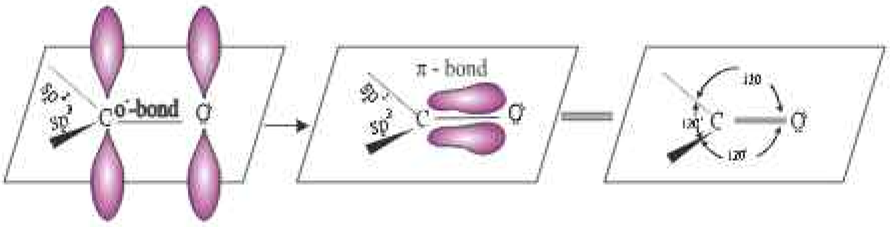
IUPAC names: replace -e by -al for aldehydes and - one for ketones e.g. CH_3-CHO is ethanal and CH_3-COCH_3 is propanone.

Carboxylic Acids

Common names: end with -ic acid e.g. CH_3CH_2COOH is propionic acid

IUPAC names: replace -e in corresponding alkanes by -oic acid e.g. CH_3CH_2COOH is propanoic acid.

Structure of Carbonyl group



Carbonyl carbon is sp^2 Hybridised and planar in shape, with one sigma and one π bond between C=O

General Methods:

(a) **Contolled oxidation/dehydrogenation of primary and secondary alcohols**

Primary alcohol gives aldehyde, secondary gives ketones, tertiary undergoes dehydration

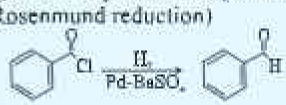
(b) **Hydration of Alkynes**

(c)Ozonolysis

Preparation of Aldehydes, Ketones and Carboxylic Acids

Aldehydes:

(a) **From acyl chloride** (acid chloride) (Rosenmund reduction)



(b) **From nitriles and esters**

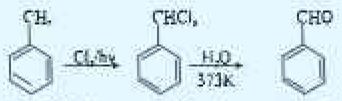
(Stephen reaction)

$R-C\equiv N+SnCl_2+HCl \rightarrow RCH=NH \xrightarrow{H_3O^+} R-CHO$

$RCH_2-CH=CH-CH \xrightarrow[\text{(ii) } H_2O]{\text{(i) DIBAL } (AlH(iBu)_2)} R-CH_2-CH-CH-CHO$

(c) **From hydrocarbons** (Etard Reaction)

(d) **(Side chain chlorination)**

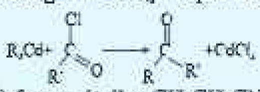


(e) **(Gatterman-Koch reaction)**

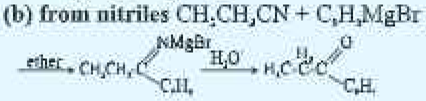
Ketones:

(a) **From acyl chlorides**

$2\ R-MgX + CdCl_2 \rightarrow R_2Cd+Mg(X)Cl$



(b) **from nitriles** $CH_3CH_2CN + C_6H_5MgBr$



(c) **From benzene (Friedel-craft acylation)**

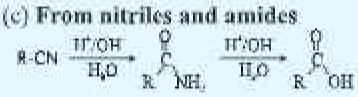
Carboxylic Acids:

(a) **From Primary alcohol/aldehyde**

$RCH_2OH \xrightarrow[H_2O]{\text{alkaline } KMnO_4} R-COOH$

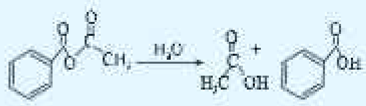
(b) **From alkylbenzene**

(c) **From nitriles and amides**



(d) **From Grignard reagent**

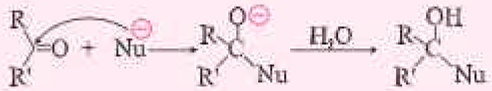
(e) **From acyl halides and anhydrides**



(f) **From esters**

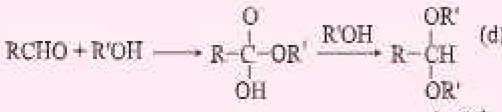
Reactions of Aldehydes, Ketones and Carboxylic Acids

Aldehyde and Ketones
Nucleophilic Addition reaction

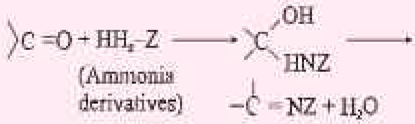


(a)  Cyanohydrin

(b) 

(c) 

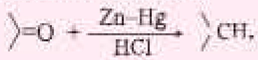
Acetal

(d) 

(Ammonia derivatives)

1. Reduction: Aldehydes and ketones converts to primary and secondary alcohols respectively in presence of $NaBH_4$ / $LiAlH_4$. $NaBH_4$ selectively reduces aldehydes and ketones only in presence of other carbonyl containing functional groups including carboxylic acids, esters etc.

   Clemmensen reduction:

   Wolf - Kishner Reduction:

2. Oxidation:

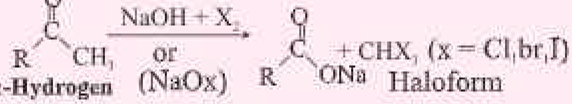
(a) Tollens' Test.

$$R\text{-}CHO + 2\,[Ag(NH_3)_2]^+ + OH^- \longrightarrow RCOO^- + 2\,Ag \text{ (silvery mirror)} + 2\,H_2O + 4\,NH_3$$

(b) Fehling's Test

$$R\text{-}CHO + 2\,Cu^{2+} + 5\,OH^- \longrightarrow R\text{-}COO^- + Cu_2O \text{ (Red ppt)} + 3\,H_2O$$

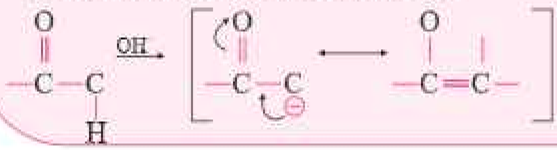
(c) Haloform reaction: given by methyl ketones 



Haloform

3. **Reaction due to α-Hydrogen**

Aldol condensation due to acidic a-Hydrogen



$$CH_3CHO \xrightarrow{\text{dil NaOH}} CH_3-\underset{OH}{\overset{H}{\underset{|}{\overset{|}{C}}}}-CH_2-CHO$$

β-hydroxy aldehyde

$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{\text{dil NaOH}} CH_3-\underset{OH}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$$

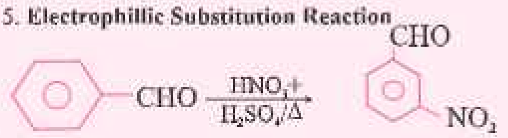
β-hydroxy ketone.

4. **Cannizzaro Reaction**

Aldehyde don't have α-Hydrogen

$$HCHO + HCHO \xrightarrow[\Delta]{\text{conc KOH}} CH_3-OH + HCOO^-K^+$$

5. **Electrophillic Substitution Reaction**



Carboxylic Acids

Acidic nature : $R\text{-}COOH + NaHCO_3 \rightarrow RCOONa + H_2O + CO_2$ (Brisk effervescence)

(Chemical test for carboxylic acid)

Formation of carboxylic acid derivatives:

$$ROOH \xrightarrow[H^+]{R'\text{-}OH} R\text{-}COOR' + H_2O$$

$$ROOH \xrightarrow[SOCl_2]{PCl_5/} R\text{-}COOCl + POCl_3/SO_2 + HCl$$

$$ROOH \xrightarrow{NH_3} R\text{-}COONH_4 \xrightarrow{\Delta} R-\overset{O}{\overset{\|}{C}}-NH_2$$

$$ROOH \xrightarrow[LiAlH_4]{B_2H_6/} R\text{-}CH_2\text{-}OH$$

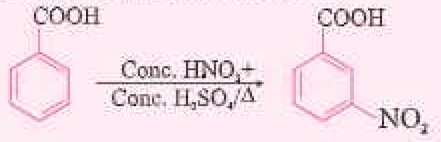
$$R\text{-}COOH \xrightarrow[NaHCO_3]{NaOH/} R\text{-}COONa \xrightarrow[\Delta]{CaO+NaOH} R\text{-}H + Na_2CO_3$$

This reaction is useful in redcing the size of carbon chain

Hell-Volhard Zelinsky reaction: $R\text{-}CH_2\text{-}COOH \xrightarrow[\text{ii) } H_3O^+]{\text{i) } X_2/\text{ Red P}} R\text{-}\underset{X}{\overset{H}{C}}\text{-}COOH$

substitution takes place at α carbon

Electrophillic Substitution Reaction



OBJECTIVE TYPE QUESTIONS

I. MULTIPLE CHOICE QUESTIONS

1. Which product is formed when benzaldehyde is treated with concentrated KOH solution?

(a) 

(b) 

(c) 

(d) 

2. Structure of 'A' and type of isomerism in the above reaction are respectively-

(a) Prop-1-en-2-ol, metamerism
(b) Prop-1 -en-1-ol, tautomerism
(c) Prop-2-en-2-ol. geometrical
(d) Prop-1-en-2-ol, tautomerism

3. Compound A and C in the following reaction are:-

$$CH_3CHO \xrightarrow[\text{(ii) } H_2O]{\text{(i)}CH_3MgBr} A \xrightarrow{H_2SO_4} B \xrightarrow[\text{ii) } H_2O_2/OH]{\text{i) } B_2H_6} C$$

(a) Identical (b) Position isomer
(c) Functional group isomer (d) Optical isomer

4. $\text{Toluene} \xrightarrow{KMnO_4} A \xrightarrow{SOCl_2} B \xrightarrow[BaSO_4]{H_2/Pd} C$

the product 'C' is:-

(a) $C_6H_5CH_2OH$ (b) C_6H_5CHO

(c) C_6H_5COOH (d) $C_6H_5CH_3$

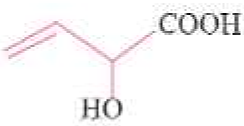
5. Among the following which has the lowest pk_a value:-

(a) CH_3COOH (b) $HCOOH$

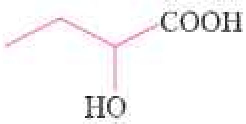
(c) $(CH_3)_2CHCOOH$ (d) CH_3CH_2OH

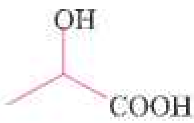
6. $CH_3CHO + HCHO \xrightarrow[\text{Heat}]{\text{dil.NaOH}} A \xrightarrow[H_2O]{HCN} B$

The structure of 'B' is:-

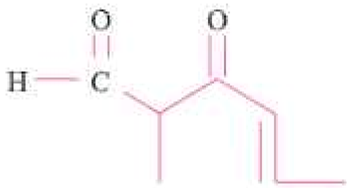
(a) 

(b) 

(c) 

(d) 

7. The IUPAC name of compound is:



(a) 2-Formylhex-2-ene-3-one

(b) 5-Methyl-4-oxohex-2-en-5-al

(c) 3-Keto-2-methylhex-5-enal

(d) 3-Keto-2-methylhex-4-enal

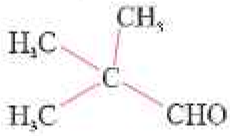
8. Which of the following reactions will not result in the formation of carbon-carbon bond?

(a) Cannizzaro reaction (b) Wurtz reaction

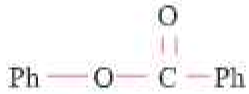
(c) Friedel Crafts reaction (d) Reimer-Tiemann reaction

9. Reduction of aldehydes and ketones into hydrocarbon using zinc amalgam and conc. HCl is called.................
   (a) Dow process (b) Cope reduction
   (c) Wolf-Kishner reduction (d) Clemmensons Reduction

10. Which of the following compound do not undergo aldol condensation?
   (a) CH_3CH_2CHO (b) CH_3CHO
   (c) CH_3COCH_3 (d)



11. The treatment of following compound with NaOH yields.............as major product.



   (i) Phenol (ii) Sodium phenoxide
   (iii) Sodium benzoate (iv) Benzophenone
   (a) I,II (b) III only
   (c) I,III (d) IV only

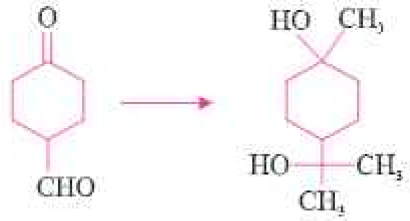
12. Which of the following will undergo Cannizzaro reaction?
   (a) Acetophenone (b) Propanone
   (c) 2,2-Dimethylpropanal
   (d) Both acetophenone and 2,2-Dimethylpropanal

13. Which of the following neither gives Fehling's test nor iodoform test?
   (a) Benzaldehyde (b) Ethanal
   (c) Propanone (d) Acetophenone

14. Which reagent(s) is/are best for following conversion?
   $CH_3\text{-}CH{=}CH\text{-}CN \rightarrow CH_3\text{-}CH{=}CH_2\text{-}CHO$
   (a) H_2, Pd-$BaSO_4$ (b) DiBAL-H
   (c) H_2/Ni (d) $NaBH_4$

15. Benzophenone can be obtained by the reaction of -
   (a) Benzoyl chloride + Benzene + anhy. $AlCl_3$
   (b) Benzoyl chloride + Diphenyl anion
   (c) Benzoyl chloride + Phenyl magnesium chloride
   (d) Benzene + carbon monoxide+$ZnCl_2$

16. Which of the following compounds will give butanone on oxidation with alkaline $KMnO_4$ solution?
    (a) Butan-l-ol
    (b) Butan-2-ol
    (c) Both of these
    (d) None of these
17. Reaction of alkene **X** with with O_3 followed by H_2O_2/ Zn forms propanone and ethanal. Alkene **X** is-
    (a) Pent-3-ene
    (b) Pent-2-ene
    (c) 2-Methylbut-2-ene
    (d) 2,2-Dimethylprop-1-ene
18. The correct sequence of the following conversion is



    (a) CH_3MgBr, $[Ag(NH_3)_2]^+OH$, H^+/CH_3OH
    (b) $[Ag(NH_3)_2]OH$, CH_3MgBr, H^+/CH_3OH
    (c) $[Ag(NH_3)_2]^+OH$, H^+/CH_3OH, CH_3MgBr
    (d) CH_3MgBr, H^+/CH_3OH, $[Ag(NH_3)_2]+OH$
19. When 2-hydroxybenzoic acid is distilled with zinc dust it gives
    (a) Phenol
    (b) Benzoic Acid
    (c) Benzaldehyde
    (d) A polymeric product
20. Tollen's reagent forms silvery mirror when it reacts with:
    (a) CH_3CHO
    (b) CH_3COOH
    (c) CH_3COCH_3
    (d) CH_3OH

II FILL IN THE BLANKS

1. Tollens' reagent is chemically known as ....
2. Reaction of phthalic acid with ammonia followed by strong heating gives................
3. Acetyl chloride may be converted into acetaldehyde by ....reduction.
4. Groups like nitro- and chloro- ....acidity of aromatic carboxylic acids.
5. Phenol and benzoic acid can be distinguished by the reaction with..........................
6. On reaction of propanal with Fehling's reagent red precipitate of .... is formed.
7. Reaction of Grignard reagent with ....results into formation of primary alcohols.
8. Lower aldehydes are soluble in water due to..........................interactions with water molecules.
9. DIBAL-H is used to reduce nitriles or esters to corresponding..........................
10. Reaction of ethyl magnesium bromide with carbon dioxide followed by acidification gives ....

III ASSERTION REASON TYPE QUESTIONS

The question given below consist of an Assertion and Reason. Use the following key to choose the appropriate answer.

(a) Assertion and reason both are correct and reason is the correct explanation of the assertion.

(b) Assertion and reason both are correct statements but reason is not correct explanation of assertion.

(c) Assertion is correct statement but reason is wrong statement.

(d) Assertion is wrong statement but reason is correct statement.

1. **ASSERTION:** Reaction of Pentanoic acid with Cl_2/ Red P followed by water gives 2-chloropentanoic acid.

   REASON: The substitution takes places at α-carbon.

2. **ASSERTION:** Carboxylic acids have higher boiling point than aldehydes and ketones of comparable molar masses.

   REASON: Due to strong intermolecular H-bonding in carboxylic acids.

3. **ASSERTION:** Nitration of benzoic acid gives *m*-nitrobenzoic acid.

   REASON: Carboxyl group increases electron density on ring.

4. **ASSERTION:** Benzaldehyde undergoes Cannizzaro reaction.

   REASON: It contains one α-hydrogen.

5. **ASSERTION :** Formaldehyde is a planar molecule.

   REASON : It contains sp^2 hybridised carbon atom.

6. **ASSERTION :** Compounds containing -CHO group are easily oxidised to corresponding carboxylic acids.

   REASON : Carboxylic acids can be reduced to alcohols by treatment with $LiAlH_4$.

7. **ASSERTION :** The α-hydrogen atom in carbonyl compounds is less acidic.

   REASON : The anion formed after the loss of α-hydrogen atom is resonance stabilised.

8. **ASSERTION :** Aromatic aldehydes and formaldehyde undergo Cannizaro reaction.

   REASON : Aromatic aldehydes are almost as reactive as formaldehyde.

9. **ASSERTION :** Aldehydes and ketones, both reacts with Tollens' reagent to form silvery mirror.

   REASON : Both, aldehydes and ketones contain a carbonyl group.

10. **ASSERTION:** Ketones are oxidised under drastic conditions.

    REASON: Oxidation of ketones gives carboxylic acids having carbons lesser than parent molecule.

IV ONE WORD ANSWER TYPE QUESTIONS

1. Name the product formed by addition of one equivalent of monohydric alcohol to aldehydes.
2. Name the product formed by the reaction of benzene with CO, HCl in presence of anhyd. $AlCl_3$
3. Which reagent is used to convert carboxylic acid to corresponding alcohol?
4. Which reaction is carried out to reduce the number of carbons from carboxylic acids?
5. Which ester will be formed by the reaction of methanol and propanoic acid?
6. Write the major product formed by the reaction of benzaldehyde and acetophenone.
7. Which reagent will be best to convert ketone to corresponding alcohol in presence of carboxylic acid?
8. Which reagent converts carboxylic acids into corresponding anhydrides?
9. Name the carboxylic acid formed by reaction of cyclohexene with $KMnO_4$-H_2SO_4 and heating.
10. Which out of each pair is expected to be stronger acid ?

    (a) CH_3COOH or $HCOOH$

    (b) $CH_2(Cl)COOH$ or $CH_2(Br)COOH$
11. Name the test which can be used to distinguish between pentan-2-one and pentan-3-one .
12. Predict the products when cyclohexancalbaldehyde reacts with zinc analgam and HCl.
13. Write the catalyst used in Rosenmund's reduction
14. Name the reagent used in following reaction

$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \longrightarrow CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-CH_3$$

15. Out of CH_3CHO and CH_3COCH_3 which one is more reactive towards HCN.

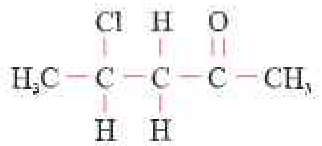
VERY SHORT ANSWER TYPE QUESTIONS (1 Marks)

1. Arrange the following compounds in increasing order of their acidic strengths:
   $(CH_3)_2CHCOOH$, $CH_3CH_2CH(Br)COOH$, $CH_3CH(Br)CH_2COOH$

Ans. $(CH_3)_2CHCOOH < CH_3CH(Br)CH_2COOH < CH_3CH_2CH(Br)COOH$

2. Draw the structure of the compound whose IUPAC name is 4-chloropentan-2-one.

Ans.



3. Which type of aldehyde can undergo Cannizzaro reaction?

Ans. Aromatic and aliphatic aldehydes which do not contain α-hydrogen.

4. Name the aldehyde which does not give Fehling's test.

Ans. Benzaldehyde.

5. Arrange the following in order of their increasing reactivity towards HCN:
   CH_3CHO, CH_3COCH_3, $HCHO$, $C_2H_5COCH_3$

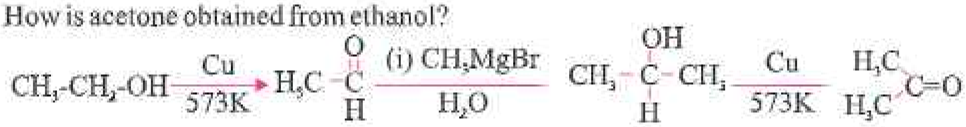
Ans. $C_2H_5COCH_3 < CH_3COCH_3 < CH_3CHO < HCHO$

6. Arrange the following compounds in increasing order of their boiling point:
   CH_3CHO, CH_3CH_2OH, CH_3OCH_3, $CH_3CH_2CH_3$

Ans. $CH_3CH_2CH_3 < CH_3OCH_3 < CH_3CHO < CH_3CH_2OH$

8. How is acetone obtained from ethanol?

Ans.



9. Why do aldehydes and ketones have lower boiling point than alcohols?

Ans. Due to presence of associated molecules with H-bonding in alcohols.

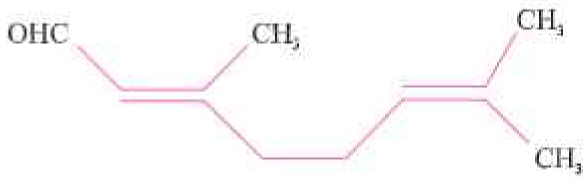
10. Write reaction between acetyl chloride and dimethyl cadmium.

Ans. $CH_3COCl + Cd[CH_3]_2 \xrightarrow[\text{ether}]{\text{dry}} H_3C-\underset{\underset{O}{\|}}{C}-CH_3 + CdCl_2$

11. What happens when CH_3CHO is treated with $K_2Cr_2O_7$ in presence of H_2SO_4?

Ans. $CH_3CHO \xrightarrow{K_2Cr_2O_7 + H_2SO_4} CH_3COOH$

12. Write IUPAC name of following compound:



Ans. 3,7-Dimethylocta-2,6-dien-1-al

13. Give balanced equation and name of products when CH_3COOH is treated with PCl_5?

Ans. $CH_3COOH + PCl_5 \rightarrow CH_3COCl + POCl_3 + HCl$

14. What product is obtained when ethyl benzene is oxidized with alkaline $KMnO_4$ followed by acidification.

Ans. Benzoic acid (C_6H_5COOH) is obtained.

15. CH_3CHO is more reactive than CH_3COCH_3 towards reaction with HCN. Give reason.

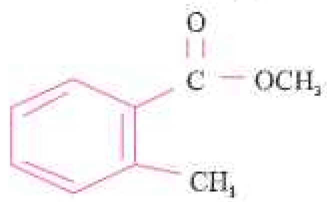
Ans. Due to presence of two $-CH_3$ group in CH_3COCH_3 which shows more +I effect and steric hindrance than CH_3CHO.

16. Write IUPAC names of the following compound:

$$HOOC - \overset{\overset{\displaystyle H}{|}}{C} = \overset{\overset{\displaystyle H}{|}}{C} - COOH$$

Ans. But-2-ene-1,4-dioic acid

17. Write the IUPAC name of following molecule:



Ans. 2-Methylmethylbenzoate

18. Why does benzoic acid does not undergo Friedel-Crafts reaction?

Ans. -COOH group in is an electron withdrawing group, which deactivates the benzene ring strongly and hence electrophilic substitution becomes difficult.

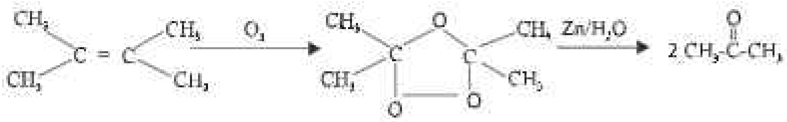
19. Benzaldehyde gives a positive test with Tollens' reagent but not with Fehling's and Benedict's solutions. Why?

Ans. It is due to stronger oxidising nature of Tollens' reagent as compared to Fehling's and Benedict's solution and cannot oxidise benzaldehyde to benzoic acid. In general, all these three can oxidise aliphatic aldehydes.

20. Write the chemical equation for Wolf-Kishner Reduction.

Ans. $CH_3CHO \xrightarrow{NH_2NH_2} CH_3\text{-}C{=}N\text{-}NH_2 \xrightarrow[\text{Ethylene glycol}]{KOH/} CH_3\text{-}CH_3 + N_2$

21. Name alkene which on ozonolysis give acetone as a product

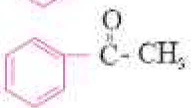


2, 3-Dimethylbut-2-ene

22. Give reason why hydrazones of RCHO and ketone are not produced in strongly acidic medium?

Ans. In acidic medium, $\ddot{N}H_2\ddot{N}H_2$ get protonated and will not act as $Nu^{\ominus}$

23. Complete the reaction

Ans. 

24. Name the aldehyde, which only exist in gaseous state.

Ans. HCHO (Formaldehyde)

25. Give reason:- During esterification between acid and alcohol, water or the ester should be removed as soon as it is formed.

Ans. Acid+alcohol $\rightleftharpoons$ ester + water

To make the reaction fast, by removing product as per Le-Chatlier principle

SHORT ANSWER TYPE QUESTIONS (2 or 3 Marks)

1. How will you convert:

   (i) $C_2H_2 \rightarrow CH_3COOH$

   (ii) $C_6H_5CONH_2 \rightarrow C_6H_5COOH$

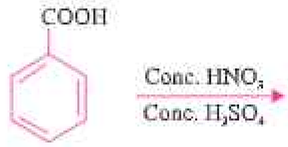
Ans. (i) $C_2H_2 \xrightarrow[HgSO_4]{H_2SO_4} CH_3CHO \xrightarrow[\text{dil. } H_2SO_4]{KMnO_4} CH_3COOH$

(ii) $C_6H_5CONH_2 \xrightarrow[\Delta]{OH^-/H^+} C_6H_5COOH + NH_3 + NaCl$

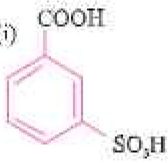
2. Complete the following:

(i)

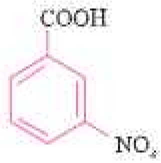
(ii)



Ans.(i)



(ii)



3. An organic compound 'X' has molecular formula $C_6H_{10}O$. It does not reduce Fehling's solution but forms a bisulphite compound. It also gives positive Iodoform test. What are possible structure of 'X'? Explain.

Ans. 'X' gives positive test with Iodoform. It is methyl ketone.

$$H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-CH_3 \quad \text{and} \quad H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{H_3C}{\overset{H}{C}}-CH_3$$

are possible structures of the compound.

4. Give the chemical test to distinguish between:

   (i) CH_3CHO and $H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$

   (ii) CH_3CHO and C_6H_5CHO

Ans. (i) CH_3CHO produce silver mirror with Tollens' reagent.

$$CH_3CHO + 2AgNO_3 + 2NH_4OH \rightarrow CH_3COOH + 2Ag + 2NH_4NO_3 + 2H_2O$$

(ii) CH_3CHO gives brick red ppt. in Fehling test

$$CH_3CHO + 2CuSO_4 + 4NaOH \rightarrow CH_3COOH + \underset{\text{Brick red ppt.}}{Cu_2O} + Na_4SO_4 + 2H_2O$$

5. Is benzaldehyde more reactive or less reactive towards nucleophilic addition reactions than propanal ? Explain your answer.

Ans. Carbon atom of carbonyl is C_6H_5CHO is less reactive than that of propanal. C_6H_5CHO is less polar due to resonance.

6. Which acid of each pair shown here would you expect to be stronger ?

(i) CH_3CO_2H or CH_2FCO_2H

(ii) CH_2FCO_2H or CH_2ClCO_2H

(iii) $CH_2FCH_2CH_2CO_2H$ or $CH_3CHFCH_2CO_2H$

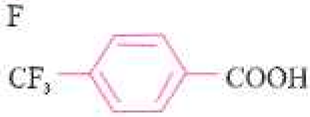
(iv)

Ans. (i) FCH_2COOH

(ii) CH_2FCOOH

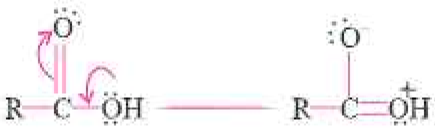
(iii) $H_3C-CH(F)-CH_2COOH$

(iv)



7. Carboxylic acids do not give reactions of aldehydes and ketones why?

Ans. It is due to resonance

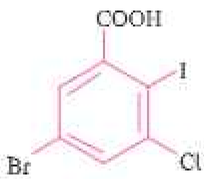


Positions of $>C=O$ group keep changing.

8. Write IUPAC name of the following :

(i)

(ii)



Ans. (i) 3,5-dimethylphenylethanoate.

(ii) 5-Bromo-3-chloro-2-iodobenzoic acid.

9. Give chemical test to distinguish between following pair of compounds:

(i) C_2H_5OH and CH_3CHO

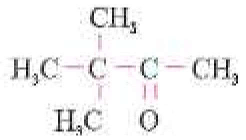
(ii) $C_6H_5COCH_3$ and $C_6H_5CH_2CHO$

Ans. (i) CH_3CHO gives silvery mirror with Tollens' reagent while C_2H_5OH does not.

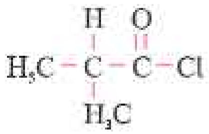
(ii) Acetophenone will give yellow ppt. of iodoform while $C_6H_5CH_2CHO$ will not.

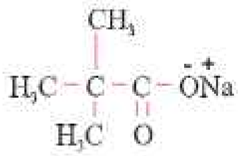
10. Complete the following reactions by identifying A, B and C :

$$\text{(i) } A + \text{Hydrogen(g)} \xrightarrow{Pd/BaSO_4} (CH_3)_2CHCHO$$

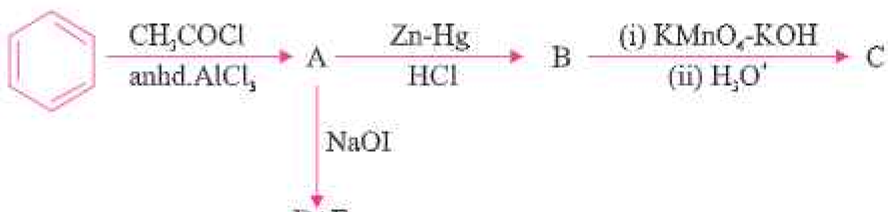
(ii)  $+ NaOI \longrightarrow B + C$

Ans.

(i) 'A' is 

(ii) 'B' is CHI_3 and 'C' is 

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



Ans. A=$C_6H_5COCH_3$

B=$C_6H_5CH_2CH_3$

C=C_6H_5COOH

D=$C_6H_5COO^-\overset{+}{Na}$

E=CHI_3

12. Aldehydes usually do not form stable hydrates but chloral normally exists as chloral hydrate. Give reason.

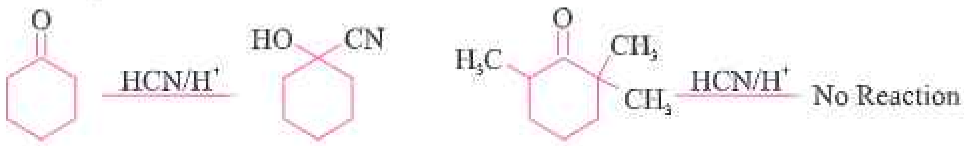
Ans. In case of aldehyde reaction is reversible.

$$\underset{H}{\overset{R}{>}}C=O + H_2O \rightleftharpoons \underset{H}{\overset{R}{>}}C\underset{OH}{\overset{OH}{<}}$$

In case of CCl_3CHO, Cl atoms increases positive charge on carbonyl carbon. Therefore, weak nucleophiles like water readily added to the carbonyl group.

13. Give possible explanation for the following:
   (i) Cyclohexanone forms cyanohydrins in good yield but 2,2,6-trimethyl cyclohexanone does not.
   (ii) There are two - NH_2 groups in semicarbazide. However,only one is involved in formation of semicarbozone.

Ans. (i) Due to steric hindrance for CN^- at C=O due to 3-methyl groups at α-position.



(ii) Only one $-NH_2$ group attached to C=O is involved in resonance. As result electron density on these $-NH_2$ group decreases and hence does not act as nucleophile.

14. Convert the following in not more than two steps:
   (i) Benzoic acid to Benzadehyde
   (ii) Propanone to Propene

Ans. (i) $C_6H_5COOH \xrightarrow{SOCl_2} C_6H_5COCl \xrightarrow[Pd\text{-}BaSO_4]{H_2} C_6H_5CHO$

(ii) $CH_3COCH_3 \xrightarrow{NaBH_4} CH_3\text{-}\underset{OH}{\underset{|}{C}H}\text{-}CH_3 \xrightarrow{conc.\ H_2SO_4} CH_3\text{-}CH{=}CH_2$

15. Write the reactions involved in the following reactions:

(i) Clemmensen reduction

(ii) Cannizzoro reaction

Ans. (i) 

(ii) 

16. Convert the following

(i) Ethylbenzene to Benzoic acid

(ii) Ethanal to But-2-enal

Ans. (i) $C_6H_5C_2H_5 \xrightarrow{K_2Cr_2O_7/H^+} C_6H_5COOH$

(ii) $2CH_3CHO \xrightarrow{\text{dil. NaOH}} \underset{\displaystyle OH}{CH_3\overset{}{C}HCH_2CHO} \xrightarrow{\text{heat}} CH_3\text{-}CH{=}CH\text{-}CHO$

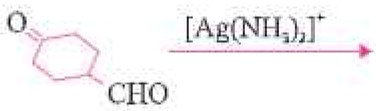
17. Predict the organic products of the following reactions:

(i) 

(ii) 

(iii) 

(iv) 

(v) 

(vi) 

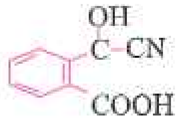
Ans. (i) 

(ii) 

(iii) 

(iv) 

(v) 

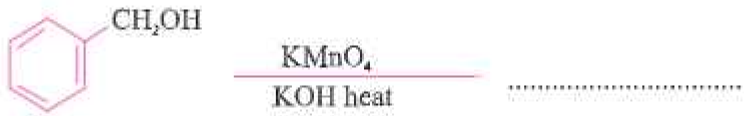
(vi) 

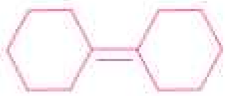
18. Complete the following as missing starting material, reagent or products:

(i)......................

(ii)

(iii)



Ans.(i)  (ozonolysis)

1,2-Dicyclohexylethene

(ii) B_2H_6/THF.H_2O_2/(Hydroboration) OH^-, then PCC

(iii) 

(Oxidation)

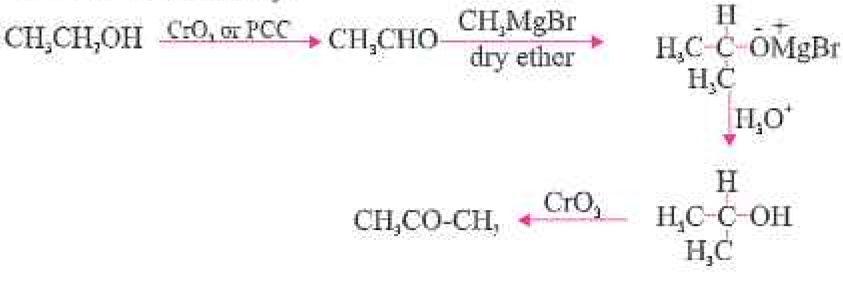
Patassium benzoate

19. Mention the reactions involved for the following conversion.

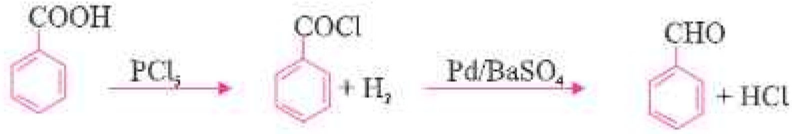
(i) Ethanol→Acetone

(ii) Benzene→Acetophenone

(iii) Benzoic acid → Benzaldehyde

Ans.(i) 

(ii) 

(iii) 

20. Give reason for the following:

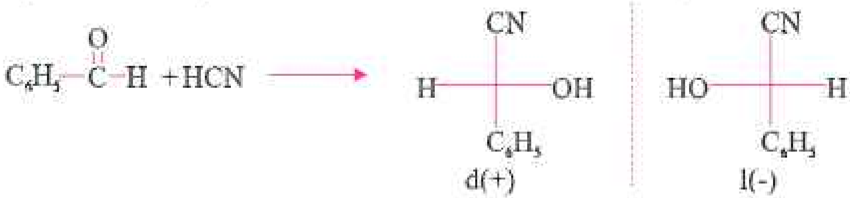
(i) Why are carboxylic acid more acidic than alcohol or phenols although all of then have H–atom attached to oxygen atom (—O—H)?

(ii) Treatment of C_6H_5CHO with HCN gives a mixture of two isomers which cannot be separated even by fractional distillation.

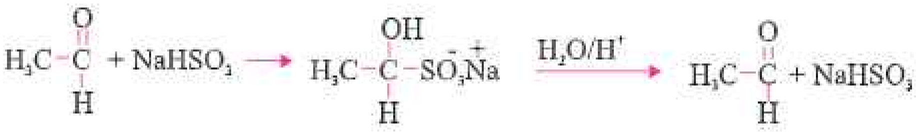
(iii) Sodium bisulphite is used for purification of ketones and aldehydes.

Ans. (i) Then is resonance in carboxylate ion, negative charge disperse over oxygen atom. But there is no resonance in alcohol(R–OH). Also in phenol less dispersal of negative change in phenolate ion as compare to carboxylate.

(ii) Due to two optical isomers fractional distillation is not possible.



(iii) Due to formation of addition compound of aldehydes and ketones with $NaHSO_3$ whereas impurities do not.



21. Write chemical tests to distinguish between following pair of compounds:

(i) CH_3CHO and C_6H_5CHO

(ii) C_6H_5-OH and CH_3COOH

(iii) Pentanal and Pentan-2-one

Ans. (i) CH_3CHO gives brick red ppt. with Fehling while C_6H_5CHO does not.

(ii) Phenol does not give brisk effervescence but CH_3COOH gives this test with $NaHCO_3$.

(iii) Pentanal forms silver mirror but Pentan-2-one does not. Or pentan-2-one give positive do form test

22. Convert the following:

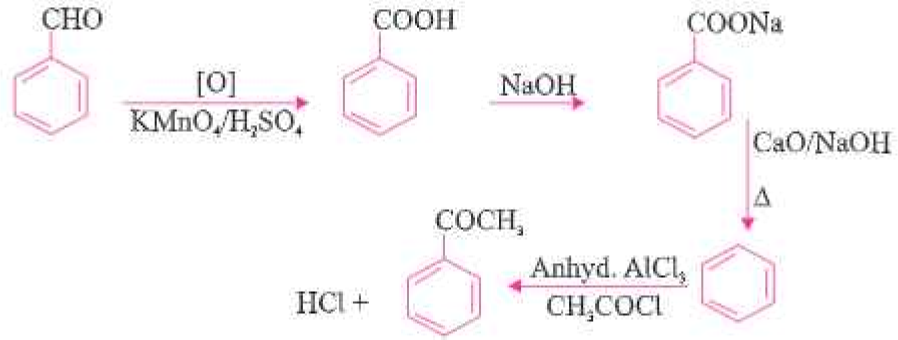
(i) Benzaldehyde to Acetophenone

(ii) Malonic acid to Acetic acid

(iii) Acetaldehyde to Butan-2-ol

Ans.

(i)



(ii) $$H_2C\begin{matrix}\diagup COOH\\ \diagdown COOH\end{matrix} \xrightarrow{\text{heat}} CH_3COOH + CO_2$$

(iii) $$2CH_3CHO \xrightarrow{OH} CH_3-\underset{OH}{\overset{OH}{C}}H\text{-}CH_2\text{-}CHO \xrightarrow[H_2SO_4/\Delta]{\text{Conc.}} H_3C-\overset{H}{C}=\overset{H}{C}-CHO$$

$$\xrightarrow{LiAlH_4} \underset{\text{Butanol-2-ol}}{CH_3CH_2CH_2CH_2OH}$$

LONG ANSWER TYPE QUESTIONS (5 Marks)

1. Write chemical reaction to perform the following conversion:

(i) Butan-1-ol to Butanoic acid

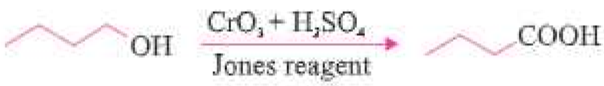
(ii) Benzyl alcohol to Phenylethanoic acid

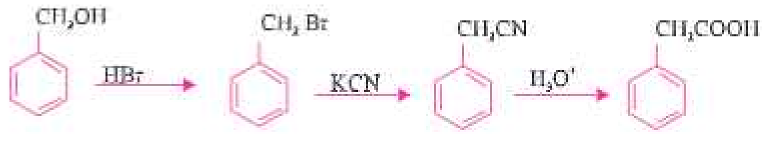
(iii) 3-Nitrobromobenzene to 3-Nitrobenzoic acid

(iv) 4-Methylacetophenone to Terephthalic acid

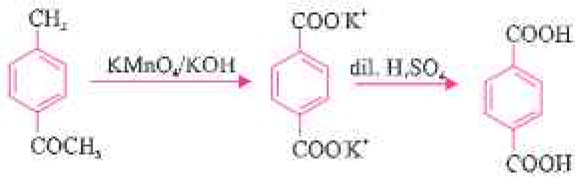
(v) Cyclohexene to Hexane-1,6 dioic acid

Ans.

(i) 

(ii) 

(iii) 

(iv) 

(v) 

2. Draw the structure of the following derivatives:

(i) 2.4-Dinitrophenylhydrazone of C_6H_5CHO

(ii) Cyclopropanone oxime

(iii) Acetaldehyde Dimethylacetal

(iv) Semicarbazone of Cyclobutanone

(v) Ethylene ketal of Hexan-3-one

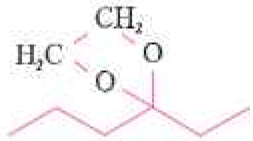
(vi) Methylhemiacetal of formaldehyde

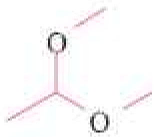
Ans.

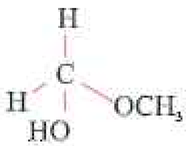
(i) 

(iv) 

(ii) 

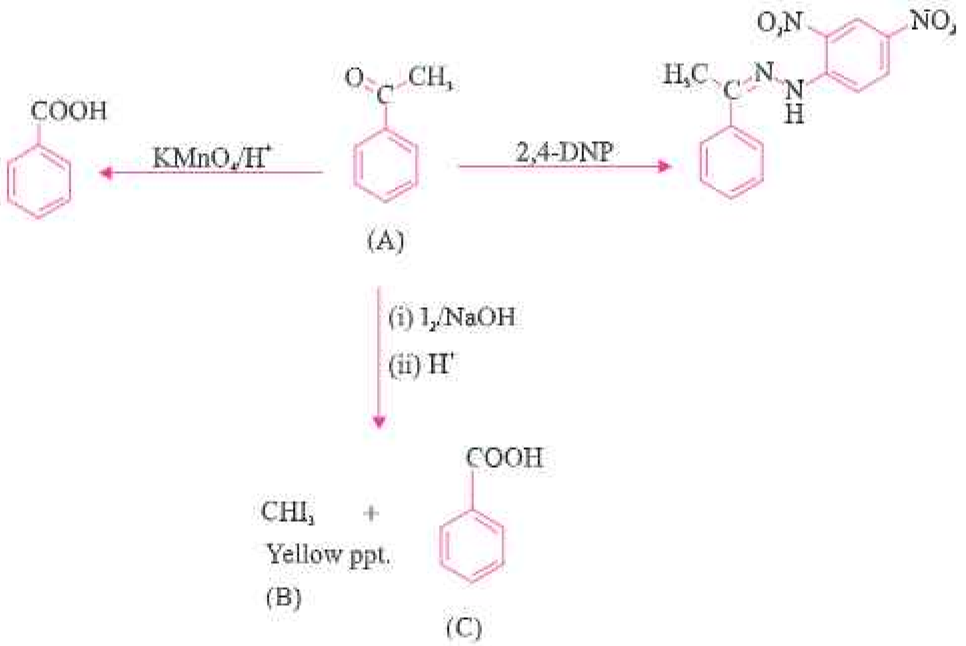
(v) 

(iii) 

(vi) 

3. An aromatic compound 'A' (Molecular formula C_8H_8O) gives positive 2, 4-DNP test. It gives a yellow precipitate of compound 'B' on treatment with iodine and sodium hydroxide solution. Compound 'A' does not give Tollens' or Fehling's test. On drastic oxidation with potassium permanganate it forms a carboxylic acid 'C' (Molecular formula $C_7H_6O_2$), which is also formed along with the yellow compound in the above reaction. Identify A, B and C and write all the reactions involved.

Ans:

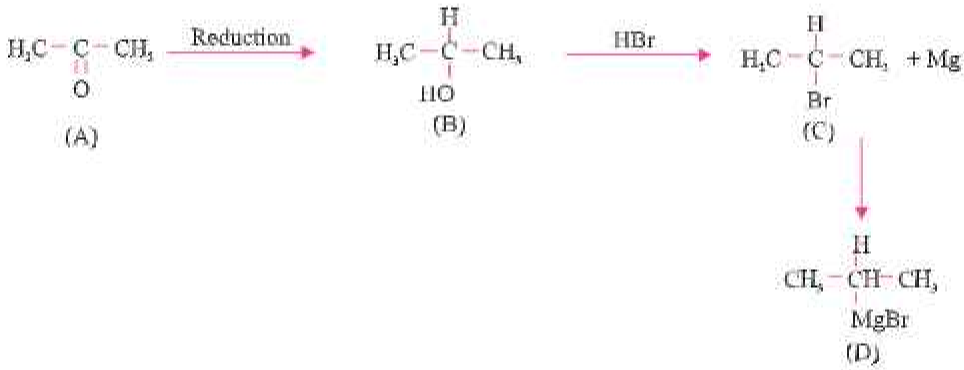


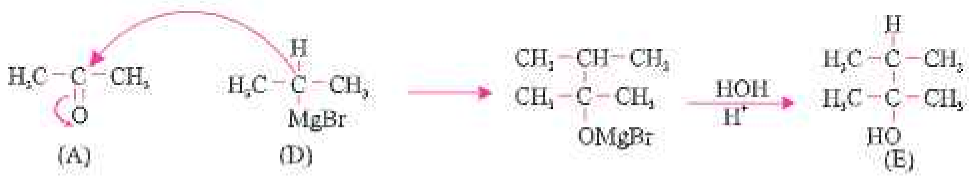
4. Give reason for the following:
   (i) C_6H_5COOH is weaker acid than formic acid.
   (ii) HCOOH and CH_3CHO can not be distinguished by Tollens' reagent.
   (iii) R-COOH do not give characteristic reaction with >C=O.
   (iv) Carboxylic acids are stronger acids than phenols.
   (v) Acid amides are weakly basic in nature.

Ans. (i) In C_6H_5COOH, carboxylate ion is resonance stabilised
   (ii) Presence of -CHO group in both.
   (iii) >C=O group is sterically hindered in carboxylic acid.
   (iv) Dispersal of negative charge on carboxylate ions is more than phenoxide ion.
   (v) Acid amides are weak basic due to involvent lone pair in conjugation with give of electrons on nitrogen atom. 

5. An organic compound 'A' (C_3H_6O) is resistant to oxidation but forms compound 'B' (C_3H_8O) on reduction. 'B' reacts with HBr to form the compound 'C'. 'C' with Mg forms Grignard's reagent 'D' which reacts with 'A' to form a product which on hydrolysis gives 'E'. Identify 'A' to 'E'.

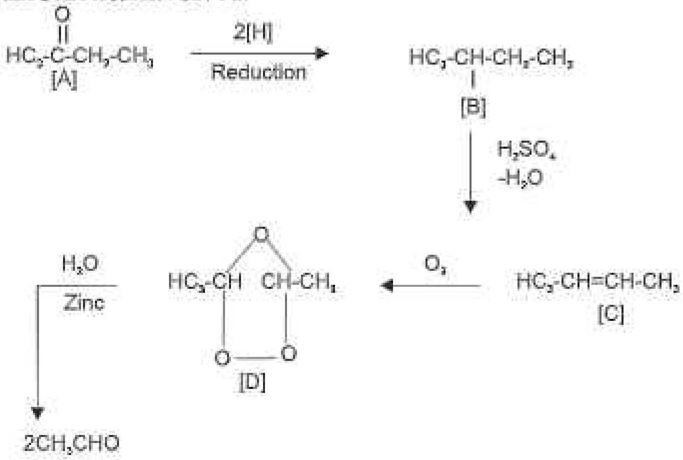
Ans. 'A' must be ketone.





6. A ketone [A] which undergoes haloform reaction gives compound [B] on reduction. [B] on heating with H_2SO_4 gives compound [C] which forms monozonide [D] by reacting with ozone. [D] on hydrolysis in the presence of Zinc dust gives acetaldehyde. Identify [A], [B], [C], [D]. Write the reaction involved.

Ans.



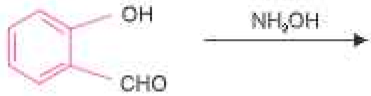
7. Complete the following reaction

(a) $CH_3CHO + HOCH_2CH_2OH \longrightarrow$

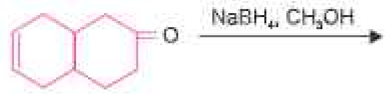
(b) $C_6H_5COCl + H_2 \xrightarrow{Pd/BaSO_4}$

(c)

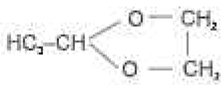
(d)



(e)

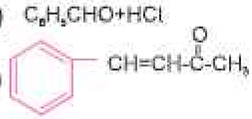


Ans. (a)



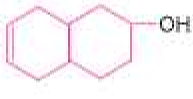
(b) $C_6H_5CHO+HCl$

(c)



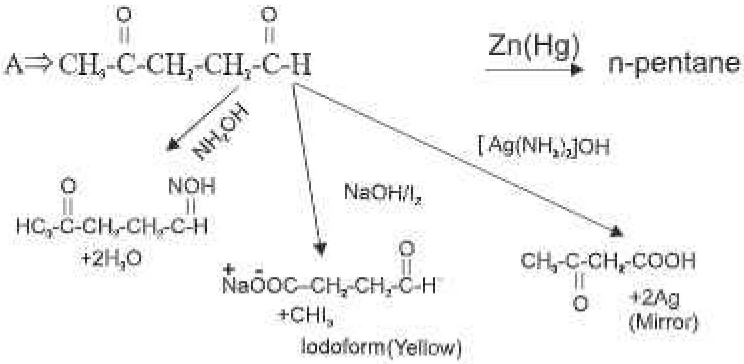
(d)

(e)



8. An organic compound [A] with molecular formula $C_5H_8O_2$ is reduced to n-pentane on treatment with Zn-mg/HCl. The compound [A] forms a dioxime with hydroxyle amine and gives a positive iodo form test and Tollen's test. Identify the compound [A] and deduce its structure.

Ans.



(9). Complete the missing products

(a) $HCHO \xrightarrow{H_2/Ni} [A] \xrightarrow{PCl_5} [B] \xrightarrow{KCN} [C] \xrightarrow{H_3O^+} [D]$

(b) $CH\equiv CH \xrightarrow[H_2SO_4/HgSO_4]{H_2O} [A] \xrightarrow{[O]} [B] \xrightarrow{SOCl_2} [C]$

(c) $CH_2{=}CH_2 \xrightarrow{HBr} [A] \xrightarrow{KCN} [B] \xrightarrow{H_2O/H^+} [C] \xrightarrow{LiAlH_4} [D]$

Ans. (a) A = CH_3OH, B = CH_3Cl, C = CH_3CN, D = CH_3COOH
(b) A = CH_3CHO, B = CH_3COOH, C = CH_3COCl
(c) A = CH_3CH_2-Br, B = CH_3CH_2-CN, C = CH_3CH_2COOH,
D = $CH_3CH_2CH_2OH$

10. [A], [B] and [C] are three non-cyclic functional isomer of a carbonyl compound with molecular formula C_4H_8O. Isomer [A] and [C] gives positive Tollen's test whereas Isomer [B] does not give tollen's test but give positive iodoform test. Isomer [A], [B] on reduction with Zn[Hg]/conc. HCl give same product [D]. Identify A, B, C, D.

Ans. A = $CH_3CH_2CH_2CHO$ Butan-1-al

B = $CH\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_2\text{-}CHO$ Butan-2-one

C = $CH_3\text{-}\underset{CH_3}{\underset{|}{C}}\text{-}CHO$ 2-Methylpropanal

D = $CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_3$ Butane

CASE-STUDY BASED QUESTIONS

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

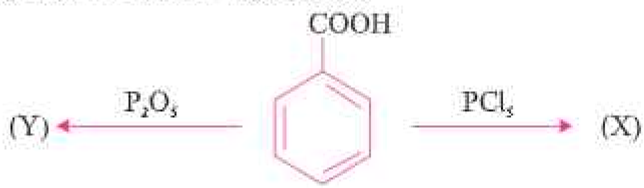
Carboxylic acids are compounds with excellent chemical and physical properties, the most particular characteristics of this type of organic compounds, is their high solubility in polar solvents, as water, or alcohols, methanol, ethanol, etc. Chemical structure contains a carbonyl function (-C=O) and an hydroxyl group (OH), these groups interact easily with polar compounds, forming bridges of H, obtaining high boiling points. The carbonyl group (C=O) is considered a one of the most functional groups involved in many important reactions. The carboxylic acids are the most important functional group that present C=O.

This type of organic compounds can be obtained by different routes, some carboxylic acids, such as citric acid, lactic acid or fumaric acid are produced from by fermentation, most of these type of carboxylic acids are applied in the food industry. Historically, some carboxylic acids were produced by sugar fermentation. Synthetics route, there are different synthesis reactions such as reactions of oxidation from alcohols in the presence of strong oxidants such as $KMnO_4$, oxidation of aromatic compounds among other routes. For example, citric acid is a carboxylic acid, can be obtained by different routes, synthetic, enzymatic and naturally occurring, is considered harmless and cheap, used in the food industry, because is non-toxic, has a thermal stability to the 175°C. Bian et al., in 2017, reported the use of citric acid impregnated in porous material for the synthesis of Ni particles. They showed, that the presence of citric acid, is important in the dispersion of the Ni particles when are incorporate in porous materials, thus inhibiting the agglomeration.

Derivatives of carboxylic acid, as alkyl halides, esters, and amides, present different and important application in diverse areas. In the case of esters, these are obtained from the reaction between carboxylic acids and alcohols in presence of an acid catalyst usually H_2SO_4 with heat, this type of reaction is known as esterification. In the case of the amides, it is obtained in the presence of an amine, may be primary and secondary, with a carboxylic acid, in this reaction also can be used a catalyst and heat to accelerate the reaction.

Reference : Aide Sienz-Galindo, Lluvia I. Lopez-Lopez, Fabiola N. de la Cruz- Duran, Adali O.Castafieda-Facio, Leticia A. Ramirez-Mendoza, Karla C. Cordova-Cisneros and Denisse de Loera-Carrera (March 15th 2018). **Applications of Carboxylic Acids in Organic Synthesis, Nanotechnology and Polymers, Carboxylic Acid-Key Role in Life Sciences**, Georgiana Ileana Badea and Gabriel Lucian Radu, *IntechOpen*, DOI: 1 0.5772/intechopen.74654.

(A) Identify A and B in following reaction:



(B) Assertion: Carboxylic acids are highly acidic.

Reason: Carboxylate ion is resonance stabilised.

(a) Assertion and reason both are correct and reason is the correct explanation of the assertion.

(b) Assertion and reason both are correct statements but reason is not correct explanation of assertion.

(c) Assertion is correct statement but reason is wrong statement.

(d) Assertion is wrong statement but reason is correct statement.

(C) What happens when phthalic acid reacts with ammonia followed by strong heating?

(D) How acetyl chloride may be converted to ethanoic acid?

2. **Read the passage and answer the following questions:**

'Tetrahydrofuran (THF) is a bulk chemical, which can be obtained from various feedstocks including biomass. In addition, the C5 carboxylic acids are much more expensive than THF. Therefore, we adopted THF as model ether to study the catalytic system (Table 1). The reaction could be efficiently accelerated by IrI_4 catalyst and LiI promoter in AcOH solvent at 170 °C, and the yield of C5 carboxylic acids reached 70% after 16 h (entry1). The products contained two isomers, i.e., pentanoic acid and 2-methylbutanoic acid, and their molar ratio was 58:42. A little C6 carboxylic acids were also formed in the reaction. The rest of the THF substrate was converted to butane.

In addition, trace of methane was also detected. We also tried different Ir catalyst precursors, such as $Ir(CO)(PPh_3)_2Cl$, $Ir(CO)_2(acac)$, and $IrCl_3$, the results indicated that they were not as efficient as IrI_4. We set the reaction time at 8 h and tested other catalytic systems. The IrI_4 catalyst was essential to the reaction because no target product was observed without it. The Rh catalyst was effective for synthesis of carboxylic acids via olefin and/or alcohol hydrocarboxylation with CO_2 and H_2. Whereas in this work no product was obtained when RhI,

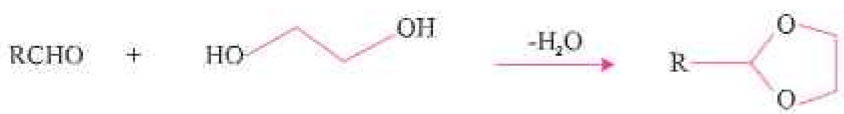
$$R{-}O{-}R' + CO_2 + H_2 \xrightarrow[170^\circ C,\ \text{in AcOH}]{IrI_4,\ LiI} R/R\text{-}COOH$$

(A) How ethers can be distinguished from carboxylic acid?

(B) Propanol on reaction with............and.............gives propanal and propane respectively.

3. **Read the passage and answer the following questions:**

The acetal is the most common protecting group for aldehydes and 1,3-dioxolanes are the most commonly encountered type of acetal, usually prepared by reaction of the aldehyde with ethylene glycol with azeotropic removal of water (eq1). Regeneration of the carbonyl is normally out with aqueous acid.



(1)

We have been concerned with the general problem of converting dioxolanes into Carboxylic acids without employing acid to first remove the protective group (eq 2). The non-acidic alternative to eq 2 would allow the introduction of acid groups into a molecule containing.

(2)

various acid-sensitive functionalities. Our solution to this problem is outlined in eq 3. Prugh and McCarthy in 1966 showed that cyclic acetals are converted into bromo esters when treated with N-bromosuccinimide (NBS). Indeed, a

(3)

variety of dioxolanes give good yields of the corresponding 2-bromoethyl esters when refluxed with NBS in CCl_4. For example, 3-phenyl-1,3-dioxolane gives a 98% yield Of 2-bromoethyl benzoate (88% after distillation).

The transformation of eq 3 is completed by a zinc-induced elimination which yields the acid upon workup. Despite the precedent for this second step, a variety of reaction conditions failed to give any acid from 2-bromoethyl benzoate.

Zinc in refluxing THF gave no reaction. Even zinc which had activated with copper sulfate was ineffective and ultraactive zinc from the potassium metal or sodium naphthalenide reduction of zinc chloride also failed to promote elimination. Zinc in refluxing methanol or ethanol gives 42-46% benzoic acid plus 47-52% of transesterification product. Ester interchange can be avoided by using zinc in refluxing THF to give a 44% yield of benzoic acid and a recovery of starting material. Addition of catalytic sodium iodide improves the yield of benzoic acid from this reaction to with only of starting material recovered.

Reference : Lawrence C. Anderson, Harold W. Pinnick, **Preparation of carboxylic acids from protected aldehydes** *J. Org. Chem.* **1978**, 43, 17, 3417-3418 **https://doi.orq/10.1021/io00411a044**

(A) The formation of acetal from aldehyde is an example of .... reaction.

(B) Which of the following reagent(s) can be used to convert butan-1-ol to butanoic acid?

(a) 1. $KMnO_4$—KOH 2. H^+

(b) CrO_3—H_2SO_4

(c) Both i) and ii)

(d) None of these

(C) Write the structure of the product formed when propanal reacts with methanol.

(D) What happens when propanal reacts with ethyl magnesium iodide followed by reaction with dilute acid?

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

Nucleophilic additions to a carbonyl group leading to tetrahedral species which are products or intermediates in a mechanistic sequence occupy a central place in biochemistry as well as in organic chemistry. It has been shown recently that the structural pathway for the nucleophilic addition of an amino group to carbonyl can be mapped on the basis of crystal structure data. However, from structural data alone no direct information about the energy variation along the reaction pathway can Obtained. Furthermore, it was not entirely clear to what extent steric requirements of substituents on the nucleophile and the carbonyl group, as well as crystal packing effects, influence the arrangement of the reactive centers. An an attempt to till these gaps we have carried out calculations on the reaction path of the simple model system.

$$CH_2=O + H^- \rightarrow CH_3O^-$$

corresponding to nucleophilic addition of hydride anion to formaldehyde to produce methanolate anion. A calculation has also been made for the system consisting of an ammonia and a formaldehyde molecule at a of 20 nm.

Reference : H. B. Buergi, J. M. Lehn, G. Wipft, **Ab initio study of nucleophilic addition to a carbonyl group**, *J. Am. Chem. Soc*. 1974, 96, 6, 1956-1957, Publication Date: March 1, 1974 https://doi.org/10.1021/ja00813a062

(A) Which of the following nucleophilic addition reaction generates chiral carbon?

(a) Benzaldehyde + KOH

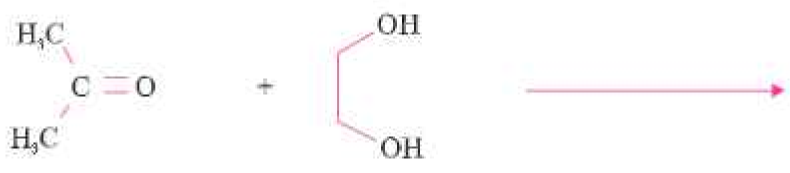
(b) Benzaldehyde + ammonia

(c) Propanone + KOH

(d) Propanone + ammonia

(B) Write the major product on reaction of acetophenone with CH_3-NH_2?

(C) Complete the reaction:



(D) Which will undergo reaction with 2,4-dinitrophenylhydrazine at fastest rate?

(a) Acetophenone (b) Propanone

(c) Benzaldehyde (d) Propanal

ANSWERS

I MULTIPLE CHOICE QUESTIONS

1. (b) 2. (d) 3. (b). 4. (b) 5. (b) 6. (a) 7. (d) 8. (a) 9. (d) 10. (d) 11. (c) 12. (c) 13. (a) 14. (b). 15. (a) 16. (b) 17. (c) 18.(c) 19.(b) 20.(a)

II FILL IN THE BLANKS

1.	Ammoniacal silver nitrate	2.	Phthalimide	3.	Rosenmund
4.	Increases	5.	$NaHCO_3$	6.	Cu_2O
7.	Methanal/Formaldehyde	8.	H-bonding.	9.	Aldehydes
10.	Propanoic acid				

III ASSERTION REASON TYPE QUESTIONS

III. 1. (a) 2. (a) 3. (c) 4. (c) 5. (a) 6. (b) 7. (d) 8. (c) 9. (d) 10. (b)

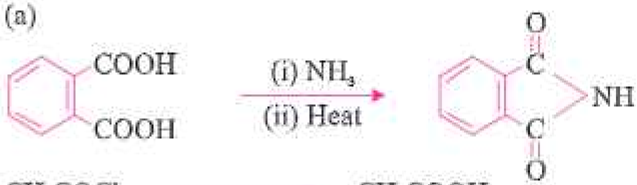
IV ONE WORD ANSWER TYPE QUESTIONS

1.	Hemiacetal	2.	Benzaldehyde	3.	$LiAlH_4$ or B_2H_6
4.	Decarboxylation	5.	Methyl propanoate		
6.	1,3-Diphenylprop-2-en-l-one or Benzalacetophenone				
7.	$NaBH_4$	8.	P_2O_5 or H^+/Δ	9.	Hexane-1,6-dioic acid
10.	a) HCOOH, (b) $CH_2(Cl)COOH$			11.	Iodoform Test
12.	Methycyclohexane	13.	$Pd/BaSO_4$	14.	$CH_3MgBr/H_2O/H+$
15.	CH_3CHO				

CASE STUDY BASED QUESTIONS

1. (A) $X = C_6H_5COCl$ $Y = (C_6H_5CO)_2O$

(B) (a)

(C) 

(D) $CH_3COCl \xrightarrow[H_2O/H^+]{} CH_3COOH$

2. (A) With $NaHCO_3$ carboxylic acids give brisk effervescence, whereas ethers cannot.

(B) PCC

PASSAGE :3

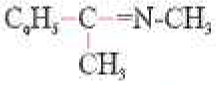
3. (A) Nucleophilic addition reaction

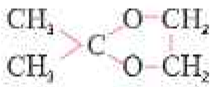
   (B) (c)

   (C) $CH_3CH_2CH(OCH_3)_2$

   (D) $(C_2H_5)_2$ CHOH

4. (A) (c)

   (B) 

   (C) 

   (D) (d)

UNIT TEST-1

Aldehydes, ketones and carboxylic acid

Maximum Marks : 20 **Time : 1 Hrs.**

1. Identify the correct product in following reaction:

(a) 

(b) 

(c) 

(d) 

2. Which of the following reagent(s) is most suitable for following conversion?

Propanone → Propane

(a) PCC (b) $LiAlH_4$

(c) (I). $KMnO_4$-KOH (ii). H^+ (d) Zn(Hg)/HCl

3. The highest pK_a value is observed in-

(a) Phenol (b) Benzoic acid

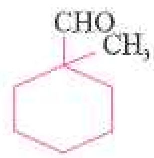
(c) 4-Nitrobenzoic acid (d) Ethanoic acid

4. Which of the following undergoes nucleophilic addition reaction at fastest rate?

(a) Benzaldehyde (b) Acetophenone

(c) Methanal (d) Ethanal

5. Cannizzaro reaction is not shown by-

(a) 

(b) 

(c) HCHO (d) CH_3CHO

6. Give a chemical test to distinguish between following compounds: 2

(a) Benzaldehyde and Acetophenone

(b) Benzoic acid and Phenol

7. How butanoic acid can be synthesised using appropriate: 2

(a) Grignard reagent

(b) Amide

8. Arrange following in ascending order of given properties: 2

   (a) Ethanal, Ethanol, Methoxymethane, Propane (boiling point)

   (b) Propanal, Benzaldehyde, Acetophenone (reactivity towards nucleophilic addition reaction)

9. Complete the reaction sequence by writing structures of A-E. Also name the reaction involved in the conversion of A to B. 2

$$C_6H_6 \xrightarrow[\text{Anhyd. } AlCl_3]{CH_3COCl} A \xrightarrow{\text{Zn-Hg / Conc.HCl}} B \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } KMnO_4\text{ - }KOH,\ \Delta} C$$

$$A \xrightarrow{NaOH} D + E$$

10. Explain following: 3

    (a) α- hydrogens in aldehydes and ketones are acidic in nature.

    (b) There are two $-NH_2$ groups in semicarbazide. However only one involves in the formation of semicarbazone.

    (c) Propanone is less reactive than propanal towards nucleophilic addition reactions.

11. How will you carry out following conversions? 3

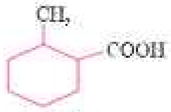
    (a) Bromobenzene to 1-Phenylethanol

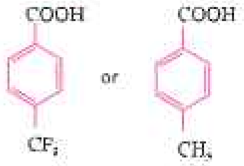
    (b) Benzoic acid to *m*- Nitrobenzyl alcohol

    (c) Propanone to Propene

UNIT TEST- 2
Aldehydes, ketones and carboxylic acid

Maximum Marks : 20 **Time : 1 Hrs.**

1. Give the IUPAC of 

2. Which acid will be more acidic  1

3. Write product of CH_3CHO with hydrazine. 1
4. Which will have higher boiling point CH_3CHO or CH_3COOH. 1
5. How many mole of hydrazine will be used with one mole of Phthaldehyde 1
6. Write chemical distinguish test to seperate following. 1
   (a) Pentan-2-one and Pentan-3-one
   (b) Benzophenone and Benzoic acid
7. Write short not on 1
   (a) Hell-Volhard-Zelinsky Reaction
   (b) Etard Reaction
8. How will you synthesise (i) Acetone from propene. (ii) Salicylic acid from benzene. 2
9. Arrange the following compound in increasing order of their properties.
   (a) CH_3COOH, $C_6H_5COCH_3$, CH_3CHO [Reactivity towards nucleophilic addition reaction]
   (b) $Cl\text{-}CH_2\text{-}COOH$, $F\text{-}CH_2\text{-}COOH$, $CH_3\text{-}CH_2\text{-}COOH$ (acidic character)
   (c) CH_3CHO, CH_3CH_3, CH_3COOH, CH_3CH_2OH (boiling point)
10. Give reason. 3
    (a) Cyclohexanone forms cyanohydrin in good yield but 2,2,6- trimethyl cyclohexanone does not.
    (b) There are two-NH_2 group in semicarbazide howere only one is involved in the formation of semicarbazone.
11. (a) Convert the following 3
    (i) Benzaldehyde to 3-Phenylpropan-1-ol
    (ii) Benzole acid to m-Nitrobenzyl alcohol
    (b) An organic compound with molecular formula $C_9H_{10}O$ from 2,4-DNP derivatives, reduce Tollen's reajent and undergoes cannizarro's reaction. on vigrous oxidation it gives 1,2- Benzene-dicarboxylic acid. Identify the compound.

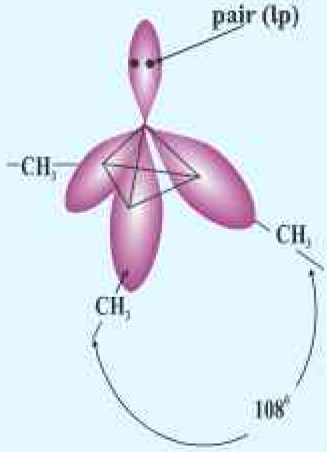
UNIT 13

AMINES

Points to Remember

Geometry

Pyramidal shape



Classification and Nomenclature of Amines

Nomenclature

Common Names:- Amine is used as suffix after alkyl group e.g. $CH_3CH_2NH_2$ is ethylamine

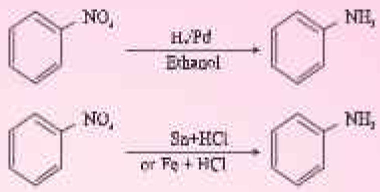
IUPAC names:- e is replaced by - amine e.g. $CH_3CH_2NH_2$ is Ethanamine.

Classification

$$NH_3 \rightarrow \underset{\text{Primary}(1^0)}{RNH_2} \rightarrow \underset{\text{Primary}(2^0)}{\begin{matrix}R\\R\end{matrix}\rangle R\text{-}H} \rightarrow \underset{\text{Primary}(3^0)}{\begin{matrix}R\\R\end{matrix}\rangle N\text{-}R''}$$

Method of Preparation

1. Reduction of Nitro compounds



2. Ammonolysis Alkyl Halides

$$\ddot{N}H_3 + R\text{-}X \longrightarrow R\,NH_3^+\,X^-$$

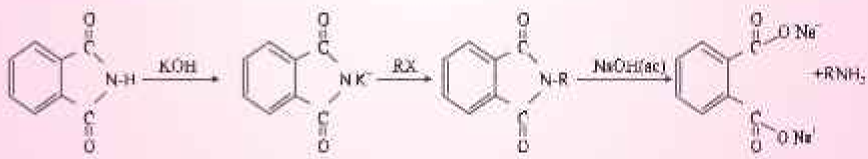
3. Reduction of nitriles

$$R-C\equiv N \xrightarrow[Na(Hg)/C_2H_5OH]{H_2/Ni} R\text{-}CH_2NH_2$$

4. Reduction of amide

$$R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[(ii)\ H_2O]{(i)\ LiAlH_4} R\text{-}CH_2NH_2$$

5. Gabriel phthalimide sythesis



Basic character in gaseous phase:

6. Hoffmann bromamide degeneration reaction.

$$R-\overset{O}{\overset{\|}{C}}-NH_2 + Br_2 + 4NaOH \longrightarrow R\text{-}NH_2 + Na_2CO_3 + 2NaBr + H_2O$$

Chemical Reactions:

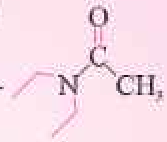
(i) **Reactions Basic character:** Due to presence of lone pair of electrons on N of $-NH_2$ group they acts as base

$3° > 2° > 1° >$ ammonia (due to + I effect of alkyl group)

Basic Character in aqueous phase:

$\underset{2°}{(C_2H_5)_2NH} > \underset{3°}{(C_2H_5)_3N} > \underset{1°}{C_2N_5NH_2} > NH_3$ (R is other than $-CH_3$)

$\underset{2°}{(CH_3)_2NH} > \underset{1°}{(CH_3NH_2)} > \underset{3°}{(CH_3)_3N} > NH_3$ (R is $-CH_3$)

(ii) **Acylation** $(C_2H_5)_2NH + H_3C\text{-}\overset{O}{\overset{\|}{C}}\text{-}Cl \xrightarrow{\text{Base}}$  $+ \; HCl$

(iii) **Carbylamine reaction:**

$R\text{-}NH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta} R\text{-}NC + 3KCl + 3H_2O$

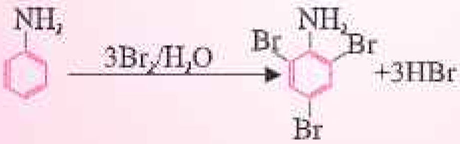
(iv) **With nitrous acid**

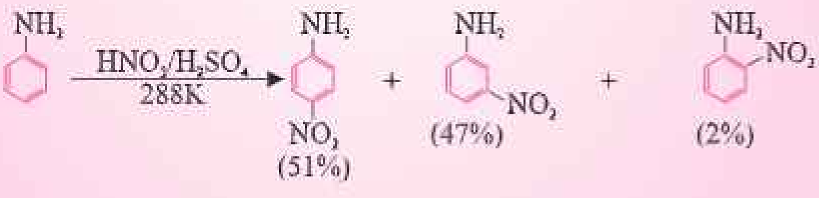
$RNH_2 \xrightarrow{NaNO_2 + HCl} [R\text{-}\overset{+}{N_2}\overset{-}{Cl}] \xrightarrow{H_2O} ROH + N_2 + HCl$

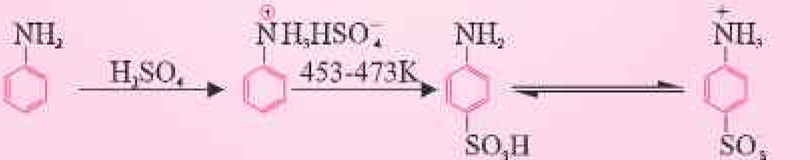
$C_6H_5NH_2 \xrightarrow[273\text{-}278K]{NaNO_2 + HCl} C_6H_5\overset{+}{N_2}\overset{-}{Cl} + NaCl + 2H_2O$

(v) **With Benzene sulphonyl chloride**

(vi) **Electrophilic Substitution**







Zwitter ion

Diazonium salt

X^- may be Cl^-, Br^-, HSO_4^-, BF_4^-

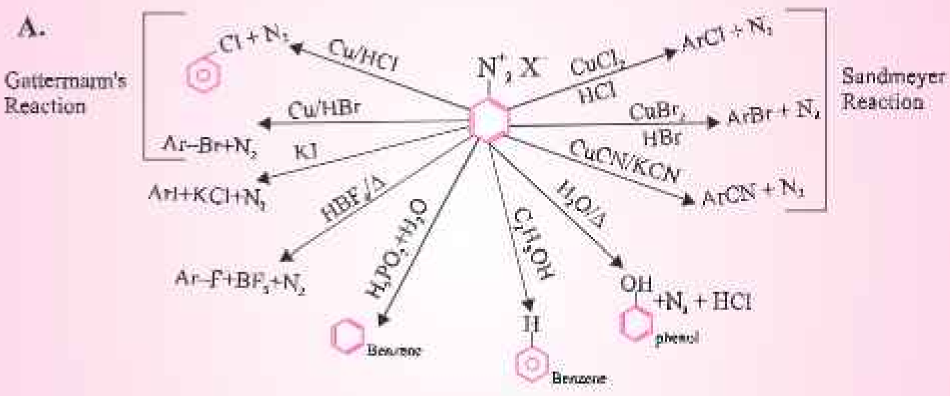
Benzenedrazonium salt

Preparation:

$$C_6H_5NH_2 + NaNO_2 + NCl \xrightarrow{0-5^\circ C} C_6H_5\overset{+}{N}_2Cl^- + NaCl + H_2O$$

Reaction:

A.



B. Coupling Reaction

(i) 

OrangDye
p-Hydroxyazobenzen.

(ii) 

Yellow Dye
(p-Aminozobenzune)

OBJECTIVE TYPE QUESTIONS

I MULTIPLE CHOICE QUESTIONS

1. In the nitration of benzene using conc. H_2SO_4 and conc. HNO_3 the species which initiates the reaction is:

   (a) NO^+ (b) NO_2^+

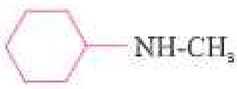
   (c) NO_2^- (d) NO_3^-

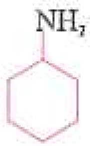
2. The correct IUPAC name of $CH_2=CH-CH_2NHCH_3$

   (a) Allylmethyl amine (b) 2-Aminopent-4-ene

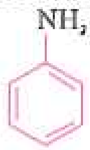
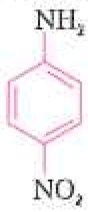
   (c) 4-Aminopent-1-ene (d) N-Methylprop-2-enamine

3. Which is the weakest base?

   (a)  (b) 

   (c)  (d) H_3C-NH_2

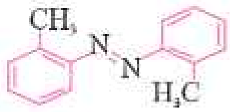
4. The correct order of basic strength for the following compound is:

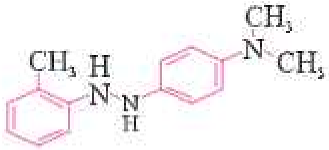
   (i)  (ii)  (iii) 

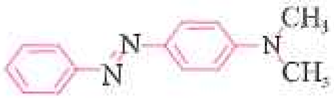
   (a) ii < iii < i (b) iii < i < ii

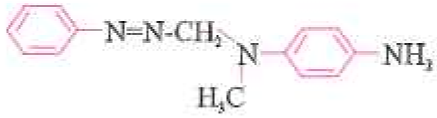
   (c) iii < ii < i (d) ii < i < iii

5. The structure of 'C' in following reaction sequence would be -

(a) 

(b) 

(c) 

(d) 

6. Which of the following statement about primary amine is false?

   (a) Aryl amines react with nitrous acid to produce phenol

   (b) Alkyl amines are stronger base than ammonia

   (c) Alkyl amines are stronger base than aryl amines

   (d) Alkyl amines react with nitrous acid to produce alcohol

7. Which of the following is most stable diazonium salt?

   (a) $CH_3N_2^+X^-$ (b) $C_6H_5N_2^+X^-$

   (c) $CH_3CH_2N_2^+X^-$ (d) $C_6H_5CH_2N_2^+X^-$

8. Method by which aniline can not be prepared is:

   (a) Reduction of nitrobenzene with H_2/Pd in ethanol.

   (b) Potassium salt of phthalimide treated with chlorobenzene

   (c) Hydrolysis of phenyl isocyanide with acidic solution

   (d) Degradation of benzamide with bromine in alkaline medium solution.

9. In the chemical reaction:

   $CH_3CH_2NH_2 + CHCl_3 + 3KOH \rightarrow$ 'A' + 'B' + $3H_2O$

   The compound 'A' and 'B' are respectively:

   (a) $CH_3CH_2CONH_2$ and 3KCl

   (b) CH_3CH_2NC and K_2CO_3

   (c) CH_3CH_2NC and 3KCl

   (d) CH_3CH_2CN and 3KCl

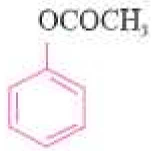
10. An amide (A) reacts with bromine in aqueous NaOH and forms amine containing three carbons. Identify (A):

(a) 2-Methylpropanamide (b) Propanamine

(c) Butanamide (d) None of these

11. Which of the following compound will give significant amount of *meta* product during mononitration reaction?

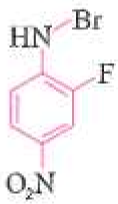
(a) 

(b) 

(c) 

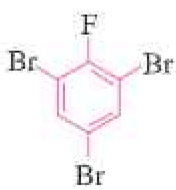
(d) 

12. The final product C in the following sequence of reaction is:

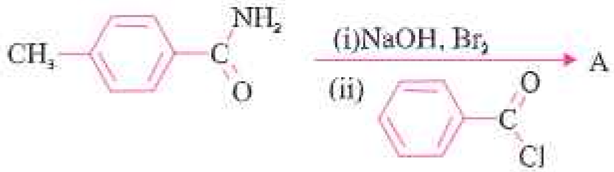
(a) 

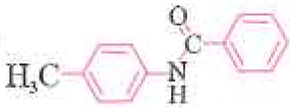
(b) 

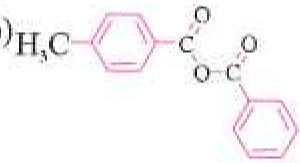
(c) 

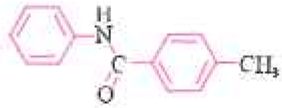
(d) 

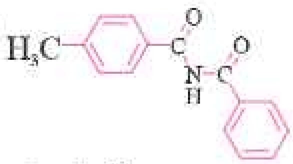
13. In the reaction, the structure of product A is:



(a) 

(b) 

(c) 

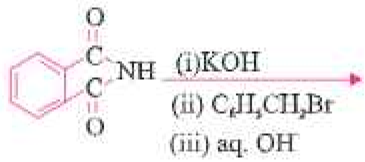
(d) 

14. Which of the following reactions forms benzylamine?

(a) 

(b) $C_6H_5CONH_2 \xrightarrow{NaOBr}$

(c) $C_6H_5CN \xrightarrow{H^+ / H_2O}$

(d) 

15. Bromobenzene can be prepared from benzene diazonium chloride by its treatment with-
   (a) Cu/HBr
   (b) Br_2, hv
   (c) CuBr/HBr
   (d) Br_2/CCl_4

16. Acetamide and Ethylamine can be distinguish by reacting with
   (a) aq. HCl and heat
   (b) aq. NaOH and heat
   (c) Acidified $KMnO_4$
   (d) Bromine Water

17. The order of reactivity of halides with amines is
    (a) RI > RBr > RCl
    (b) RBr > RI> RCl
    (c) RCl > RBr > RI
    (d) RBr > RCl > RI
18. Which of the following does not affect the K_b of an organic base?
    (a) +I or -I effect
    (b) solvation effect
    (c) density
    (d) steric hinderance
19. Which of the following on reduction with $LiAlH_4$ yields a secondary amine?
    (a) Methyl isocyanide
    (b) Acetamide
    (c) Methyl cyanide
    (d) Nitroethane
20. In diazotisation of aniline with $NaNO_2$ and HCl acid the excess of acid is used primarily to
    (a) suppress the concentration of free aniline
    (b) suppress the hydrolysis to phenol
    (c) ensure a stoichlometric amount of HNO_2 acid
    (d) neutralise the base liberated.

II FILL IN THE BLANKS

1. Reaction of nitrobenzene with Fe + HCl results into the formation of...................
2. Aromatic amines are..............bases while aliphatic amines are..................bases than ammonia.
3. Gabriel phthalimide synthesis is used for synthesis of ....amines.
4. Benzenesulphonyl chloride is also known as..............reagent.
5. Butanamide on reaction with $LiAlH_4$ forms.................
6. To reduce activation of aniline it is deactivated by..................reaction.
7. Nitration of aniline forms *para* and .... isomers of nitroaniline as major products.
8. Benzene diazonium chloride may be converted into phenol by reaction with ....at 283 K.
9. Primary amines are soluble in water due to..............................

III ASSERTION REASON TYPE QUESTIONS

In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(a) Both assertion and reason are correct statements and reason is correct explanation of assertion.

(b) Both assertion and reason are correct statements but reason is not correct explanation of assertion.

(c) Assertion is correct statement but reason is wrong statement.

(d) Assertion is wrong statement but reason is correct statement.

1. **ASSERTION** : Acylation of amines gives a monosubstituted product whereas alkylation of amines gives polysubstituted product.
   REASON : Acyl group sterically hinders the approach of further acyl groups.
2. **ASSERTION :** Hoffmann bromamide degradation reaction results into formation of primary amines.
   REASON : Primary amines are more basic than secondary amines.
3. **ASSERTION :** N-Ethylbenzenesulphonamide is soluble in alkali.
   REASON : Hydrogen attached to nitrogen in sulphonamide is strongly acidic.
4. **ASSERTION :** N, N-Diethylbenzenesulphonamide is insoluble in alkali.
   REASON : Sulphonyl group attached to nitrogen atom is strong electron withdrawing group.
5. **ASSERTION :** Only a small amount of HCl is required in the reduction of nitro compounds with iron scrap and HCl in the presence of steam.
   REASON : $FeCl_2$ formed gets hydrolysed to release HCl during the reaction.
6. **ASSERTION :** Aromatic 1° amines can not be prepared by Gabriel phthalimide synthesis.
   REASON : Aryl halides undergoes nucleophilic substitution with anion formed by phthalimide.
7. **ASSERTION :** Acetanilide is less basic than aniline.
   REASON : Acetylation of aniline results in decrease of electron density on nitrogen.
8. **ASSERTION:** n-Propylamine has higher boiling point than trimethylamine.
   REASON: Among n-Propylamine molecules, there is hydrogen bonding but there is not hydrogen bonding in trimethylamine.
9. **ASSERTION:** Aniline does not undergoes Friedel Crafts reaction.
   REASON: Friedel Crafts reaction is an electrophilic substitution reaction.
10. **ASSERTION:** Ethylamine is more basic than aniline.
    REASON: Due to +I effect of ethyl group electron density on nitrogen increases.

IV ONE WORD TYPE QUESTIONS

1. Name the reaction in which primary amines reacts with $CHCl_3$ and KOH forming foul smelling substance.
2. Write the IUPAC name of white precipitate formed by reaction of aniline with bromine water.
3. Write the product formed by the Hoffmann bromamide degradation of benzamide.
4. Is CH_3CONH_2 weaker or stronger base than $CH_3CH_2NH_2$?
5. Write the structure of reagent used to protect amino group in aniline.
6. Name the product formed when benzene diazonium chloride reacts with H_3PO_2.
7. Name the reaction which is used to convert diazonium salt into corresponding halide by reacting with Cu(I) halides.
8. Which type of reaction involves in the cleavage of C-X bond in ammonolysis ?
9. What is the pH during coupling reaction between phenol and benzendiazonium salt.
10. Write the reagent which can be used to convert nitrobenzene to aniline
11. How many structural isomer are possible for $C_4H_{11}N$ compound?
12. Name the reagent for the conversion of amide to amine containing same number of carbon atom.
13. What kind of substitution involved in Gabriel phthalimide systhesis?
14. Name the solvent which we used in acetylation of aniline using acetic anhydride.

VERY SHORT ANSWER TYPE QUESTIONS (1 Marks)

1. Convert *m*-dinitrobenzene to m-nitroaniline.

Ans. 

2. Write IUPAC name of $CH_3-N(CH_3)-C(CH_3)(CH_2-CH_3)-CH_2-CH_3$

Ans. 3-Methyl-N,N-dimethylpentanamine

3. Give one use of quaternary ammonium salts.

Ans. It is used as detergents, e.g., $[CH_3(CH_2)_{15}N(CH_3)_3]^+Cl^-$

4. Mention the chemical formula of Hinsberg's reagent.

Ans. Benzene sulphonyl chloride, $C_6H_5-SO_2Cl$

5. Why aniline dissolves in HCl?

Ans. $C_6H_5NH_2 + HCl \rightarrow [C_6H_5NH_3]^+Cl^-$

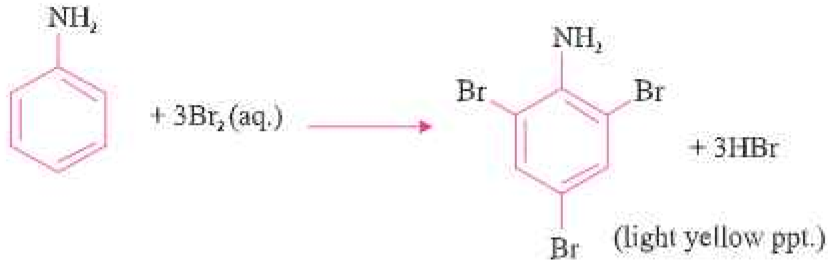
It dissolves due to its basic nature.

6. How will you test the presence of primary amine?

Ans. By carbylamine test.

$RNH_2 + CHCl_3 + 3KOH \rightarrow R-NC + 3H_2O$

7. What happens when aniline is treated with bromine?

Ans. 

8. Write a chemical equation to illustrate the ammonolysis.

Ans. For alcohols:

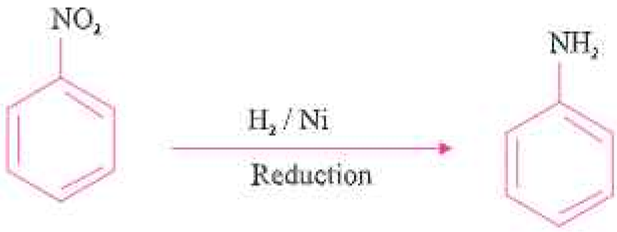
$$C_2H_5OH \xrightarrow[Al_2O_3 / 620K]{NH_3} C_2H_5NH_2 \xrightarrow[-H_2O]{C_2H_5OH} (C_2H_5)_2NH \xrightarrow{C_2H_5OH} (C_2H_5)_3N$$

For alkyl halides:

$$C_2H_5I \xrightarrow[-HI]{NH_3 / 373K} C_2H_5NH_2 \xrightarrow[-HI]{C_2H_5I} C_2H_5)_2NH_2 \xrightarrow[-HI]{C_2H_5I} (C_2H_5)_3N \xrightarrow[-HI]{C_2H_5I} [(C_2H_5)_4N]^+I^-$$

9. Convert nitrobenzene into aniline.

Ans.



10. Convert C_6H_5COOH to $C_6H_5NH_2$

Ans.

11. Write the name of isomerism exhibited by different amines.

Ans. Chain, position, metamerism, functional.

12. Arrange the following compounds in increasing order of solubility in water:

$C_6H_5NH_2 < (C_2H_5)_2NH < C_2H_5NH_2$

13. What is the role of HNO_3 in the nitrating mixture used for nitration of benzene.

Ans. HNO_3 provides NO_2^+ electrophile.

14. Why $C_6H_5\overset{+}{N_2}\overset{-}{Cl}$ not stored and is used immediately after its preparation?

Ans. It is highly unstable

15. What is the best reagent to convert $C_6H_5CONH_2$ into aniline?

Ans. $Br_2 + NaOH$

16. Write of IUPAC of

Ans. 2,4-Dinitrobenzamine/2,4 Dinitroaniline

17. Write the structure of N-Ethyl-N-methyl ethanamine

Ans. CH_3-CH_2-N-CH_3
$\quad\quad\quad\quad|$
$\quad\quad\quad CH_2$-CH_3

18. Rearrange the following compound in an increasing order of their basic strength.
Aniline, p-nitroaniline, P- toluidine.

Ans. p-Nitroaniline < Aniline < p-Toluidine

19. Ammonolysis of alkyl halide does not give amine in pure state why.

Ans. Because 2° and 3°, amines are also formed

20. A poisonous gas is formed by the reaction of R-NH_2 with $CHCl_3$, KOH. Give the name of the test.

Ans. Carbylamine test

21. Out of Pentan-1-ol and pent-1-amine which is more soluble.

Ans. pentan-1-ol

22. Identify A and B:
$CH_3COO\,C_2H_5 \xrightarrow{NH_3} A \xrightarrow{Br_2/KOH} B$

Ans. A- CH_3-$CONH_2$ B- CH_3-NH_2

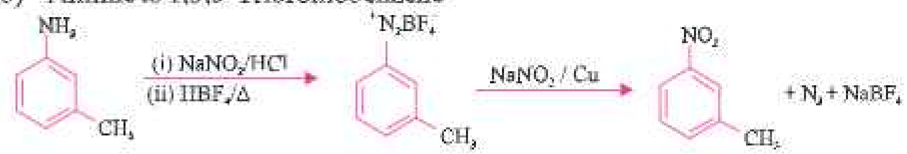
23. Write the name of test to distinguish between ethanamine and N-ethyle ethananine

Ans. Hinsberg Test.

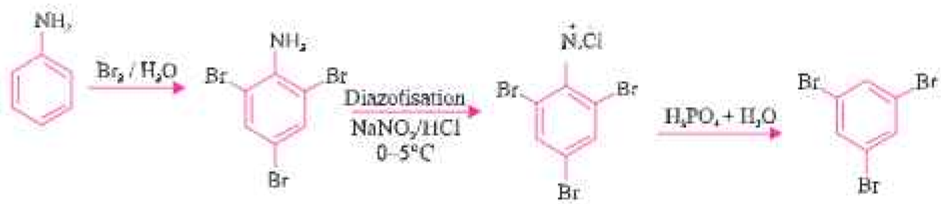
SHORT ANSWER TYPE QUESTIONS (2 or 3 Marks)

1. How will you convert following :
   (a) 3-Methlylaniline to 3-Nitrotoluene
   (b) Aniline to 1,3,5-Tribromobenzene

(a)



(b)



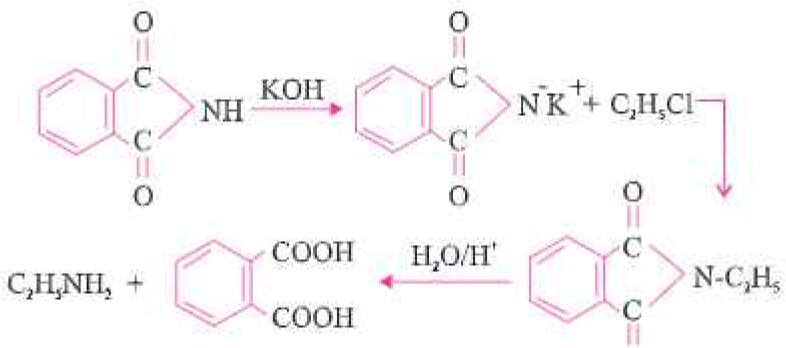
2. A compound 'A' having molecular formula C_3H_7ON reacts with Br_2 in presence of NaOH to give compound. 'B' This compound 'B' reacts with HNO_2 to form alcohol and N_2 gas. Identify compound 'A' and 'B' and write the reactions involved.

$$\underset{(A)}{CH_3CH_2CONH_2} \xrightarrow[NaOH]{Br_2} CH_3CH_2NH_2 \xrightarrow{HNO_2} \underset{(B)}{C_2H_5OH + N_2 + H_2}$$

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

Ans. (i) It is because aniline is protonated to form anilinium cation, in which $-NH_3^+$ group is *meta*-directing.
   (ii) It is because aniline is Lewis base can form adduct with $AlCl_3$ which deactivates the ring.

4. How will you synthesise ethanamine by Gabriel phthalimide synthesis?



phthalic acid

5. Write short notes on following:
   (a) Coupling reaction
   (b) Ammonolysis

Ans : (a) 

Ammonolysis : $R-X + NH_3 \rightarrow R-NH_2 + HX$

$RNH_2 + R-X \rightarrow (R)_2NH + HX$

$(R)_2NH + R-X \rightarrow (R)_3N + HX$

$(R)_3N + R-X \rightarrow [R_4N^+]X^-$

6. Account for the following :

(b) (a) Electrophilic substitution in aromatic amines takes place more readily than benzene.

(b) Nitro compounds have higher boiling points than hydrocarbons having almost same molecular mass.

Ans. (a) - NH_2 is electron releasing group so electrophilic substitution takes place faster.

(b) Nitro compounds are more polar than hydrocarbons therefore have more depole Waals forces of attraction.

7. Write the structure of reagents/organic compounds 'A' to 'E' :

Ans :

A B C D E

8. What happens when :

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

(b) An alkyl halide is treated with AgCN and product is hydrolysed.

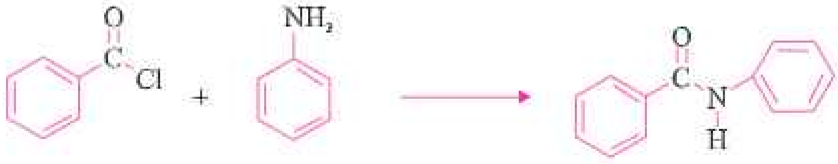
(c) Methyl magnesium bromide is treated with cyanogen chloride.

Ans. (a) $R-X + AgNO_2 \xrightarrow[-AgX]{} R-NO_2 \xrightarrow[{[H]}]{Sn/HCl} R-NH_2$

(b) $R-X + AgCN \xrightarrow[-AgX]{} RNC \xrightarrow{H_2O/H^+} RNH_2 + HCOOH$

(c) $CH_3MgBr + CN-Cl \rightarrow CH_3CN + Mg\begin{matrix} Cl \\ Br \end{matrix}$

9. Write reaction for benzoylation of aniline.

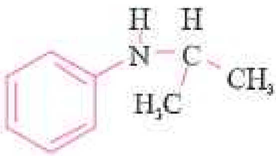
Ans :  + HCl

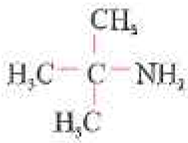
N-phenyl benzamide

10. Draw structure of the following compounds:

(a) N-Isopropylaniline

(b) t-Butylamine

Ans : (a) 

(b) 

11. Give reasons:

(a) Electrophilic substitution in aromatic amines takes place more readily than benzene

(b) Ethylamine and acetamide both contain amino group but acetamide does not show basic nature.

Ans: (a) -NH_2 group in aromatic amines shows +R effect and increases electron density on ring and facilitating the attack of electrophile.

(b) In acetamide the electron pair on nitrogen is in resonance with carbonyl group so electrons are less readily available than ethylamine.

12. An organic aromatic compound 'A' with the molecular formula C_6H_7N is sparingly soluble in water. 'A' on treatment with dil. HCl gives a water soluble compound 'B'. 'A' also reacts with chloroform in presence of alcoholic KOH to form an obnoxious smelling compound 'C'. 'A' reacts with benzene sulphonyl chloride to form alkali soluble compound 'D'. 'A' reacts with $NaNO_2$ and HCl to form a compound `E' which on reaction with phenol forms an orange dye. Elucidate the structures of the organic compounds from 'A' to 'F'.

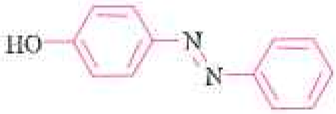

A


B


C


D

E


F


13 Write chemical distinguish test between following pair of compound.

(i) Aniline and N-Methylaniline

(ii) $(CH_3)_2$ NH and $(CH_3)_3N$

Ans. (i) Aniline + $CHCl_3$+KOH $\rightarrow$  Foul smell

N-Methyl aniline + $CHCl_3$ + KOH $\rightarrow$ No reaction

(ii) $(CH_3)_2$ NH+HNO_2 Yellow oily compound

$(CH_3)_3N$ + HNO_2 Salt soluble in water

14. Write the main product when benzene dyazonium salt reacts with following reagent

(i) HBF_4/Δ (ii) Cu/HBr (iii) H_2O

Ans. (i)


(ii)

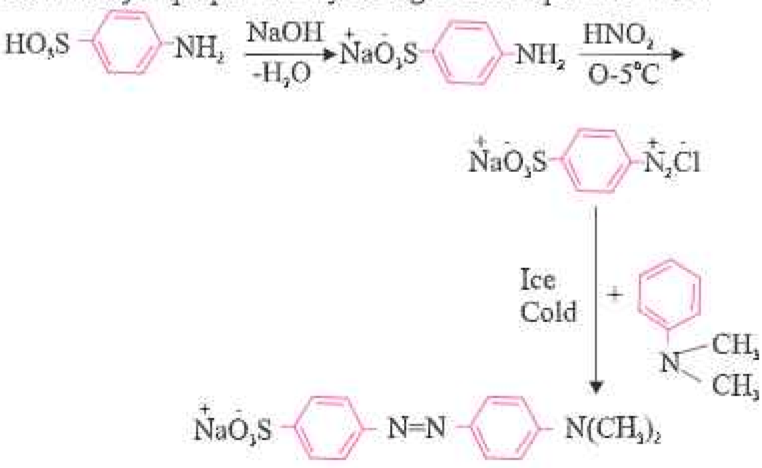

(iii)


15. Write the method to prepare a pure sample of primary amine having one more carbon than the alkyl halide used ?

Ans. $R\text{-}X \xrightarrow{KCN\ (Alc)} R\text{-}CN \xrightarrow[\text{(Reduction)}]{LiAlH_4} R\text{-}CH_2\text{-}NH_2$

16. How will you prepare methyl orange from sulphanilic acid ?

Ans.



Methyl Orange

17. Why methylamine in water react with ferric chloride to precipitate hydrated ferric oxide.

Ans: Methylamine form soluble hydroxide in reacting with water the $\overline{O}H$ ion released combine with Fe^{3+} ion to give forric hydroxide.

$$CH_3NH_2 + H_2O \longrightarrow CH_3N^+H_3 + \overline{O}H$$

$$2Fe^{3+} + 6\ddot{O}H^- \longrightarrow 2Fe(OH)_3 \text{ or } Fe_2O_3.3H_2O$$

18. Complete the following reactions:

(i) $R\text{-}\overset{O}{\overset{\|}{C}}\text{-}NH_2 \xrightarrow[H_2O]{LiAlH_4}$

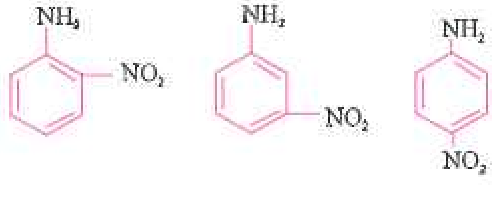
(ii) $C_6H_5N_2Cl + H_3PO_2 + H_2O \longrightarrow$

(iii) $C_6H_5\ NH_2 +$ Conc. $HNO_3 \longrightarrow$

Ans. (i) $R\text{-}CH_2\text{-}NH_2$

(ii) C_6H_6

(iii)



19. Give reason why trimethylamine reacts with BF_3 while triphenylamine does not.

Ans: In trimethylaniline $(Me)_3N$, the methyl group show +I effect , hence increase the reactivity towards Lewis acid (BF_3). While in $(Ph_3)_3$ N, Phenyls group (C_6H_5) show -I effect which decrease the e^- density over N atom. hence reactivity decreases towards Lewis acid (BF_3)

20. Justify with suitable reason: Why is para nitroaniline is weaker base than m-nitro aniline?

Ans. Because Nitro group at para position exhibits a strong electron withdrawing effect dut to –R and –I effects and hence decreases electron density from $-NH_2$ as compared to nitro group at m-position, where it only exhibits –I effect.

LONG ANSWER TYPE QUESTIONS (5 Marks)

1. Arrange the following :
   (a) In decreasing order of pK_b value
   $C_2H_5NH_2, C_6H_5NHCH_3, (C_2H_5)_2NH$ and $C_6H_5NH_2$
   (b) In increasing order of basic strength:
   (i) Aniline , *p*-Nitroaniline and *p*- Toluidine
   (ii) $C_6H_5NH_2$, $C_6H_5NHCH_3$, $C_6H_5CH_2NH_2$
   (c) In decreasing order of basic strength :
   $C_6H_5NH_2$, $(CH_3)_2NH$, CH_3NH_2
   (d) Decreasing order of basic strength in gas phase :
   $C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$, NH_3
   (e) Increasing order of boiling point :
   C_2H_5OH, $(CH_3)_2NH$, $C_2H_5NH_2$

Ans : (a) $C_6H_5NH_2 > C_6H_5NHCH_3 > C_2H_5NH_2 > (C_2H_5)_2NH$
   (b) (i) *p*- Nitroaniline < Aniline < *p* -Toluidine
   (ii) $C_6H_5NH_2 < C_6H_5NHCH_3 < C_6H_5CH_2NH_2$
   (c) $(CH_3)_2NH > CH_3NH_2 > C_6H_5NH_2$
   (d) $(C_2H_5)_3N > (C_2H_5)_2NH > C_2H_5NH_2 > NH_3$
   (e) $(CH_3)_2NH < C_2H_5NH_2 < C_2H_5OH$

2. How will you convert the following compound:
   (i) Ethanoic acid into Methanamine
   (ii) Hexanenitrile into 1- Aminopentane
   (iii) Nitromethane to Dinethylamine
   (iv) Ethanamine into Methanamine

Ans. (i) $\underset{\text{Methanol}}{CH_3COOH} \xrightarrow{NH_3} CH_3CONH_2 \xrightarrow[NaOH]{Br_2} CH_3NH_2$

(ii) $\underset{\text{Hexane nitrile}}{CH_3(CH_2)_4CN} \xrightarrow[\text{partial hydrolysis}]{\text{Conc. HCl}} \underset{\text{Hexanamide}}{CH_3(CH_2)_4CONH_2} \xrightarrow{Br_2/KOH} \underset{\text{1-Aminopentane}}{CH_3(CH_2)_4NH_2}$

(iii) $\underset{\text{Methanol}}{CH_3NO_2} \xrightarrow{H_2/Ni} CH_3NH_2 \xrightarrow{CHCl_3/KOH} CH_3NC \xrightarrow{H_2/Ni} \underset{\text{Ethanoic acid}}{CH_3NH{-}CH_3}$

(iv) $\underset{\text{Ethanamine}}{CH_3CH_2NH_2} \xrightarrow[(NaNO_2 + HCl)]{HNO_2} CH_3CH_2OH \xrightarrow{KMnO_4/H^+} CH_3COOH \xrightarrow{aq.\ NH_3} CH_3COONH_4$

$\xrightarrow{heat} CH_3CONH_2 \xrightarrow{Br_2/KOH} \underset{\text{Methanamine}}{CH_3NH_2}$

3. Write short note on the following :-

(a) Carbylamine reaction

(b) Diazotization

(c) Hoffmann bromamide reaction

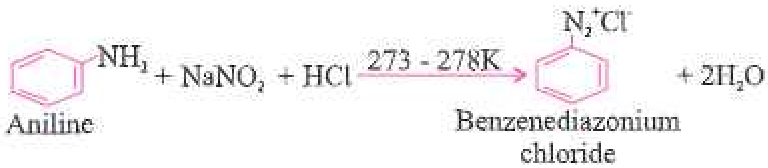
(d) Coupling reaction

(e) Ammonolysis

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

$$RCH_2NH_2 + CHCl_3 + 3KOH\ (alc.) \longrightarrow RCH_2NC + 3KCl + 3H_2O$$

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



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

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

$$R-\overset{\overset{O}{\|}}{C}-NH_2 + Br_2 + 4KOH \longrightarrow RNH_2 + K_2CO_3 + 2KBr + 2H_2O$$

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

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

Benzendiazonium chloride — Phenol — *p*-Hydroxyazobeneze (Azo dye)

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

$$RCH_2Cl + NH_3 \xrightarrow[-HCl]{} RCH_2NH_2 \xrightarrow[-HCl]{RCH_2Cl} (RCH_2)_2NH \xrightarrow[-HCl]{} (RCH_2)_3N \xrightarrow[-HCl]{RCH_2Cl} (RCH_2)_4\overset{+}{N}\overset{-}{Cl}$$

4. Complete the following reaction :-

(i) $C_6H_5NH_2 + H_2SO_4(\text{conc.}) \rightarrow$

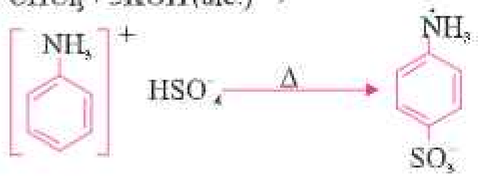
(ii) $C_6H_5N_2Cl + C_2H_5OH \rightarrow$

(iii) $C_6H_5NH_2 + (CH_3CO)_2O \rightarrow$

(iv) $C_6H_5N_2Cl + H_3PO_2 + H_2O \rightarrow$

(v) $C_6H_5NH_2 + CHCl_3 + 3KOH\,(\text{alc.}) \rightarrow$

Ans: (i)



(ii) $C_6H_6 + N_2 + HCl + CH_3CHO$

(iii) $C_6H_5NHCOCH_3 + .CH_3COOH$

(iv) $C_6H_6 + H_3PO_3 + HCl + N_2$

(v) $C_6H_5NC + 3KCl + 3H_2O$

5. Accomplish the following conversion :-

(i) $C_6H_5NO_2 \rightarrow C_6H_5COOH$

(ii) Benzene → *m*-Bromophenol

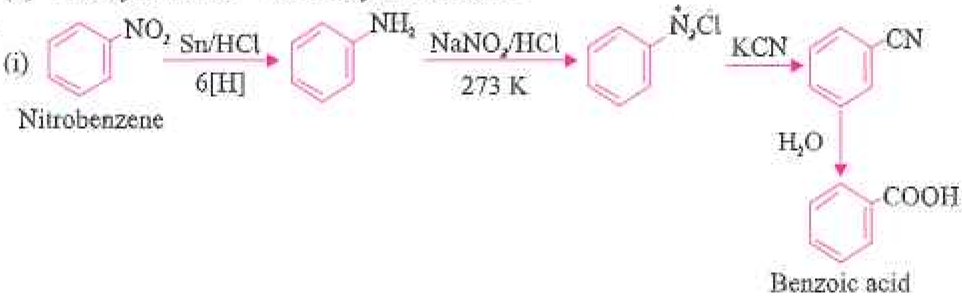
(iii) $C_6H_6COOH \rightarrow C_6H_5NH_2$

(iv) Aniline → 2,4,6 -Tribromoaniline

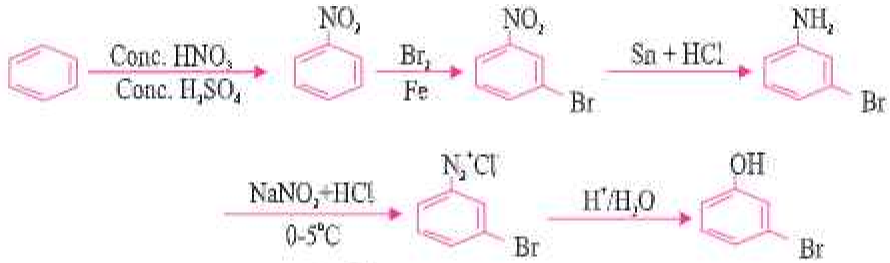
(v) Benzylchloride → 2-Phenylethanamine

Ans:-

(i)



(ii)



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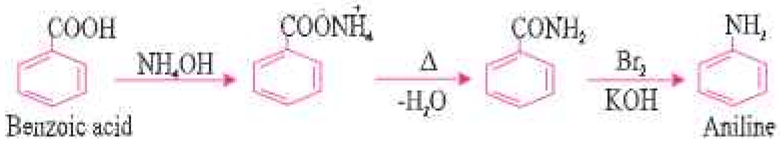

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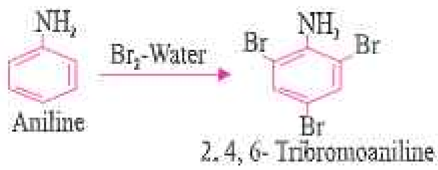

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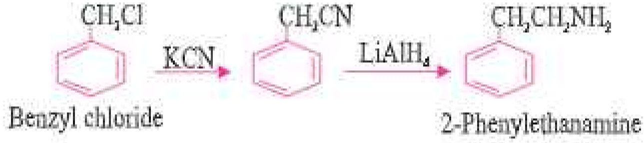


7. Write A,B and C in the given reaction sequences;

(i) $C_6H_5N_2Cl \xrightarrow{CuCN} A \xrightarrow{H_2O/H^+} B \xrightarrow{NH_3} C$

(ii) $CH_3CH_2Br \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow{HNO_2} C$

(iii) $C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow[273K]{HNO_2} B \xrightarrow[\Delta]{H_2O/H_+} C$

(iv) $CH_3COOH \xrightarrow[\Delta]{NH_3} A \xrightarrow{NaOBr} B \xrightarrow{NaNO_2/HCl} C$

(v) $CH_3CH_2I \xrightarrow{NaCN} A \xrightarrow[\text{Partial hydrolysis}]{OH^-} B \xrightarrow{NaOH/Br_2} C$

Ans. (i) C_6H_5CN, C_6H_5COOH, $C_6H_5CONH_2$

(ii) CH_3CH_2CN, $CH_3CH_2CH_2NH_2$, $CH_3CH_2CH_2OH$

(iii) $C_6H_5NH_2$, $C_6H_5\overset{+}{N}_2\overset{-}{Cl}$, C_6H_5OH

(iv) CH_3CONH_2, CH_3NH_2, CH_3OH

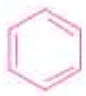
(v) CH_3CH_2CN, CH_3CH_2-CO-NH_2, CH_3-CH_2-NH_2

8. An organic compound 'A' on treatment with aqueous ammonia and heating forms compound 'B' which on heating with Br_2 and KOH forms a compound 'C' of molecular formula C_6H_7N. Write the structure and IUPAC of compound A, B and C.

Ans.

9. Write the structure of compound **A** to **E** in the following sequence of reaction. E is N-methyaniline

$$[A] \xrightarrow[H_2SO_4]{HNO_3} [B] \xrightarrow[\Delta]{Sn/HCl} [C] \xrightarrow[KOH/\Delta]{CHCl_3} [D] \xrightarrow{H_2/Pt} [E]$$

Ans. A= 

Benzene

B=  Nitrobenzene

C=  Aniline

D=  Phenylisocyanide

E=  N-methylaniline

10. Write the structure A, B, C, D, E in the given reaction.

$$C_6H_5NH_2 \xrightarrow[\text{Pyridine}]{CH_3COCl} [A] \xrightarrow[\Delta]{Br_2\ CH_3COOH} [B] \xrightarrow{H^+} [C]$$

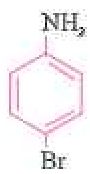
$$C_6H_5NH_2 \xrightarrow{CHCl_3+KOH} D$$

$$[A] \xrightarrow{HNO_3+\ H_2SO_4} E$$

Ans.

A= $C_6H_5NHCOCH_3$

B= 

C= 

D= 

E= 

CASE-STUDY BASED QUESTIONS

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

Friedel-Crafts (FC) reaction is an important method to incorporate carbon skeletons into aromatic system. Great successes have been achieved for the hydroarylation of neutral arenes (such as toluene, anisole, and their homologues). Because the FC reactions typically require Lewis acid catalysts, for arenes containing nitrogen atom, the substrate scope of FC reactions are quite limited due to the coordination between amine and Lewis acid catalyst, except indole and pyrrole. Being profited from the extremely weak basic properties, acid-catalyzed additions of indole and pyrrole to alkenes have obtained great achievements. However, the hydroarylation of alkaline arenes to alkenes still remains many challenges. Some researches have shown the possibility of hydroarylation between the parent anilines $C_6H_5NH_2$ and alkenes. However, the reaction of arenes with stronger basicity (such as N,N-dimethylaniline and N,N-diethylaniline) still is a big problem, due to their ability to coordinate with Lewis acid catalyst which can lead to deactivation of the aromatic ring. Furthermore, alkaline arenes can trap the proton in the C-H activation process and the reaction will be terminated as result.

Recently, Bertrand et al. reported an anti-Bredt cyclic diaminocarbene which showed increased λ-accepting character without diminishing its cs-donor property. We found that Gold(I) compound derived from this new carbene can be used as effective catalyst for the FC reaction between alkenes and N,N-dialkylanilines. Now, these new FC reactions are receiving more and more research interests. As we known, most of the electrophilic substitution reactions followed the Markovnikov rule. For the FC reaction of alkenes, the reactions following the Markovnikov rule should form branched product. Only several examples were reported on the formation of linear product by anti-Markovnikov rule. For the FC reactions between alkenes and N, N-dialkylanilines catalyzed by carbene Gold(I), both Markovnikov and anti-Markovnikov hydroarylations were observed and all these reactions gave high para-selectivity products. The selectivity to the branched or linear product was highly depended on the structure of alkenes.

Reference : Wu, H., Zhao, T. & Hu, X. **Friedel-Crafts Reaction of N,N-Dimethylaniline with Alkenes** *Catalyzed by Cyclic Diaminocarbene-Gold(I) Complex. Sci Rep* 8, 11449 (2018). https://doi.org/10.1038/s41598-018-29854-0

(A) Why aniline does not undergoes Friedel-Crafts reaction?

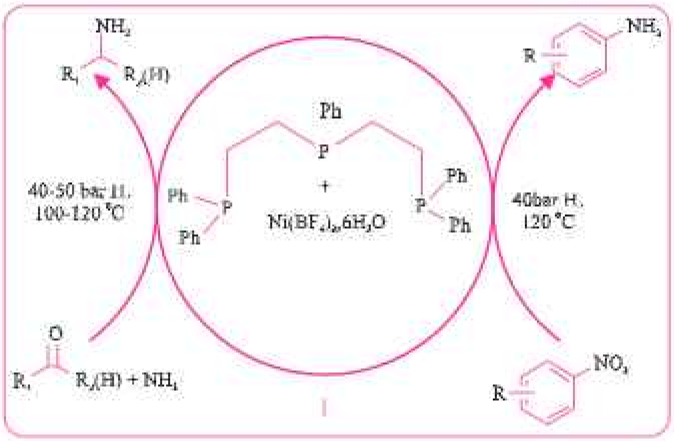
(B) Write reaction to convert aniline into N,N-dimethylaniline.

(C) How *p*- Nitroaniline can be synthesised from Aniline?

(D) Why -NH_2 group in aniline is *ortho-*, *para-* directing?

2. **Read the passage and answer the following questions:**

The development of base metal catalysts for industrially relevant amination and hydrogenation reactions by applying abundant and atom economical reagents continues to be important for the cost-effective and sustainable synthesis of amines which represent highly essential chemicals. In particular, the synthesis of primary amines is of central importance because these compounds serve as key precursors and central intermediates to produce value-added fine and bulk chemicals as well as pharmaceuticals, agrochemicals and materials. Here we report a Ni-triphos complex as the first Ni-based homogeneous catalyst for both reductive amination of carbonyl compounds with ammonia and hydrogenation of nitroarenes to prepare all kinds of primary amines. Remarkably, this Ni-complex enabled the synthesis of functionalized and structurally diverse benzylic, heterocyclic and aliphatic linear and branched primary amines as well as aromatic primary amines starting from inexpensive and easily accessible carbonyl compounds (aldehydes and ketones) and nitroarenes using ammonia and molecular hydrogen. This Ni-catalyzed reductive amination methodology has been applied for the amination of more complex pharmaceuticals and steroid derivatives. Detailed DFT computations have been performed for the Ni-triphos based reductive amination reaction, and they revealed that the overall reaction has an inner-sphere mechanism with H_2 metathesis as the rate determining step.



Reference : Kathiravan Murugesan, Zhihong Wei, Vishwas G. Chandrashekhar, Haijun Jiao, Matthias

Beller, Rajenahally V. Jagadeesh **General and selective synthesis of primary amines using Ni-based homogeneous catalysts**_*Chem. Sci.*, 2020, 11, 4332-4339

(A) Convert nitrobenzene to chlorobenzene.

(B) What happens when butanone reacts with ammonia according to scheme given above.

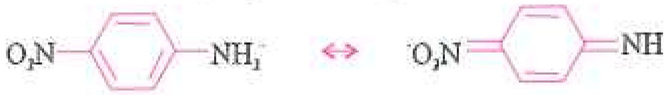
(C) Mention one method, other than mentioned here for conversion of nitrobenzene to aniline.

3. **Read the passage and answer the following questions:**

For a group of nitro-substituted amilines and diphenylamines, a plot of PICHA (ordinate) against $pK_{BH}{}^{+}$ gave a straight line of slope 0.6. That is, the acidities of the amines seemed to be affected to a smaller extent by ring substitution than were their basicities.

$$ArNH_3^+ \xleftarrow{H^+} ArNH_2 \xrightarrow{-H^+} ArNH^-$$

This result was somewhat surprising because, although resonance with the nitro group occurs in both the neutral amine and the anion, and hence affects both equilibria, it involves a very important charge delocalization in the amide anion.



It has been suggested that the nitro substituent has an anomalous effect in acid mixtures (2), where some of the pK_{BH}^{+} values had been determined. In the course of extending the H— scale to very basic values, we had the opportunity to use amines containing substituents other than nitro (3) and to determine if the unusual effect of substituents on acidity vis-a-vis basicity was due to the presence of nitro groups. In accompanying papers the pK_{BH}^{+} values (4) and the pK_{HA} values of these aromatic amines are reported. (The basicities of amines are described, as is customary, in terms of the acidity of their conjugate acids.)

Reference : Ross Stewart and Douglas Dolman. **A comparison of the acidity and basicity of aromatic amines**. *Canadian Journal of Chemistry*. 45(9): 925-928. https://doi.org/10.1139/v67-156

(A) Which of the following has highest pK_b value?

(a) Aniline

(b) *p*-Nitoaniline

(c) *m*-Nitroaniline

(d) *o*-Nitroaniline

(B) Why basic strength of aliphatic amines are higher than ammonia?

(C) What will be the correct order of basic strength of following: Et NH_2, $(Et)_2$ NH, $(Et)_3$N

(D) What happens when aniline reacts with sulphuric acid?

ANSWERS

I MULTIPLE CHOICE QUESTIONS

1. b 2. d 3. a 4. d 5. c 6. a 7. b 8. c 9. c 10. a
11. c 12. d 13. a 14. a 15. c 16. b. 17. a. 18. c 19. a 20. c

II FILL IN THE BLANKS

1.	Aniline	2.	weaker, stronger
3.	Primary aliphatic	4.	Hinsberg
5.	Butanamine	6.	Acetylation
7.	*meta*	8.	Water.
9.	H-bonding		

III ASSERTION REASON TYPE QUESTIONS

1. c 2. c 3. a 4. b 5. a 6. c 7. a 8. a 9. b 10. a

IV ONE WORD ANSWER TYPE QUESTIONS

1.	Carbylamine reaction	2.	2,4,6-tribromoaniline
3.	Aniline	4.	weaker
5.	Friedel-Crafts reaction	6.	Benzene
7.	Sandmeyer	8.	S_N2
9.	pH-9 to 10	10.	Sn + HCl
11.	8	12.	$LiAlH_4$
13.	S_N1/S_N2		
14.	Pyridine		

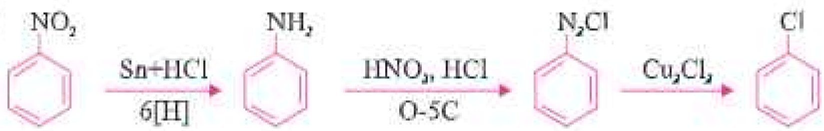
CASE STUDY BASED QUESTIONS

1: (A) Aniline forms salt with anhydrous $AlCl_3$.

(B) 

(C) Refer NCERT

(D) Due to +R effect of $-NH_2$ group.

2: (A) 

(B) $$CH-\overset{\displaystyle O}{\overset{\|}{C}}-CH_2-CH_3 \xrightarrow[\text{(ii) } H_2/Ni]{\text{(i) } NH_3} CH_3-\underset{\displaystyle NH_2}{\underset{|}{CH}}-CH_2-CH_3$$

(C) 

3: (A) (d)

(B) Due to +I effect of -R groups present in aliphatic amines

(C) $(Et)_2NH$, $(Et)_3N$, $EtNH_2$

UNIT TEST-1
Amines

Maximum Marks : 20 **Time Allowed : 1 Hour**

1. Benzamide reacts with Br_2 and NaOH forming.................................. 1
2. The correct order of basicity of amines is: 1
   (a) Ammonia > Ethanamine > Aniline
   (b) Ethanamine > Ammonia > Aniline
   (c) Ammonia > Aniline > Ethanamine
   (d) Ethanamine > Aniline > Ammonia
3. When aniline reacts with $NaNO_2$/HCl then reaction with CuCN followed by acidic hydrolysis. What will be the final product of the reaction? 1
   (a) Nitrobenzene (b) Benzaldehyde
   (c) Benzoic acid (d) Phenol
4. Assertion: Aniline forms 2,4,6-tribromoaniline on reaction with bromine water.
   Reason: $-NH_2$ is *ortho, para-* directing. 1
   (a) Both assertion and reason are correct statements and reason is correct explanation of assertion.
   (b) Both assertion and reason are correct statements but reason is not correct explanation of assertion.
   (c) Assertion is correct statement but reason is wrong statement.
   (d) Assertion is wrong statement but reason is correct statement.
5. Assertion: Primary amines cannot be synthesised by Gabriel phthalimide synthesis.
   Reason: Due to steric hindrance caused by bulky group substitution is not possible.
   (a) Both assertion and reason are correct statements and reason is correct explanation of assertion. 1
   (b) Both assertion and reason are correct statements but reason is not correct explanation of assertion.
   (c) Assertion is correct statement but reason is wrong statement.
   (d) Assertion is wrong statement but reason is correct statement.
6. How will you synthesise Butanamine by Gabriel phthalimide synthesis? 2
7. Write chemical test distinguish to between following pair of compounds: 2
   (a) Aniline and Benzylamine

(b) Methylamine and Dimethylamine

8. How will you convert the following compound: 2

(a) Ethanoic acid to methanamine

(b) Aniline to *p*-Bromoaniline

9. An aromatic compound 'A' on treatment with aqueous ammonia and heating forms compound 'B' which on heating with Br_2 and KOH forms a compound 'C' of molecular formula $C_6H_{15}N$. Write the structures and IUPAC names of compounds A, B and C. 3

10. Write short notes on following: 3

(a) Benzoylation reaction

(b) Hoffmann bromamide degradation reaction

(c) Carbylamine reaction

11. Explain with suitable reason: 3

(a) Acetylation of aniline reduces its activation effect.

(b) CH_3NH_2 is more basic than CH_3CONH_2.

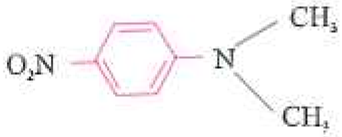
(c) Nitration of aniline gives significant amount of *meta*-Nitroaniline in addition to *o*- and *p*-Nitroaniline.

UNIT TEST-II

Amines

Maximum Marks : 20 **Time Allowed : 1 Hr**

1. Give the IUPAC of following compound. 1



2. Give reason:- aniline does not undergo friedel craft alkylation. 1
3. How will you convert Benzene into aniline 1
4. What is Hinsberg reagent. 1
5. Out of butan-1-ol and but-1-amine which one has higher boiling point? 1
6. Write short note on following: 2

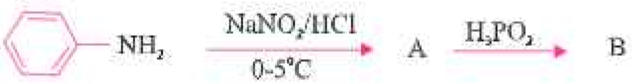
   (i) Gabriel pnthalinide synthesis

   (ii) Diazotisation
7. Write chemical distinguish test between following pair. 2

   (a) Aniline and benzylamine

   (b) Ethane amine and N, N-dimethylethanamine.
8. Complete the following reaction. 2

   (i) 

   (ii) 

9. Arrange the following as per mentioned properties. 3

   (a) Ethane amine, N-ethylethaneamine, N-N-diethylethnane amine (Basic strength in aqueous medium)

   (b) Aniline, p-Nitroaniline, p-Tolidine (increasing basic character)

   (c) $C_6H_5NH_2$, $(C_2H_5)_2NH$, $C_2H_5NH_2$ – increasing order of solubility in water.
10. Convert the following compounds: 3

    (a) Benzamide to toluene

    (b) Aniline to 2,4,6 - Tribromofluorobenzene

    (c) Chlorobenzene to *p*-chloroaniline.
11. Two isomeric compound 'A' and 'B' having molecular formula $C_4H_{11}N$, both lose N_2 on treatment with HNO_2 and gives compound 'C' and 'D' respectively. 'C' is resistant to oxidation but immediately respond to Lucas reagent. Whereas 'D' respond to Lucas reagent after 5 minutes and gives a positive iodoform test. Identify A, B, C, D. 3

UNIT 14

BIOMOLECULES

Points to Remember

Biomolecules

These are the macromolecules essential for survival of life, e.g. carbohydrotes, proteins, etc.

Carbohydrates

These are polyhydroxy aldehydes or ketones or their derivatives, e.g. glucose.

Sugars

These are the carbothydrates having sweet taste.
They may be reducing or non-reducing.

Glucose

- It is obtained by hydrolysing starch or cane sugar.
- its reactions are as:

Glucose $\xrightarrow[\Delta]{HI}$ n-hexane:

$\xrightarrow[3\ mol]{NH_2OH}$ Oxime

$\xrightarrow{Br_2 Water}$ Gluconic acid

$\xrightarrow[CH_3COCl]{Acetylation}$ Pentaacetate

$\xrightarrow{HNO_3}$ Saccharic Acid

Sucrose

- It contains D-(+)glucose and D(-) fructose joined together by β -1,2-glycosidic linkage.
- It is also called invert sugar.

Proteins

These are polymers of α-amino acids.

Amino Acids

These contain amino as well as carboxyl functional group.
They may be essential or non-essential,

Zwitter Ion

Ion containing positive as well as negative charge is called zwitter ion.

e.g. $R-\underset{{}^{+}NH_3}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-O^-$

Denaturation

- It is the process of destroying 2° or 3° structure of protein by heating and by changing pH.
- Due to this, protein losts its biological activity.
- e.g. coagulation of egg white on boiling.

Vitamins, Nucleic Acids and Hormones

Vitamins

These are essential but in very small amounts. Vitamins A, D, E and K are fat soluble while rest are water soluble.

Deficiency Diseases

Vitamin	Deficiency Disease
A	Xerophthalmia
B_1	Beri-beri
B_{12}	Pernicious anaemia
C	Scurvy
D	Rickets
E	Infertility
K	Icreased blood clotting time
H	Loss of hair

Nucleic acid: These are the polymer of nucleotides(Sugar + base+ Phosphoric acid)

DNA	RNA
i) Double helical.	i) Single stranded.
ii) Sugar is 2-deoxyribose.	ii) Sugar is ribose.
iii)Bases : A, T, G, C.	iii)Bases : A,U,G,C.
iv)Property of replication.	iv)Do not replicate.
v) It is responsible for transmission of heredity Character	v) Helps in protein biosynthesis.

Hormones: These are the chemicals secreted by Endocrine glands.

Starch
- It contains two components: amylose (water soluble, 20%) and amylopectin (80%, water insoluble).
- It is the reserve food of plants.

Cellulose
- Most abundant in plants and contains glucose units, joined together by β-1, 4-glycosidic linkage.

Enzymes: There are the proteins which catalyse reaction occuring in human body, they are also known as biocatalysts e.g. Invertase, Zymase etc.

Structure of Proteins

Primary structure: It shows the sequence of amino acids in a Polypeptide chain

Secondary structure: It is formed due to H-bonding and may be α-helix or β-pleated sheet structure.

Tertiary structure: Represents overall folding of the polypeptide chain.

Quaternary structure: Protein can be composed of two or more polypeptide chains called sub-units. The spatial arrangement of these sub-units with respect to each other is quaternary structure of the protein.

TYPES OF PROTEINS

Fibrous Protein: Polypeptide chains run parallel or anti-parallel and held together by hydrogen and disulphide bonds. e.g. keratin, collagen

Globular Protein : Chains of polypeptide coil around to give a spherical shape. e.g. insulin, albumin

1. **Carbohydrates :** These are optically active polyhydroxy aldehydes or ketones or the compounds which produce these on hydrolysis.

2. **Classification :**

   (i) Monosaccharides : Those carbohydrates which cannot be hydrolysed into further simpler carbohydrates. e.g, glucose, fructose, galactose etc.

   (ii) Disaccharides : Those carbohydrates which produces two monosaccharides on hydrolysis. e.g, sucrose, maltose and lactose.

   (iii) Oligosaccharides : Those carbohydrates which give two to ten monosaccharides on hydrolysis.

   (iv) Polysaccharides : Those carbohydrates which on hydrolysis gives large number of monosaccharides on hydrolysis. e.g, starch, cellulose, glycogen.

3. **Sugar :** Carbohydrates which are sweet in taste.

   (i) Reducing sugars : Those which reduce Fehling's or Tollens' reagent due to availability of free aldehydic groups. e.g, glucose, fructose, galactose.

   (ii) Non-reducing sugars : Those which do not reduce Fehling's or Tollens' reagent. They do not have free aldehydic group. e.g, sucrose.

4. **Glucose :** It is a monosaccharide with molecular formula $C_6H_{12}O_6$.

5. **Preparation of Glucose:**

   (i) From sucrose :

$$\underset{}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6} \quad \text{(only from sucrose)}$$

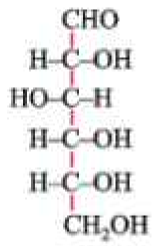
   (ii) From starch :

$$(C_6H_{10}O_5)_n + nH_2O \rightarrow C_{12}H_{22}O_{11} + H_2O \rightarrow \underset{\text{glucose}}{2C_6H_{12}O_6}$$

6. **Structure :**

   Fischer structure :

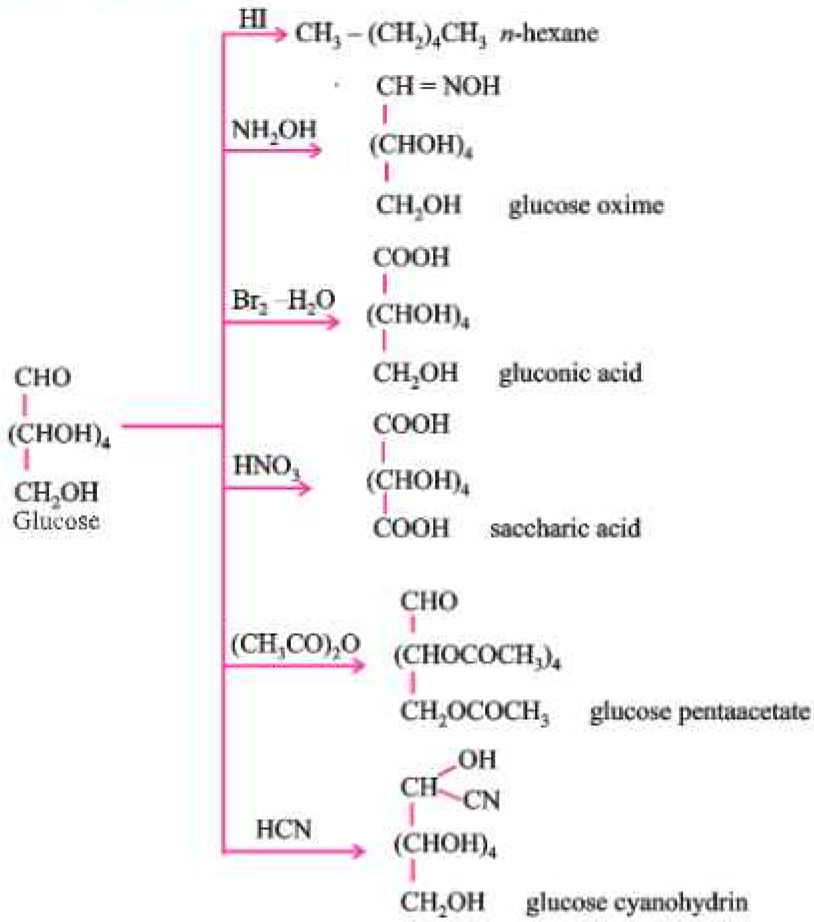
   (+) glucose has 'D' configuration as shown :



D-(+)-glucose

'D'- means – OH group on first chiral 'C' from the bottom is on right hand and (+) means it is dextrorotatory *i.e.,* it rotates plane polarized light towards right.

Reactions of glucose :



Objections against open chain structure of glucose

The open chain structure was unable to explain the following reactions :

(a) It does not give the 2, 4-DNP test, Schiff's test and does not form the **hydrogensulphite** addition product with $NaHSO_3$

(b) The pentacetate of glucose does not react with NH_2OH, indicating the absence of free aldehydic group.

(c) Glucose exist in 2 different crystalline forms α and β forms. These are called anomers. They differ in optical rotation, they also differ in melting point.

After which a close chain (cyclic) structure of glucose was proposed by Haworth.

* Anomers are isomers which have a different configuration at C-1 functional group

7. **Glycosidic linkage :** The linkage between two monosaccharide units through oxygen is called the glycosidic linkage.

8. **Proteins :** These are macro molecules made up of amino acids joined by amide linkage (– CONH –) is called as peptide linkage. These are required for growth and development of the body.

9. **Amino acids :** These contain an amino (- NH_2) and an acidic (- COOH) group and are therefore amphoteric in nature. In solution, they exist in the form of zwitter ion (a dipolar ion).

10. **Native state of protein :** The parental state or the natural state in which the protein is found.

11. **Denaturation of protein :** Destruction of the native state of protein is denaturation. It can be brought by physical and chemical methods. The 2° and 3° structures are destroyed, only 1° structure is retained.

Enzymes : These are biocatalyst and generally globular proteins *e.g.,* invertase, zymase, phenylalanine hydroxylase, urease etc.

Main characteristics of enzymes :

(i) It speed up the biological reaction upto million times.

(ii) It is highly specific and work on lock and key theory.

(iii) It is highly sensitive to pH and temperature.

12. **Nucleic acids :** These are biomolecules which are long chain polymers of nucleotides. They are of two types :

(i) Deoxyribonucleic acid (DNA)

(ii) Ribonucleic acid (RNA)

13. Nuceloside = Base + Sugar

Nucleotide = Base + Sugar + Phosphoric acid

OBJECTIVE TYPE QUESTIONS

I MULTIPLE CHOICE QUESTIONS

1. Which of the following acids is a vitamin?

(a) aspartic acid (b) ascorbic acid

(c) oxalic acid (d) saccharic acid

2. Non-reducing sugar out of following is -

(a) Glucose (b) Sucrose

(c) Maltose (d) Lactose

3. In a protein molecule amino acids are linked together by:

(a) Peptide linkage (b) Coordinate bond

(c) Glycosidic linkage (d) Phospodiester linkage

4. One strand of DNA has the sequence. ATGCTT, the sequence of complementary strand would be:

(a) TCCGAA (b) TACGTA

(c) TACGAA (d) TAGCTA

5. Which of the following vitamin is water soluble?

(a) Vitamin C (b) Vitamin D

(c) Vitamin K (d) Vitamin E

6. In both DNA and RNA, base and phosphate ester linkage are at -

(a) C'_5 and C'_2 respectively of sugar molecule

(b) C'_2 and C'_5 respectively of sugar molecule

(c) C'_5 and C'_5 respectively of sugar molecule

(d) C'_5 and C'_1 respectively of sugar molecule

7. The two functional groups present in a typical carbohydrates are:

   (a) -OH and -COOH (b) -CHO and -COOH

   (c) >C=O and -OH (d) -CHO and -COCl

8. The presence or absence of hydroxyl group on which carbon atom of sugar differentiates RNA and DNA.

   (a) 1st (b) 2nd

   (c) 3rd (d) 4th

9. The carbohydrate known as invert sugar is -

   (a) Lactose (b) Sucrose

   (c) Maltose (d) Glucose

10. Pick the disaccharide from following:

    (a) Maltose (b) Cellulose

    (c) Maltase (d) Starch

11. Which one of the following is not an aldose?

    (a) Glucose (b) Ribose

    (c) Fructose (d) Galactose

12. Biomolecule containing transition metal is-

    (a) Vitamin C (b) Chlorophyll

    (c) Haemoglobin (d) RNA

13. Which of the following does not have glycosidic linkage?

    (a) Maltose (b) Amylose

    (c) Galactose (d) Sucrose

14. Fibrous proteins are present in:

    (a) Haemoglobin (b) Albumin

    (c) Collagen (d) Insulin

15. Hydrolysis of lactose with dilute acid yields

    (a) equimolar mixture of D-glucose and D-fructose

    (b) equimolar mixture of D-glucose and D-galactose

    (c) equimolar mixture of D-galactose and D-fructose

    (d) equimolar mixture of D-galactose and D-sucrose

16. Match the carbohydrate in Column I with its characteristic given in Column II

Column-I	Column-II
(A) Lactose	(p) Ketohexose
(B) Starch	(q) Disaccharide
(C) Sucrose	(r) Polysaccharide
(D) Fructose	(s) on hydrolysis gives β-D-glucose and β-D-galactose

(a) A - s, B - r, C - p, D - q
(b) A - p, B - q, C - r, D - s
(c) A - r, B - s, C - p, D - q
(d) A - s, B - r, C - q, D - p

17. Match the carbohydrate in Column I with its characteristic given in Column II

Column-I	Column-II
(A) Keratin	(p) protein
(B) Haemoglobin	(q) β-pleated protein
(C) Riboflavin	(r) α-amino acid
(D) Glycine	(s) Water soluble vitamin

(a) A-p, B-q, C-s, D-r
(b) A-q, B-p, C-s, D-r
(c) A-q, B-p, C-r, D-s
(d) A-s, B-r, C-q, D-p

18. The number of chiral carbon present in β-D-(+)-glucose is:
(a) 2 (b) 4 (c) 5 (d) 1

19. Which of the following nitrogenous base is not present in RNA?
(a) Adenine (b) Uracil (c) Cytosine (d) Thymine

20. Hormone produced under stress which stimulates glycogenolysis in the liver of human being ?
(a) Thyroxin (b) Insulin (c) Adrenaline (d) Estradiol

II FILL IN THE BLANKS

1. The disease beri-beri is caused due to lack of ....
2. Scurvy is caused due to deficiency of ....
3. ....(carbohydrate) is not digested by human beings but digested by herbivorous animals.
4. ....on hydrolysis gives D-glucose and D-galactose.

5. Amylose and amylopectin are the two components of.........................
6. Carbohydrates which yields a large number of monosaccharide units on hydrolysis are called ....
7. Carbohydrates which reduce Tollens' reagent are called ....
8. Deficiency of .... leads to xerophthalmia and night blindness.
9. ....contains pentose sugar, and base whereas.........................contains pentose sugar, base as well as phosphate group.
10. The pair of stereoisomers which differ only in the configuration of the hydroxyl group at C-1 are called ....

III ASSERTION-REASON TYPE QUESTIONS

In each of the following questions, a statement of Assertion (A) is given followed by a corresponding statement of Reason (R) just below it. Of the statements, mark the correct answer as

(a) Both assertion and reason are correct, and reason is the correct explanation of the assertion.

(b) Both assertion and reason are correct, but reason is not the correct explanation of the assertion.

(c) Assertion is correct, but reason is incorrect.

(d) Assertion is incorrect but reason is correct.

1. **ASSERTION :** A solution of sucrose in water is dextrorotatory but on hydrolysis in presence of little HCl it becomes laevorotatory.

   REASON : Sucrose on hydrolysis gives unequal amount of glucose and fructose as a result sign of rotation changes.
2. **ASSERTION** : Fructose does not contain aldehyde group but still reduce Tollens' reagent.

   REASON : In the presence of base, fructose undergoes rearrangement to form glucose and mannose.
3. **ASSERTION :** D-(+)-Glucose is dextrorotatory in nature.

   REASON : 'D' represents its dextrorotatory nature.
4. **ASSERTION :** Vitamin D can be stored in our body.

   REASON : Vitamin D is fat soluble vitamin.

5. **ASSERTION :** All naturally occurring α-amino acids except glycine are optically active.

   REASON : Most naturally occurring amino acids have D-configuration.

6. **ASSERTION :** In presence of enzyme, substrate molecule can be attacked by the reagent effectively.

   REASON : Active sites of enzymes hold the substrate, molecule in a suitable position.

7. **ASSERTION:** Sucrose is a non-reducing sugar.

   REASON : It has glycosidic linkage.

8. **ASSERTION:** Vitamin C has to be continuously supplied through diet.

   REASON: Vitamin C is a water soluble vitamin, excreted by urine

9. **ASSERTION :** Cellulose is not digested by human beings.

   REASON : Cellulose is a polymer of β-D-glucose.

10. **ASSERTION:** Non-essential amino acids are not necessary for protein synthesis.

    REASON: Non-essential amino acids are produced in the human body.

IV ONE WORD ANSWER TYPE QUESTIONS

1. Name the component of starch which is water soluble.
2. Write the product formed when glucose is treated with HI.
3. What are the products of hydrolysis of maltose?
4. Name the purines present in DNA.
5. Write the name of linkage joining two amino acids.
6. The deficiency of which vitamin causes the disease pernicious anaemia.
7. Name the nitrogenous base that is found in nucleotide of RNA only.
8. Name the vitamin whose deficiency is responsible for poor coagulation of blood.
9. Write the product formed on reaction of D-glucose with Br_2 water.
10. Name the polysaccharide which is stored in the liver of animals.

VERY SHORT ANSWER TYPE QUESTIONS (1Marks)

Q. 1. What structural feature is required for a carbohydrate to behave as reducing sugar ?

Ans. The carbonyl group of any one monosaccharide present in carbohydrate must be free.

Q. 2. Give the significance of (+) sign in the name D-(+)-glucose.

Ans. (+) sign indicates dextro-rotatory nature of glucose.

Q. 3. Glucose is an aldose sugar but it does not react with sodium hydrogen sulphite. Give reason.

Ans. The – CHO group reacts with – OH group at C-5 to form a cyclic hemiacetal.

Q. 4. Why is sucrose called invert sugar ?

Ans. When sucrose is hydrolysed by water, the optical rotation of solution changes from positive to negative.

Q. 5. Name the amino acid which is optically inactive.

Ans. Glycine.

Q. 6. Give reason : Amylase present in the saliva becomes inactive in the stomach.

Ans. HCl present in stomach decreases the pH.

Q. 7. Name the interactions responsible for the stability of α-helical structure of proteins

Ans. Hydrogen bonding.

Q. 8. Which nucleic acid is responsible for carrying out protein synthesis in the cell ?

Ans. RNA (Ribonucleic acid)

Q. 9. When RNA is hydrolysed, there is no relationship among quantities of different bases obtained. What does this fact suggest about structures of RNA ?

Ans. RNA is single stranded.

Q. 10. What type of linkage holds together the monomers of DNA and RNA ?

Ans. Phosphodiester linkage.

Q. 11. Give the Haworth projection of D-glucopyranose.

Ans. 

α-D(+) Glucopyranose β-D(+) Glucopyranose

Q. 12. Where does the water present in the egg go after boiling the egg ?

Ans. On boiling, during denaturation process water gets absorbed in denaturated proteins.

Q. 13. Name two protein which is insoluble in water.

Ans. Keratin. Myosin

Q. 14. Mention two important functions of carbohydrates in plants.

Ans. Major energy source, storage molecules like starch in plants.

Q. 15. Name the different types of RNA molecules found in cells of organisms.

Ans. tRNA, mRNA, rRNA.

Q. 16. Why are carbohydrates generally optically active ?

Ans. Because they contain one or more chiral carbon.

Q. 17. During curdling of milk, what happens to sugar present in it ?

Ans. Lactose changes to lactic acid.

Q. 18. The two strands in DNA are not identical but complementary. Explain.

Ans. Base pairing rule is followed; A = T and G ≡ C. (Hydrogen bonding between complementary bases)

Q. 19. If one strand of DNA has the sequence 5'-G-G-A-C-T-A-C-T-3', what is the sequence of bases in the complementary strand ?

Ans. 3'-C-C-T-G-A-T-G-A-5'

Q. 20. What are monosaccharides ?

Ans. Sugars which cannot be hydrolysed to give simpler units or compounds.

Q. 21. What is the difference between native protein and denatured protein ?

Ans. Proteins found in a biological system with unique 3D-structure and biological activity is called native protein. When native protein is subjected to physical and chemical change, protein loses its biological activity and is called denatured protein.

SHORT ANSWER TYPE QUESTIONS (2 or 3 Questions)

Q. 1. Define the following terms in relation to proteins :

(i) Peptide linkage (ii) Denaturation

Ans. (i) Peptide linkage : A link between two amino acids with loss of water – CO – NH – peptide linkage.

(ii) A process that changes the three dimensional structure of native protein is called denaturation of protein. It results into breaking of hydrogen bonds and disulphide linkages. Thus, a completely denatured protein has a shape of random coil.

Q. 2. List the reactions of glucose which cannot be explained by its open chain structure.

Ans. (i) Despite having the aldehyde group, glucose does not give 2, 4 DNP test or Schiff's test.

(ii) It does not form hydrogensulphite addition product with $NaHSO_3$.

(iii) The penta acetate of glucose does not react with hydroxylamine indicating the absence of free – CHO group.

Q. 3. Explain what is meant by :

(i) Biocatalyst (ii) Glycosidic linkage

Ans. (i) Biocatalysts are the catalysts which increases the rate of metabolism biochemical reactions.

(ii) The linkage between the monosaccharide units through oxygen is called glycosidic linkage.

Q. 4. Explain the following terms :

(i) Invert sugar **(ii) Polypeptides**

Ans. (i) An equimolar mixture of glucose and fructose produced on hydrolysis of sucrose is called invert sugar. It is called so because sucrose is dextrorotatory whereas its hydrolysis product is laevorotatory.

(ii) Polypeptides are polymers of amino acids containing less than 100 amino acids. For example, oxytocin, vasopressin, etc.

Q. 5. Name the product of hydrolysis of sucrose. Why is sucrose not a reducing sugar ?

Ans. On hydrolysis, sucrose gives equimolar mixture of D-(+)-glucose and D-(–)-fructose. Sucrose is not a reducing sugar as glucose and fructose are linked through their reducing centres in structure of sucrose.

Q. 6. Explain nucleotides and nucleosides.

Ans. A nucleoside contain only two basic components of nucleic acids *i.e.,* pentose sugar and nitrogenous base.

A nucleotide contains all the three basic components of nucleic acids *i.e.,* a phosphoric acid group, pentose sugar and nitrogenous base.

Q. 7. Describe primary structure and secondary structure of proteins.

Ans. Primary structure of proteins : The protein in which amino acids linked with each other in a specific sequence is said to be the primary structure of that protein.

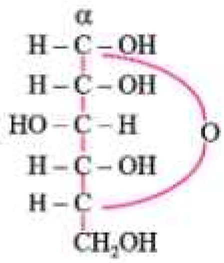
Secondary structure of proteins : It refers to the shape in which a long polypeptide chain can exist *i.e.,* α-helix and β-pleated structure.

Q. 8. What is essentially the difference between α-form of glucose and β-form of glucose ? Explain.

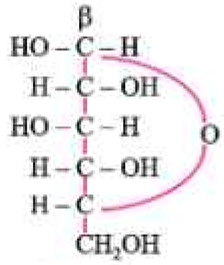
Ans. α-form of glucose and β-form of glucose differ only in the configuration of the hydroxyl group at C_1 in cyclic structure of glucose/hemiacetal form of glucose.

Q. 9. What are anomers ? Give the structures of two anomers of glucose.

Ans. Monosaccharides which differs in configuration at C_1 e.g., α-glucose and β-glucose.



α-Glucose



β-Glucose

Q. 10. Write the obtained by hydrolysis of:

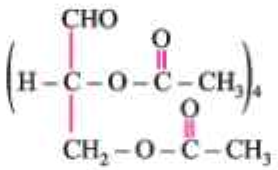
(i) Maltose **(ii) Cellulose**

Ans. (i) α-D-glucose (ii) β-D-glucose

Q. 11. (i) Acetylation of glucose with acetic anhydride gives glucose penta-acetate. Write the structure of penta acetate.

(ii) Explain why glucose penta acetate does not react with hydroxylamine ?

Ans. (i)



Glucose pentaacetate

(ii) The molecule of glucose penta acetate has a cyclic structure in which – CHO is involved in ring formation.

Q. 12. Write the products of oxidation of glucose with :

(i) Bromine water

(ii) Nitric acid

Ans. (i)

Glucose Gluconic acid

(ii)
$$\begin{array}{c} CHO \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \\ \text{Glucose} \end{array} \xrightarrow{HNO_3} \begin{array}{c} COOH \\ | \\ (CHOH)_4 \\ | \\ COOH \\ \text{Saccharic acid} \end{array}$$

Q. 13. State two main differences between globular and fibrous proteins.

Ans.

Globular protein	Fibrous protein
(i) They form a α-helix structure.	(i) They have β-pleated structure.
(ii) They are water soluble.	(ii) They are water insoluble.

Q. 14. What are essential and non-essential amino acid ? Give two examples of each type.

Ans. Essential amino acids are those which are not produced in our body and required to be supplied from outside, *e.g.*, valine, leucine.

Non-essential amino acids are those which are produced by our body, *e.g.*, glycine, alanine.

Q. 15. Coagulation of egg white on boiling is an example of denaturation of protein. Explain it in terms of structural changes.

Ans. Protein albumin present in egg white gets denatured *i.e.*, 2° & 3° structures are destroyed and 1° structure is retained.

Q. 16. Describe two important functions of nucleic acids.

Ans. (i) DNA is responsible for transfer of heredity information from one generation to another.

(ii) RNA is responsible for protein synthesis.

Q.17. (i) **What type of linkage is responsible for the formation of proteins ?**

(ii) **Write the product formed when glucose is treated with HI.**

Ans. (ii) Peptide linkage.

(iii) n-hexane.

Q.18. **Differentiate between the following :**

(i) Secondary and tertiary structure of protein

(ii) α-helix and β-pleated sheet structure of protein

Ans. (i) **Secondary structure** is responsible for the shape of protein α-helix and β-pleated sheets in which polypeptide chains have peptide bonds.

Tertiary structure represents overall folding of polypeptide chain and give rise to the fibrous or globular molecular shape.

(ii) **α-helix structure :** The peptide chains coiled up to form right handed helix involving H-bonding (Intramolecular).

β-pleated sheets : The peptide chains lie side by side together by intermolecular hydrogen bonding.

Q.19. **(i) Name the four bases present in DNA.**

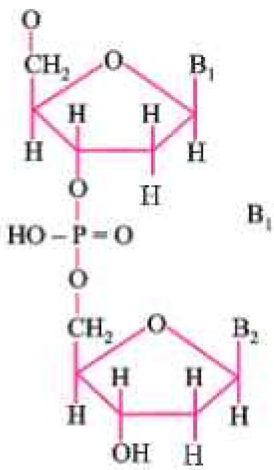
(ii) Which of them is not present in RNA ?

(iii) Give the structure of a nucleotide of DNA.

Ans. (i) Adenine, Guanine, Thymine, Cytosine.

(ii) Thymine.

(iii)



B_1 & B_2 = Nitrogeneous base (Adenine, guanine, Cytosine or thymine)

Q.20. Glucose or sucrose are soluble in water but cyclohexane and benzene are insoluble in water. Explain.

Ans. Glucose contain 5 – OH groups and sucrose contain eight – OH groups, because of this they form intermolecular hydrogen bonding, so they are soluble in water. But benzene and cyclohexane doesn't contain – OH groups hence doesn't form intermolecular hydrogen bonding, so they are not soluble in water.

CASE STUDY BASED QUESTIONS

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

Living systems are made up of various complex biomolecules like carbohydrates, proteins, nucleic acids, lipids, etc. Proteins and carbohydrates are essential constituents of our food. Carbohydrates are the main source of energy that is ingested by the human body . Brain mainly utilizes the glucose. Red blood cells also use glucose only. Fiber in the diet is not digested by human body due to lack of cellulase enzyme. Glucose is the major enegy source in the body. Glycogen is the storage form of glucose and glycogen is stored in skeletal muscles and liver. If glucose intake exceeds than it is utilized in the body it is converted into fat. Riboses are utilized in formation of deoxyribonucleic acid . Carbohydrates are polyhydroxy alcohol with potentially active carbonyl group which may be aldehyde or keto group. Carbohydrates can be classified on the basis of carbon atom present in the carbohydrates. Carbohydrates are classified into four types monosaccharides, disaccharides, oligosaccharides, polysaccharides. Monosaccharides cannot be hydrolyzed further into simpler form. They may contain 3-7 carbon atoms but monosaccharides containing 5-6 carbon atoms are more abundant in nature. All monosaccharides reduce Tollens' reagent as well as Fehling's solution and hence are called reducing sugars. Pentoses and hexoses have cyclic structures, furanose and pyranose. Disaccharides give two monosaccharides on hydrolysis. Polysaccharides may be homopolysaccharides and heteropolysaccharides. Plants produce carbohydrates by photosynthesis. In most animals, carbohydrates are the quickly accessible reservoir of energy. The main function of carbohydrates is to provide energy, but they also play an important role in the structure and function of the body organs and nerve cells.

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

(A) Which of the following statements is **not** true about glucose?

(a) It is an aldohexose.

(b) On heating with HI it forms n-hexane.

(c) It is present in furanose form.

(d) It does not give 2, 4-DNP test.

(B) The α- and β-forms of glucose are

(a) isomers of D(+) glucose and L(–) glucose respectively

(b) anomers of glucose

(c) isomers which differ in the configuration of C-2

(d) isomers which differ in the configuration of C-5

(C) The monosaccharide constituents of lactose are:

(a) α-D-glucose and β-D-fructose

(b) α-D-glucose only

(c) β-D-glucose only

(d) β-D-glucose and β-D-galactose

(D) Glycogen is a branched chain polymer of α-D-glucose units in which chain is formed by C1-C4 glycosidic linkage whereas branching occurs by the formation of C1– C6 glycosidic linkage. Structure of glycogen is similar to___________.

(a) Amylose (b) Amylopectin

(c) Cellulose (d) Glucose

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

Proteins are very important biomolecules of living systems. α-Amino acids are the building blocks of proteins. About 20 α-amino acids have been isolated by the hydrolysis of proteins. Ten amino acids which the body cannot synthesize are called essential amino acids. The remaining ten are called non-essential amino acids. Proteins are complex nitrogeneous polymers of amino acids connected through peptide bonds. Protein is very important in sports performance as it can boost glycogen storage , reduce muscle soreness and promote muscle repair. For those who are active regularly , there may be benefit from consuming a portion of protein at each mealtime and spreading protein intake throughout the day. Protein intake that exceeds the recommended daily allowance is widely accepted for both endurance and power athletes. The various techniques utilized to rate protein will be discussed. Traditionally, sources of dietary protein are seen as either being of animal or vegetable origin. Animal sources provide a complete source of protein (i.e. containing all essential amino acids), whereas vegetable sources generally lack one or more of the essential amino acids. Animal sources of dietary protein, despite providing a complete protein and numerous vitamins and minerals, have some health professionals concerned about the amount of saturated fat common in these foods compared to vegetable sources. The advent of processing techniques has shifted some of this attention and ignited the sports supplement marketplace with derivative products such as whey, casein and soy. Individually, these products vary in quality and applicability to certain populations.

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

(A) Correct statement about amino acids is-
- (a) All amino acids are optically active
- (b) All amino acids except glycine are optically active.
- (c) All amino acids except glutamic acid are optically active.
- (d) All amino acids except lysine are optically active.

(B) Proteins are found to have two different types of secondary structures viz. α-helix and β-pleated sheet structure. α-helix structure of protein is stabilised by:
- (a) Peptide bonds
- (b) van der Waals forces
- (c) Hydrogen bonds
- (d) Dipole-dipole interactions

(C) Example of Globular proteins is -
- (a) Myosin
- (b) Albumin
- (c) Collagen
- (d) Fibroin

(D) Which of the statements about denaturation given below are correct?
- (1) Denaturation of proteins causes loss of secondary and tertiary structures of the protein.
- (2) Denaturation leads to the conversion of double strand of DNA into single strand.
- (3) Denaturation affects primary structure which gets distorted.

(a) (2) and (3)	(b) (1) and (3)
(c) (1) and (2)	(d) (1), (2) and (3)

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

The particles in the nucleus of cell, responsible for heredity, are called chromosomes which are made up of proteins and another type of biomolecules called nucleic acids. Nucleic acids are long chain polymers of nucleotides. Nucleotides are low molecular weight intracellular compounds that play major roles in physiological and biological functions, They act as precursors for nucleic acid synthesis and are also fundamental for intermediary metabolism. The two types of nucleic acids found in the chromosomes of cells of mammals are called 'deoxyribonucleic acid' and 'ribonucleic acid'. They are usually abbreviated as DNA and RNA respectively. As they are found in the nuclus of cells , they are called nucleic acids.Nucleotides and nucleic acids turn over rapidly, especially in growing tissues or those undergoing constant cell renewal. Tissues that grow have a net formation of new DNA and a rapid turnover of RNA . Nucleotides consists of a nitrogenous base (purine or pyrimidine), a pentose (ribose or deoxyribose), and one or more phosphate groups. The nitrogenous bases are derived from two parent heterocyclic molecules. The major purines found in living organisms are adenine and guanine, while cytosine, thymine, and uracil are the major pyrimidine bases. Nitrogenous bases can be formed from amino acid precursors or reutilized after their release from nucleic acid breakdown via the salvage pathway. The purine ring carbon atoms formed from the dispensable amino acids glycine, glutamic acid, and aspartame. The carbon atoms pyrimidines are derived from carbamoyl phosphate and aspartame. It has been concluded that there are about six billion base pairs in the DNA of a single human cell.

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

(A) Dinucleotide is obtained by joining two nucleotides together by phosphodiester linkage. Between which carbon atoms of pentose sugars of nucleotides are these linkages present?

(a) 5' and 3' (b) 1' and 5'

(c) 5' and 5' (d) 3' and 3'

(B) In DNA, the complementary bases are:

(a) Uracil and adenine; cytosine and guanine

(b) Adenine and thymine; guanine and cytosine.

(c) Adenine and thymine; guanine and uracil

(d) Adenine and guanine; thymine and cytosine.

(C). The correct statement regarding RNA and DNA is:
- (a) The sugar component RNA is arabinose and sugar in DNA is ribose
- (b) The sugar component in RNA is 2rdeoxyribose and the sugar component in DNA is arabinose.
- (c) The sugar component in RNA is arabinose and the sugar component in DNA is 2'-deoxyribose.
- (d) The sugar component in RNA is ribose and sugar component in DNA is 2' deoxyribose

(D). Which one of the following is not present in RNA ?

(a) Uracil	(b) Ribose
(c) Thymine	(d) Phosphate

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

Adenosine triphosphate (ATP) is the energy-carrying molecule found in the cells of all living things. ATP captures chemical energy obtained from the breakdown of food molecules and releases it to fuel other cellular processes. ATP is a nucleotide that consists of three main structures:the nitrogenous base, adenine; the sugar, ribose; and a chain of three phosphate groups bound to ribose. The phosphate tail of ATP is the actual power source which the cell taps. Available energy is contained in the bonds between the phosphates and is released when they are broken, which occurs through the addition of a water molecule (aprocess called hydrolysis). Usually only the outer phosphate is removed from ATP to yield energy; when this occurs ATP is converted to adenosine diphosphate (ADP), the form of the nucleotide having only two phosphates. The importance of ATP (adenosine triphosphate) as the main source of chemical energy in living matter and its involvement in cellular processes has long been recognized. The primary mechanism whereby higher organisms, including humans, generate ATP is through mitochondrial oxidative phosphorylation. For the majority of organs, the main metabolic fuel is glucose, which in the presence of oxygen undergoes complete combustion to CO_2 and H_2O:

$C_6H_{12}O_6 + 6O_2 \rightarrow 6O_2 + 6H_2O + \text{energy}$

The free energy (ΔG) liberated in this exergonic (ΔG is negative) reaction is partially trapped as ATP in two consecutive processes: glycolysis (cytosol) and oxidative phosphorylation (mitochondria). The first produces 2 mol of ATP per mol of glucose, and the second 36 mol of ATP per mol of glucose. Thus, oxidative phosphorylation yields 17-18 times as much useful energy in the form of ATP as can be obtained from the same amount of glucose by glycolysis alone. The efficiency of glucose metabolism is the ratio of amount of energy produced when 1 mol of glucose oxidised in cell to the enthalpy of combustion of glucose. The energy lost in the process is in the form of heat. This heat is responsible for keeping warm.

Reference : Erecinska'. M., & Silvet, I. k..(1989). TP and Brain Function Journal of Cerebral Blood Flow & Metabolism, 9(1), 2-19.
https://doi.org/10.10381jcbfm.1989. 2 and
https://www,britannica.com/science/adenosine-triphosp hate)

(A) Cellular oxidation of glucose is a:

(a) spontaneous and endothermic process
(b) non spontaneous and exothermic process
(c) non spontaneous and endothermic process
(d) spontaneous and exothermic process

(B) What is the efficiency of glucose metabolism if 1 mole of glucose gives, 38ATP energy?(Given: The enthalpy of combustion of glucose is 686 kcal, 1ATP= 7.3kcal)

(a) 100%
(b) 38%
(c) 62%
(d) 80%

(C) Which of the following statement is true?

(a) ATP is a nucleoside made up of nitrogenous base adenine and ribose sugar.
(b) ATP consists the nitrogenous base, adenine and the sugar, deoxyribose.
(c) ATP is a nucleotide which contains a chain of three phosphate groups bound to ribose sugar.
(d) The nitrogenous base of ATP is the actual power source.

(D) Nearly 95% of the energy released during cellular respiration is due to:

(a) glycolysis occurring in cytosol
(b) oxidative phosphorylation.
(c) glycolysis occuring in mitochondria
(d) oxidative phosphorylation occurring in mitochondria

(E) Which of the following statements is correct?

(a) ATP is a nucleotide which has three phosphate groups while ADP is a nucleoside which has three phosphate groups.
(b) ADP contains a nitrogenous bases adenine, ribose sugar and two phosphate groups bound to rihose.
(c) ADP is the main source of chemical energy in living matter.
(d) ATP and ADP are nucleosides which differ in number of phosphate groups.

5. **Read the passage and answer the following questions:**

EVIDENCE FOR THE FIBROUS NATURE OF DNA

The basic chemical formula of DNA is now well established. it consists of a very long chain, the backbone of which is made up of alternate sugar and phosphate groups, joined together in regular 3' 5' phosphate di-ester linkages. To each sugar is attached a nitrogenous base, only four different kinds of which are commonly found in DNA. Two of these—adenine and guanine--- are purines, and the other two thymine and cytosine-are pyrimidines. A fifth base, 5-methyl cytosine, occurs in smaller amounts in certain organisms, and a sixth, 5-hydroxy-methyl-cytosine, is found instead of cytosine in the T even phages. It should be noted that the chain is unbranched, a consequence of the regular internucleotide linkage. On the other hand the sequence of the different nucleotides is, as far as can be ascertained, completely irregular. Thus, DNA has some features which are regular, and some which are irregular. A similar conception of the DNA molecule as a long thin fiber is obtained from physicochemical analysis involving sedimentation, diffusion, light scattering, and viscosity measurements. These techniques indicate that DNA is a very asymmetrical structure approximately 20 A wide and many thousands of angstroms long. Estimates of its molecular weight currently center between 5×10^{6} and 10^{7} (approximately 3×10^{4} nucleotides). Surprisingly each of these measurements tend to suggest that the DN is relatively rigid, a puzzling finding in iew of e large number of single bonds (5 per nucleotide) in the phosphate-sugar back bone. Recently these indirect inferences have been confirmed by electron microscopy.

Reference: Watson, J. D., & Crick, F. H. (1953, January). The structure of DNA In Cold spring Harbor symposia on quantitative biology (Vol. 18, pp. 123-131) old Spring Harbor Laboratory Press.

(A) Purines present in DNA are:

(a) adenine and thymine

(b) guanine and thymine

(c) cytosine and thymine

(d) adenine and guanine

(B) DNA molecule has__________ internucleotide linkage and Purines sequence of the different nucleotides

(a) regular, regular

(b) regular, irregular

(c) irregular, regular

(d) irregular, irregular

(C) DNA has a______backbone.
(a) phosphate -purine
(b) pyrimidines- sugar
(c) phosphate- sugar
(d) purine- pyrimidine

(D) Out of the four different kinds of nitrogenous bases which are commonly found in DNA, ________has been replaced in some organisms.
(a) adenine
(b) guanine
(c) cytosine
(d) thymine

ANSWERS

I MULTIPLE CHOICE QUESTIONS

I 1. (b) 2. (b) 3. (a) 4. (c) 5. (a) 6. (c) 7. (c) 8. (b) 9. (b) 10. (a) 11. (c) 12. (c) 13. (c) 14. (c) 15. (b) 16. (d) 17. (b) 18. (b) 19.(d) 20.(c)

II FILL IN THE BLANKS

1. Amylose 2. n-Hexane 3. α-D-glucose 4. Adenine and guanine

5. Peptide linkage. 6. Vitamin B_{12} 7. Uracil 8. Vitamin K. 9. Gluconic acid

10. Glycogen.

III ASSERTION REASON TYPE QUESTIONS

1. (c) 2. (a) 3. (c) 4. (a) 5. (c) 6. (a) 7. (b) 8. (a) 9. (b) 10. (d)

IV ONE WORD ANSWER TYPE QUESTIONS

1. Vitamin B 2. Vitamin C 3. Cellulose 4. Lactose 5. Starch 6. Polysaccharides

7. Reducing sugars 8. vitamin A 9. Nucleoside, nucleotide 10. Anomers

CASE STUDY BASED QUESTIONS

1.	A. (c)	B. (b)	C. (d)	D. (b)	
2.	A. (b)	B. (c)	C. (b)	D. (c)	
3.	A. (b)	B. (b)	C. (d)	D. (c)	
4.	A. (d)	B. (b)	C. (c)	D. (d)	E.(b)
5.	A. (d)	B. (b)	C. (c)	D. (c)	

UNIT TEST-1

Biomolecules

Maximum Marks : 20 **Time Allowed : 1 Hours**

1. Name polysaccharide which is stored in the liver of animals. (1)
2. Name the enantiomer of D-glucose. (1)
3. Why is sucrose called invert sugar? (1)
4. Name the building blocks of proteins. (1)
5. Give the structure of simplest optically active amino acid. (1)
6. What are anomers? Give the structures of two anomers of glucose. (2)
7. Write the products obtained by hdydrolysis of (2)
   (i) maltose (ii) cellulose
8. What are vitamins? Give two examples of water soluble vitamin. (2)
9. What do you understand by following: (3)
   (i) denaturation of protein
   (ii) reducing sugar
10. Differentiate between the following (3)
    (i) secondary and tertiary structure of protein.
    (ii) α-helix and β-pleated sheet structure of protein.
    (iii) nucleoside and nucleotide
11. (i) Name four bases present in DNA. (3)
    (ii) Which of them is not present in RNA?
    (iii) Name the linkage responsible for stability of strands of DNA.

UNIT TEST-2
Biomolecules

Maximum Marks : 20 **Time Allowed : 1 Hours**

1. Name the following: (1)
   (i) Nitrogenous base present in RNA but not in DNA.
   (ii) Optically inactive amino acid
2. Explain- Amino acids shows amphoteric behaviour. (1)
3. Mention two examples of disachharides. (1)
4. The linkage responsible for stability of primary structure of protein is (1)
5. Name the diseases associated with the deficiency of vitamin A and vitamin B_{12}. (1)
6. Write any three reactions which cannot be explained by linear structure of D-glucose. Write cyclic structure of glucose. (2)
7. Discuss the tertiary and quaternary structure of proteins. Name the intermolecular forces responsible for stability of these structures. (2)
8. Explain- denaturation of proteins. Discuss its effect on the primary, secondary, tertiary and quaternary structures of proteins. (2)
9. Differentiate following pairs giving examples: (3)
   (i) Reducing and non-reducing sugars
   (ii) Essential and non-essential amino acids
   (iii) Fibrous and globular proteins
10. Write the reactions of D-glucose with following: (3)
    (i) HI/Δ
    (ii) Bromine water
    (iii) Acetic anhydride
11. Give reasons for following: (3)
    (i) Amino acids are soluble in water.
    (ii) Tryptophan is required in diet regularly but glutamic acid does not.
    (iii) DNA is more stable than RNA.

SOLVED SAMPLE PAPER (2023-24)
CHEMISTRY THEORY CLASS XII

TIME: 3 HOURS **Maximum Marks: 70**

General Instructions

(a) There are 33 questions in this question paper with internal choice.

(b) SECTION A consists of 16 multiple-choice questions carrying 1 mark each.

(c) SECTION B consists of 5 short answer questions carrying 2 marks each.

(d) SECTION C consists of 7 short answer questions carrying 3 marks each.

(e) SECTION D consists of 2 case- based questions carrying 4 marks each.

(f) SECTION E consists of 3 long answer questions carrying 5 marks each.

(g) All questions are compulsory.

(h) Use of log tables and calculators is not allowed

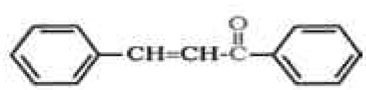
SECTION – A

The following questions are multiple -choice questions with one correct answer. Each question carries 1 mark. There is no internal choice in this section.

1. Which of the following solutions will have the highest conductivity at 298 K?

   (a) 0.01 M HCl solution (b) 0.1 M HCl solution

   (c) 0.01 M CH_3COOH solution (d) 0.1 M CH 3COOH solution

2. $A + B \xrightarrow{\text{dil NaOH}}$ 

   Identify A and B:

   (a) A = 1-phenylethanal , B = acetophenone

   (b) A = Benzophenone B = formaldehyde

   (c) A= Benzaldehyde, B = Acetophenone

   (d) A = Benzophenone , B = Acetophenone

3. The vitamins which can be stored in our body are:

   (a) Vitamin A, B, D and E (b) Vitamin A, C, D and K

   (c) Vitamin A, B, C and D (d) Vitamin A, D, E and K

4. What is IUPAC name of the ketone A, which undergoes iodo form reaction to give CH_3 CH=C(CH_3)COONa and yellow precipitate of CHI_3?

(a) 3-Methylpent-3-en-2one (b) 3-Methylbut-2-en-one

(c) 2, 3-Dimethylethanone (d) 3-Methylpent-4-one

5. Which of the following is not correct?

   (a) In haloarenes, the electron pairs on halogen atom are in conjugation with II-electrons of the ring.

   (b) The carbon-magnesium bond is covalent and non-polar in nature.

   (c) During SN1 reaction, the carbocation formed in the slow step being sp^2 hybridised is planar.

   (d) Out of $CH_2 = CH\text{-}Cl$ and $C_6H_5CH_2Cl$, $C_6H_5CH_2Cl$ is more reactive towards SN^1 reaction

6. Match the properties with the elements of 3d series:

(i) lowest enthalpy of atomisation	(p) Sc
(ii) shows maximum number of oxidation states	(q) Mn
(iii) transition metal that does not form coloured compounds	(r) Zn
	(s) Ti

   (a) (i) (r), (ii) (q), (iii) (p) (b) (i) (r), (ii) (s), (iii) (p)

   (c) (i) (p), (ii) (q), (iii) (r) (d) (i) (s), (ii) (r), (iii) (p)

7. Which of the following statement is true?

   (a) molecularity of reaction can be zero or a fraction.

   (b) molecularity has no meaning for complex reactions.

   (c) molecularity of a reaction is an experimental quantity

   (d) reactions with the molecularity three are very rare but are fast.

8. In which of the following solvents, the $C_4H_8NH_3^+X^-$ is soluble;

   (a) ether (b) acetone

   (c) water (d) bromine water

9. Which of the following observation is shown by 2 -phenyl ethanol with Lucas Reagent?

   (a) Turbidity will be observed within five minutes

   (b) No turbidity will be observed

   (c) Turbidity will be observed immediately

   (d) Turbidity will be observed at room temperature but will disappear after five minutes.

10. If the initial concentration of substance A is 1.5 M and after 120 seconds the concentration of substance A is 0.75 M, the rate constant for the reaction if it follows zero - order kinetics is:

(a) 0.00625 $molL^{-1}s^{-1}$ (b) 0.00625 s^{-1}

(c) 0.00578 $molL^{-1}s^{-1}$ (d) 0.00578 s^{-1}

11. Anisole undergoes bromination with bromine in ethanoic acid even in the absence of iron (III) bromide catalyst

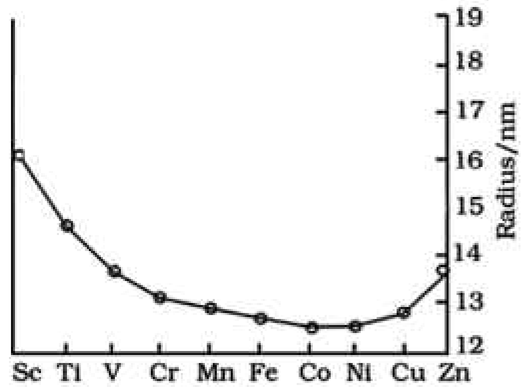
(a) Due to the activation of benzene ring by the methoxy group.

(b) Due to the de-activation of benzene ring by the methoxy group.

(c) Due to the increase in electron density at ortho and para positions

(d) Due to the formation of stable carbocation .

12. The trend of which property is represented by the following graph?



(a) ionization enthalpy (b) atomic radii

(c) enthalpy of atomization (d) melting point 3

For Visually Challenged Learners

12. Which of the following is not considered a transition element?

(a) Scandium (b) Silver

(c) Vanadium (d) Zinc

13. Given below are two statements labelled as Assertion (A) and Reason (R)

Assertion (A): Alcohols react both as nucleophiles and electrophiles.

Reason (R): The bond between C–O is broken when alcohols react as nucleophiles. Select the most appropriate answer from the options given below:

(a) Both A and R are true and R is the correct explanation of A

(b) Both A and R are true but R is not the correct explanation of A.

(c) A is true but R is false.

(d) A is false but R is true.

14. Given below are two statements labelled as Assertion (A) and Reason (R)

Assertion (A): Strong oxidising agents oxidise toluene and its derivatives to benzoic acids.

Reason (R): It is possible to stop the oxidation of toluene at the aldehyde stage with suitable reagents.

Select the most appropriate answer from the options given below:

(a) Both A and R are true and R is the correct explanation of A

(b) Both A and R are true but R is not the correct explanation of A.

(c) A is true but R is false.

(d) A is false but R is true.

15. Given below are two statements labelled as Assertion (A) and Reason (R)

Assertion : Enzymes are very specific for a particular reaction and for a particular substrate.

Reason : Enzymes are biocatalysts.

Select the most appropriate answer from the options given below:

(a) Both A and R are true and R is the correct explanation of A

(b) Both A and R are true but R is not the correct explanation of A.

(c) A is true but R is false.

(d) A is false but R is true.

16. Given below are two statements labelled as Assertion (A) and Reason (R)

Assertion (A): During electrolysis of aqueous copper sulphate solution using copper electrodes hydrogen gas is released at the cathode.

Reason (R): The electrode potential of Cu^{2+}/Cu is greater than that of H^+/H_2

Select the most appropriate answer from the options given below:

(a) Both A and R are true and R is the correct explanation of A

(b) Both A and R are true but R is not the correct explanation of A.

(c) A is true but R is false.

(d) A is false but R is true.

SECTION B

This section contains 5 questions with internal choice in one question. The following questions are very short answer type and carry 2 marks each.

17. The rate constant for a first order reaction is 60 s–1. How much time will it take to reduce the inital concentration of the reactant to its $\frac{1}{16}$th value? [log2 = 0.30, log4 = 0.60]

18. A 5% solution of $Na_2SO^4.10H_2O$ (MW = 322) is isotonic with 2% solution of non-electrolytic, non volatile substance X. Find out the molecular weight of X.

19. (a) Arrange the isomeric dichlorobenzene in the increasing order of their boiling point and melting points.

    (b) Explain why the electrophilic substitution reactions in haloarenes occur slowly and require more drastic conditions as compared to those in benzene.

20. (a) Out of p-tolualdehyde and p-nitrobenzaldehyde, which one is more reactive towards nucleophilic addition reactions, why?

    (b) Write the structure of the product formed when acetone reacts with 2,4 DNP reagent .

OR

Convert the following:

(a) Benzene to m-nitrobenzaldehyde

(b) Bromobenzene to benzoic acid

21. (a) DNA fingerprinting is used to determine paternity of an individual. Which property of DNA helps in the procedure?

    (b) What structural change will occur when a native protein is subjected to change in pH?

SECTION C

This section contains 7 questions with internal choice in one question. The following questions are short answer type and carry 3 marks each.

22. (a) Write the formula for the following coordination compound Bis(ethane-1,2-diamine) dihydroxidochromium(III) chloride

    (b) Does ionization isomer for the following compound exist? Justify your answer. $Hg[Co(SCN)_4]$

    (c) Is the central metal atom in coordination complexes a Lewis acid or a Lewis base? Explain.

23. (a) Can we construct an electrochemical cell with two half-cells composed of ZnSO solution and zinc electrodes? Explain your answer.

    (b) Calculate the λ^0_m for Cl- ion from the data given below:

    $\Lambda 0m\ MgCl_2 = 258.6\ Scm^2mol^{-1}$ and $\lambda^0_m\ Mg^{2+} = 106\ Scm^2mol^{-1}$

    (c) The cell constant of a conductivity cell is 0.146 cm-1. What is the conductivity of 0.01 M solution of an electrolyte at 298 K, if the resistance of the cell is 1000 ohm?

24. Write the name of the reaction, structure and IUPAC name of the product formed when:

    (a) phenol reacts with CHCl3 in the presence of NaOH followed by hydrolysis.

    (b) $CH_3CH_2CH(CH_3)CH(CH_3)ONa$ reacts with C_2H_5Br

25. You are given four organic compounds "A", "B", "C" and "D". The compounds "A", "B" and "C" form an orange- red precipitate with 2,4 DNP reagent. Compounds "A" and "B" reduce Tollen's reagent while compounds "C" and "D" do not. Both "B" and "C" give a yellow precipitate when heated with iodine in the presence of NaOH. Compound "D" gives brisk effervescence with sodium bicarbonate solution. Identify "A", "B", "C" and "D" given the number of carbon atoms in three of these carbon compounds is three while one has two carbon atoms. Give an explanation for y our answer.

26. When sucrose is hydrolysed the optical rotation values are measured using a polarimeter and are given in the following table:

S.No.	Time (hours)	Specific Rotation
1	0	+ 66.5°
2	∞	–39.9°

    (a) Account for the two specific rotation values.

    (b) What is the specific name given to sucrose based on the above observation .

    (c) One of the products formed during the hydrolysis of sucrose is a glucose, that reacts with hydroxylamine to give compound A. Identify compound A.

27. An organic compound A with the molecular formula (+) C_4H_9Br undergoes hydrolysis to form (+) C_4H_9OH. Give the structure of A and write the mechanism of the reaction.

28. The rate constants of a reaction at 200K and 500K are $0.02s^{-1}$ and $0.20s^{-1}$ respectively. Calculate the value of Ea (Given $2.303R = 19.15\ JK^{-1}\ mol^{-1}$)

SECTION D

The following questions are case -based questions. Each question has an internal choice and carries 4 (1+1+2) marks each. Read the passage carefully and answer the questions that follow.

29. **Crystal field splitting by various ligands**

Metal complexes show different colours due to d-d transitions. The complex absorbs light of specific wavelength to promote the electron from t_2g to eg level. The colour of the complex is due to the transmitted light, which is complementary of the colour absorbed.

The wave number of light absorbed by different complexes of Cr ion are given below:

Complex	**Wavenumber of light absorbed (cm^{-1})**	**Energy of light absorbed (kJ/mol)**
$[CrA_6]^{3-}$	13640	163
$[CrB_6]^{3+}$	17830	213
$[CrC_6]^{3+}$	21680	259
$[CrD_6]^{3-}$	26280	314

Answer the following questions:

(a) Out of the ligands "A", "B", "C" and "D", which ligand causes maximum crystal field splitting? Why?

OR

Which of the two, "A" or "D" will be a weak field ligand? Why?

(b) Which of the complexes will be violet in colour? $[CrA_6]^{3-}$ or $[CrB_6]^{3+}$ and why? (Given: If 560 – 570 nm of light is absorbed, the colour of the complex observed is violet.)

(c) If the ligands attached to Cr3+ ion in the complexes given in the table above are water, cyanide ion, chloride ion, and ammonia (not in this order)

Identify the ligand, write the formula and IUPAC name of the following:

(i) $[CrA_6]^{3-}$ (ii) $[CrC_6]^{3+}$

30. We commonly use voltaic cell as convenient, portable sources of energy. Flashlights and radios are example of devices that are often powered by the zinc-carbon dry cells or Lclanche cell. This voltaic cell has a zinc can as the anode, a graphite rod in the centre, surrounded by a paste of manganese dioxide, ammonium and zinc chloride black is the cathode. The volage of this dry cell is initially about 1.5V, but

it decreases as current is drawn off. The voltage also deteriorates rapidly in cold weather.

An alkaline dry cell is similar to the Lclanche cell but it has potassium hydroxide in place of ammonium chloride. This cell perform better under current drain and in cold weather. The half reaction are:

Anode: $Zn(s) + 2OH^- (aq) \longrightarrow ZnO(s) + H_2O(l) + 2e^-$

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

A dry cell in not truly 'dry', because the electrolyte in an aqueous paste. Once a dry cell is completely discharge, the cell is not easily reversed or reversed or recharged and is normally discarded. Lead storage cell is rechargeable cell. The spongy lead act as anode and lead dioxide as cathode. Aqueous sulphuric acid used as an electrolyte. The half reactions during discharging of lead storage cells are:

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

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

The lead storage cell can be recharged by using an external electric current. [Chemical demonstration vol 4 University of Wisconsin]

Answer the following questions:

(a) Write the cathodic reaction during the discharging of Lelanche dry cell.

(b) What is the net reacthion when the alkaline dry cell is in use and how does the cell potential depends on the concentration of KOH?

(c) How many coulombs have been transferred from anode to cathode in order to consume one mole of sulphuric acid during the discharging of lead storage cell?

OR

How much work can be extracted by using lead storage cell if each cell delivers about 2.0 V of voltage? [$F = 96500 \text{ C mol}^{-1}$]

SECTION E

The following questions are long answer type and carry 5 marks each. All questions have an internal choice

31. Attempt **any five** of the following:

(a) Which of the following ions will have a magnetic moment value of 1.73 BM.

$$Sc^{3+}, Ti^{3+}, Ti^{2+}, Cu^{2+}, Zn^{2+}$$

(b) In order to protect iron from corrosion, which one will you prefer as a sacrificial electrode, Ni or Zn? Why? (Given standard electrode potentials of Ni, Fe and Zn are – 0.25 V, – 0.44 V and – 0.76 V respectively.)

(c) The second ionization enthalpies of chromium and manganese are 1592 and 1509 kJ/mol respectively. Explain the lower value of Mn.

(d) Give two similarities in the properties of Sc and Zn.

(e) What is actinoid contraction? What causes actinoid contraction?

(f) What is the oxidation state of chromium in chromate ion and dichromate ion?

(g) Write the ionic equation for reaction of KI with acidified $KMnO_4$.

32. (a) What is the effect of temperature on the solubility of glucose in water?

(b) Ibrahim collected a 10mL each of fresh water and ocean water. He observed that one sample labeled "P" froze at 0°C while the other "Q" at –13°C. Ibrahim forgot which of the two, "P" or "Q" was ocean water. Help him identify which container contains ocean water, giving rationalization for your answer.

(c) Calculate Van't Hoff factor for an aqueous solution of $K_3[Fe(CN)_6]$ if the degree of dissociation (α) is 0.852. What will be boiling point of this solution if its concentration is 1 molal? (K_b=0.52 K kg/mol)

OR

(a) What type of deviation from Roult's Law is expected when phenol and aniline are mixed with each other? What change in the net volume of the mixture is expected? Graphically represent the deviation.

(b) The vapour pressure of pure water at a certain temperature is 23.50 mm Hg. If 1 mole of a non-volatile non-electrolytic solute is dissolved in 100g water, Calculate the resultant vapour pressure of the solution.

33. (a) Write the structure of the main products when aniline reacts with the following reagents.

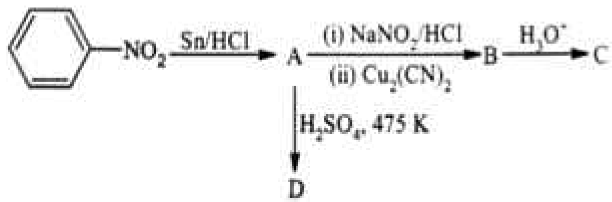
(i) Br_2 water (ii) $(CH_3CO)_2O$/pyridine

(b) Arrange the following in the increasing order of basicity in the vapour phase

(i) $C_2H_5NH_2CH_2NH_2 + CHCl_3 + KOH\ (alc) \rightarrow$

(ii) $CH_3CONH_2 + Br_2 + KOH \rightarrow$

(a) Write the structure of A to D



(b) Arrange in order of increasing boiling point $CH_3CH_2CH_2NH_2$, $CH_3CH_2NHCH_3$, $(CH_3)_3N$,

(c) (i) Prepare propylamine by Gabriel phthalimide synthesis

(ii) What happens when benzene diazonium chloride is being heated with C_2H_5OH?

SAMPLE PAPER (2023 -24)
CHEMISTRY THEORY (043)
MARKING SCHEME
SECTION A

1. (b) 0.1 M HCl solution, conductivity is higher for strong electrolyte, conductivity decreases with dilution
2. (c) A= Benzaldehyde , B= Acetophenone. This is an example of crossed Aldol condensation.
3. (d) Vitamin A,D, E and K These are fat soluble vitamins
4. (a) 3-Methylpent-3-en-2-one
5. (b) The carbon-magnesium bond is covalent and non-polar in nature .
6. (a) (i) (r) , (ii) (q), (iii) (p)

   Zinc has no unpaired electrons in 3d or 4s orbitals, so enthalpy of atomization is low

   Mn = $3d^5 4s^2$ shows +2, +3, +4, +5, +6 and+7 oxidation state , maximum number in 3d series
7. (b) molecularity has no meaning for complex reactions.
8. (c) water
9. (b) no turbidity will be observed, given compound is a primary alcohol
10. (a) 0.00625 $molL^{-1}1s^{-1}$ for zero order k = [Ro] –[R] / t = 1.5 – 0.75/120
11. (a) Due to the activation of benzene ring by the methoxy group.
12. (b) atomic radii

for visually challenged learners

12. (d) Zinc
13. (c) A is true but R is false
14. (b) Both A and R are true but R is not the correct explanation of A
15. (b) Both A and R are true and R is not the correct explanation of A.
16. (d) A is false but R is true.

    Cu will deposit at cathode

SECTION B

17. (a) k = 60 s^{-1}

$$t = \frac{2.303}{k}\log\frac{[R]}{\frac{1}{16}[R]_0} = \frac{2.303}{60}\log 16$$

$$t = \frac{2.303}{k}\log 2^4 = \frac{2.303}{60}\times 4\log 2$$

$$t = \frac{2.303}{60}\times 4\times 0.30 = 0.04606\text{ s}$$

18. $\Pi_1 = \Pi_2$

$$iC_1RT = C_2RT$$

$$\frac{3\times 5}{322} = \frac{2}{M}$$

$$M = \frac{2\times 322}{3\times 5}$$

$$M = 42.9\text{ g}$$

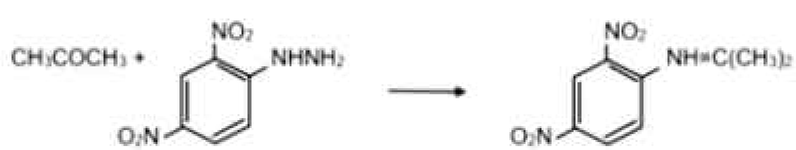
19. (a) m-dicholrobenzene < o-dicholrobenzene < p-dicholrobenze

symmetrical structure and close packing in para isomer

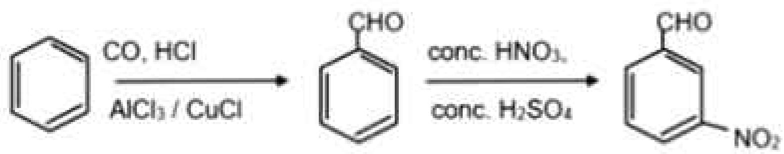
ortho has a stronger dipole dipole interaction as compared to meta

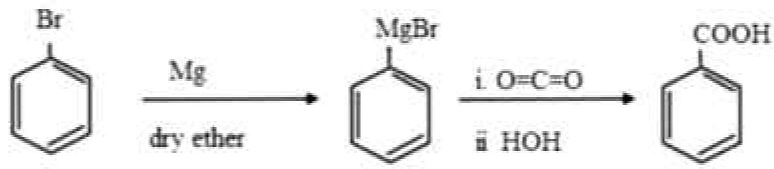
(b) the halogen atom because of its –I effect has some tendency to withdraw electrons from the benzene ring. As a result, the ring gets somewhat deactivated as compared to benzene and hence the electrophilic substitution reactions in haloarenes occur slowly and require more drastic conditions as compared to those in benzene.

20. (a) p-nitrobenzaldehyde is more reactive towards the nucleophilic addition reaction than p-tolualdehyde as Nitro group is electron withdrawing in nature . Presence of nitro group decrease electron density, hence facilitates the attack of nucleophile . Presence of -CH_3 leads to +I effect as - CH_3 is electron releasing group.

(b) 

or

(a) 

(b) 

21. (a) Replication

A sequence of bases on DNA is unique for a person and is the genetic material transferred to the individual from the parent which helps in the determination of paternity.

(b) During denaturation secondary and tertiary structures are destroyed but the primary structure remains intact.

SECTION C

22. (a) $[Cr(en)_2(OH)_2]Cl$ or $[Cr(H_2NCH_2CH_2NH_2)_2(OH)_2]Cl$

(b) No, ionization isomers are possible by exchange of ligand with counter ion only and not by exchange of central metal ion.

(c) The central atom is electron pair acceptor so it is a Lewis acid.

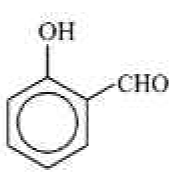
23. (a) Yes, if the concentration of $ZnSO_4$ in the two half cell is different, the electrode potential will be different making the cell possible.

(b)
$$\Lambda^0_m(MgCl_2) = \lambda^0_m(Mg^{2+}) + 2\lambda^0_m(Cl^-)$$
$$258.6 = 106 + 2\lambda^0_m(Cl^-)$$
$$\lambda^0_m(Cl^-) = 76.3\ Scm^2mol^{-1}$$

(c) cell constant $G^* = k \times R$

$$k = G^*/R = 0.146/1000 = 1.46 \times 10^{-4}\ Scm^{-1}$$

24. (a) Reimer Tiemann , (1/2)



2-Hydroxybenzaldehyde

(b) Williamson synthesis, $CH_3CH_2CH(CH_3)CH(CH_3)O\ C_2H_5$

2- Ethoxy-2-methylpentane

25. A, B and C contain carbonyl group as they give positive 2,4 DNP test

A and B are aldehydes as aldehydes reduce Tollen's reagent

C is a ketone, as it contains carbonyl group but does not give positive Tollen's test

C is a methyl ketone as it gives positive iodoform test

B is an aldehyde that gives positive iodoform test

D is a carboxylic acid

Since the number of carbons in the compounds A,B,C and D is three or two

B is CH_3CHO as this is only aldehyde which gives a positive iodoform test (1/2)

The remaining compounds A, C and D have three carbons

A is CH_3CH_2CHO, C is CH_3COCH_3 and D is CH_3CH_2COOH (1/2 each)

26. (a) The reactant Sucrose is dextrorotatory. On hydrolysis it give glucose dextrorotatory and fructose which is leavoroatatory. The specific rotation of fructose is higher than glucose Sucrose is dextrorotatory but after hydrolysis gives dextrorotatory glucose and laevorotatory fructose. Since the laevorotation of fructose (–92.4°) is more than dextrorotation of glucose (+ 52.5°), the mixture is laevorotatory.

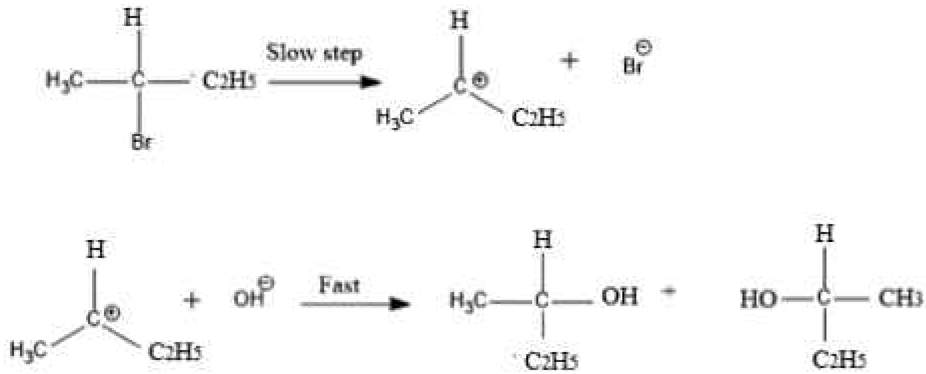
(b) Invert sugar, The hydrolysis of sucrose brings about a change in the sign of rotation, from dextro (+) to laevo (–) and the product is named as invert sugar.

(c) Glucose

$$\begin{array}{l} CH = N — OH \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array}$$

27. $$\begin{array}{l} C_2H_5 — \underset{\displaystyle |\atop \displaystyle Br}{CH} — CH_3 \end{array}$$

Mechanism:



28. $$\log\left(\frac{k_2}{k_1}\right) = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\log\frac{0.20}{0.05} = \frac{E_a}{2.303R}\left[\frac{1}{200} - \frac{1}{500}\right]$$

$$\log 10 = \frac{E_a}{19.15}\left(\frac{300}{200 \times 600}\right)$$

$$E_a = \frac{19.15 \times 200 \times 500}{300}$$

$$E_a = 6383 \text{ J/mol}$$

SECTION D

29. (a) D. Energy is directly proportional to the wave number. Maximum energy of light is required for an electron to jump from t_{2g} to eg in case of $[CrD_6]^{3-}$

OR

(a) A, The splitting caused in least in this case as the energy required for electron to jump from t_{2g} to e_g is minimum.

(b) $[CrB_6]^{3+}$, wavelength of light absorbed is 1/17830 = 560nm for the complex while 1/13640 = 733 nm for $[CrA_6]^{3-}$ complex.

(c) (i) $[CrCl_6]^{3-}$, Hexachloridochromate (III) ion (1 each)

(ii) $[Cr(NH_3)_6]^{3+}$, Hexaamminechromium(III) ion

$A = Cl^-$, $B = H_2O$, $C = NH_3$, $D = CN^-$

30. (a) Cathode reaction when Lclanche dry cell is under discharging mode is

$$MnO_2(s) + NH^+_4(aq) + e^- \longrightarrow MnO(OH)(s) + NH_3$$

(b) Net reaction is

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

Since there is no KOH appearing in the net reaction, cell potential is independent of the concentration of KOH.

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

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

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

2 mol e^- or (or 2F) have been transferred from anode to cathode to consume 2 mol of H_2SO_4 therefore, one mole H_2SO_4 requires one faraday of electricity or 96500 coulombs.

OR

$w_{max} = -nFE^\circ = -2 \times 96500 \times 2.0$

$w_{max} = -386000$ J

So, 386000 J of work can be extracted using lead storage cell when the cell is in use.

SECTION E

31. (a) Both Ti^{3+} and Cu^{2+} have 1 unpaired electron, so the magnetic moment for both will be 1.73 BM

(b) Zn, it has a more negative electrode potential so will corrode itself in place of iron

(c) Mn^+ has $3d^5 4s^1$ configuration and configuration of Cr^+ is $3d^5$, therefore, ionisation enthaply of Mn^+ is lower than Cr^+.

(d) Sc and Zn both form colourless compound and are diamagnetic.

(e) The decrease in the atomic and ionic radii with increase in atomic number of actinoids due to poor shielding effect of 5f electron.

(f) In both chromate and dichromate ion the oxidation state of Cr is +6.

(g) $10I^- + 2MnO_4^- + 16H^+ \rightarrow 2Mn^{2+} + 8H_2O + 5I_2$

32. (a) Addition of glucose to water is an endothermic reaction. According to Le Chatelier's principle, on increase in temperature, solubiltiy will increase.

(b) Q is ocean water, due to the presence of salts it freezes at lower temperature (depression in freezing point)

(c) $K_3[Fe(CN)_6]$ gives 4 ions in aqueous solution

$i = 1 + (n-1)\alpha$

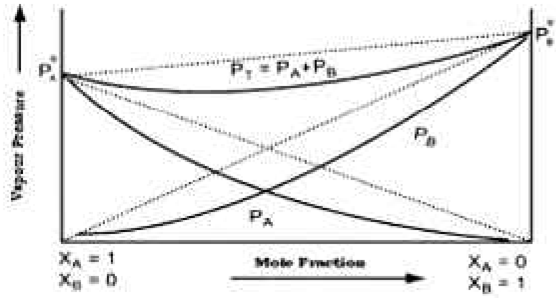
$i = 1 + (4-1) \times 0.0.852$

$i = 3.556$

$\Delta T_b = iK_b m = 3.556 \times 0.52 \times 1 = 1.85$

$T_b = 101.85^\circ$ C

(a) Negative Deviation is expected when phenol and aniline are mixed with each other. The net volume of the mixture will decrease, $\Delta V < 0$ due to stronger intermolecular interactions.



P-X Diagram for Solutions Showing Negative Deviation from Raoult's Law

(b) Relative lowering of vapour pressure = $(P^\circ - P)/P^\circ = x_2$

$x_2 = n_2/n_1$

$n_2 = 0.1$

$n_1 = 100/18$

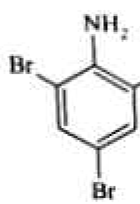
$x_2 = 0.1/5.55 + 0.1 = 0.1/5.65 = 0.018$

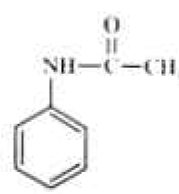
$P^\circ = 23.8$ mm Hg

Relative lowering of vapour pressure = $(23.80 - P)/23.80 = 0.018$

$23.80 - P = 0.428$

$P = 23.80 - 0.428 = 23.37$ mm Hg

33. (a) (i) 

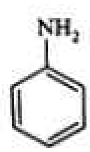
(ii) 

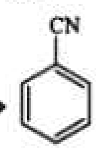
(b) $CH_3CH_2NH_2 < (CH_3CH_2)_2NH < (CH_3CH_2)_3N$

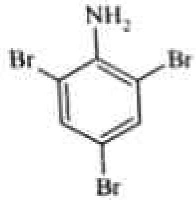
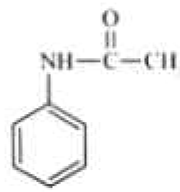
(c) (i) $CH_3CH_2CH_2NH_2 + CHCl_3 + KOH\ (alc) \xrightarrow{\text{warm}} CH_3CH_2CH_2NC + KCl + H_2O$

(ii) $CH_3CONH_2 + Br_2 + KOH \rightarrow CH_3NH_2 + KBr + K_2CO_3 + H_2O$

OR

(a) A → 

B → 

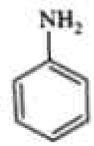
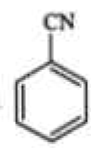
33. (a) (i)  (ii) 

(b) $CH_3CH_2NH_2 < (CH_3CH_2)_2NH < (CH_3CH_2)_3N$

(c) (i) $CH_3CH_2CH_2NH_2 + CHCl_3 + KOH\ (alc) \xrightarrow{warm} CH_3CH_2CH_2NC + KCl + H_2O$

(ii) $CH_3CONH_2 + Br_2 + KOH \rightarrow CH_3NH_2 + KBr + K_2CO_3 + H_2O$

OR

(a) A →  B → 

UNSOLVED SAMPLE PAPER–1

Maximum Marks: 70 **Time: 3 hours**

General Instructions:

Read the following instructions carefully.

(a) There are 33 questions in this question paper with internal choice.

(b) SECTION A consists of 16 multiple-choice questions carrying 1 mark each.

(c) SECTION B consists of 5 very short answer questions carrying 2 marks each.

(d) SECTION C consists of 7 short answer questions carrying 3 marks each.

(e) SECTION D consists of 2 case-based questions carrying 4 marks each.

(f) SECTION E consists of 3 long answer questions carrying 5 marks each.

(g) **All questions are compulsory.**

(h) **Use of log tables and calculators is not allowed.**

SECTION A

The following questions are multiple-choice questions with one correct answer. 1. Each questions carries 1 mark. There is no internal choice in this section.

1. 50 mL of an aqueous solution of glucose $C_6H_{12}O_6$ (Molar mass: 180 g/mol) contains 6.02×10^{22} molecules. The concentration of the solution will be

   (a) 0.1 M (b) 0.2 M

   (c) 1.0 M (d) 2.0M

2. If the standard electrode potential of an electrode is greater than zero then we can infer that its?

   (a) reduced form is more stable compared to hydrogen gas.

   (b) oxidised form is more stable compared to hydrogen gas.

   (c) reduced and oxidised forms are equally stable

   (d) reduced form is less stable than the hydrogen gas.

3. Total number of unpaired electrons present in Co^{3+} (Atomic number of Co = 27) is

   (a) 2 (b) 7

   (c) 4 (d) 5

4. Which is incorrect statement about interstitial compounds?

   (a) They are chemically reactive

   (b) They are very hard

   (c) They retain metallic conductivity.

   (d) They have high melting point

5. The correct IUPAC name of

$$\begin{array}{c} \quad\quad\; CH_3 \\ \quad\quad\; | \\ CH_3 - CH - CH_2 - CH_3 \\ \quad\quad\; | \\ \quad\quad\; OH \end{array}$$

(a) tert-butyl alcohol (b) 2, 2-Dimethylpropanol
(c) 2-Methylbutan-2-ol (d) 3-Methylbutan-3-ol

6. If a salt bridge is removed between the half cells the voltage:
(a) drops to zero (b) does not change
(c) increase gradually (d) increase repidly

7. Half life period of a first order reaction is
(a) directly propostional to the initial concentration of the reactant.
(b) Independent of initial concentration of reactions
(c) half of the rate constant
(d) None of these

8. The number of moles of $KMnO_4$ that will be needed to react with one mole of Fe^{2+} ions in acidic medium is.
(a) 5 (c) 3
(b) 2 (d) 1

9. The hydrization of the complex $[Ni(CN)_4]^{2-}$ is:
(a) Sp^3 (c) dsp^2
(b) dsp^3 (d) d^2sp^3

10. Which of the follwoing molecule is a chiral molecule?
(a) 2-Bromobutane (b) 1-Bromobutane
(c) 2-Bromopropane (d) 2-Bromopropan-2-ol

11. Which of the follwoing compound do not undergo aldol condensation?
(a) C_6H_5CHO (b) CH_3CHO
(c) CH_3COCH_3 (d) CH_3CH_2CHO

12. Which of the following is most stable diazonium salt?
(a) CH_3N_2X (b) $C_6H_5N_2X^-$
(c) $CH_3CH_2N_2X$ (d) $C_6H_5CH_2N_2\,X^+$

For questions number 13 to 16 two statements are given - one labelled Assertion (A) and the other labelled Reason (R). Select the correct answer to these questions from the codes (a) (b) (c) and (d) as given below:

(a) Both assertion (A) and reason (R) are correct statements, and reason (R) is the correct explanation of the assertion (A)

(a) Both assertion (A) and reason (R) are correct statements, but reason (R) is not the correct explanation of the assertion (A)

(c) Assertion (A) is correct, but reason (R) is incorrect statement

(d) Assertion (A) is incorrect, but reason (R) is correct statement.

13. Assertion (A): Boiling points of alkyl halides decrease in the order

$R-I > R-Br > R-Cl > R-F$

Reason(B): van der Walls forces decrease with increase in the size of halogen atom

14. Assertion (A): Low spin tetrahedral complexes are rarely observed.

Reason (B): The orbital splitting energies are not sufficiently large to forcing paring

15. Assertion (A): Benzene and hexane form ideal solution.

Reason (B): Both benzene and hexane are hydrocarbons.

16. Assertion (A): Increase in temperature increases rate of reaction

Reason(B): More reactant molecules have energy greater than threshold energy.

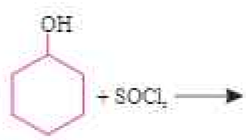
SECTION-B

17. What happens when:

(i) Propene is treated with HBr in presence of organic peroxide

(ii) Benzene is treated with CH_3Cl in presence of $AlCl_3$

18. Complete the following reactions:

(i) 

(ii) $CH_3-Br + NaI \xrightarrow{\text{Acetone}}$

19. Mention proper reasons for the following

(a) Aniline does not undergo Friedal crafts reaction.

(b) Amino group in aniline is o-and p-directing towards all electrophilic substitution reaction but aniline on nitration give a substantial amount of m-nitroaniline.

or

Arrange the following:

(a) In decreasing order of pK_b value

$CH_3CH_2NH_2, C_6H_5NH_2, (C_2H_5)_2NH, C_6H_5NHCH_3$

(b) Increasing order of boiling point:

$C_2H_5OH, (CH_3)_2NH, C_2H_5NH_2$

20. Write 'A' and 'B' in the given reactions sequences

(i) $C_6H_5\overset{+}{N}_2\overset{-}{Cl} \xrightarrow{CuCN} A \xrightarrow[\text{Complete hydrolysis}]{H_3O^+} B$

(ii) $CH_3CH_2Br \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B$

21. For a 5% solution of the (Molar mass = 60 $gmol^{-1}$) calculate the osmotic pressure at 300 K (R = 0.0821 L K^{-1} mol^{-1})

SECTION C

This section contains 7 questions will internal choice in one question. The following questions are short answer type and carry 3 marks each.

22. (a) Determine the unit of rate constant for first order reaction

(b) Show that time required for the completion of 99% the first order reaction is twice the 90% of completion.

OR

(a) What are pseudo first order reaction? Give example

(b) Rate constant k varies with temperature T according to the equation:

$$\log k = \log A - \frac{E_a}{2.303\,RT}$$

When a graph is plotted for log k vs 1/T, A straight line with a slope of 4250K is obtained. Calculate E_a for the reaction.

23. Write one chemical reaction to illustrate the following:

(a) Wiliamson synthesis (b) Kolbe's Reaction

(c) Coupling Reaction

24. (a) Give the IUPAC name and electronic configuration of central metal atom in terms of t_{2g} and e_g of $K_4[Mn(CN)_6]$.

(b) What is meant by 'Chelate effect? Give an example.

25. An antifreeze solution is prepared by dissolving 31 g of ethylene glycol (Molar mass=62 g mol^{-1}) in 600 g of water. Calculate the freezing point of the solution. (Given K_f for water=1.86 K kg mol^{-1})

26. Account for the following:

    (i) Copper (I) compounds are colourless whereas Cu(II) compounds are coloured.

    (ii) Zn, Cd and Hg are not considered as d-block elements.

    (iii) d-block elements exhibit variable oxidation stats.

27. Write the products of glucose with

    (i) $Br_2 - H_2O$ (ii) HI (iii) HCN

28. Using VBT, explain the following in relation to the paramagnetic complex $[Mn(CN)_6]^{3-}$ (Z for Mn = 25)

    (i) Type of hybridization

    (ii) Mangnetic moment value

    (iii) Type of complex - inner, outer orbital complex

SECTION D

29. Read the given passage and answer the questions follow:

    The d-block of the periodic table contains the elements of the group 3-12 and are known as transition elements. In general, the electronic configuration of these elements is (n-1) d^{1-10} ns^{1-2}. The d-orbitals of the penultimate energy level in their atoms receive electrons giving rise to the three rows of the transition metals ie., 3d, 4d and 5d series. However, Zn, Cd and Hg are not regarded as transition elements Transition elements exhibit certain characteristic properties like variable oxidation stats, complex formation, formation of coloured ions and alloys, catalytic activity, etc. Transition metals are hard (except Zn, Cd and Hg) and have a high melting are

    1. Why Zn, Cd and Hg are non-transition elements?
    2. Which transition metal of 3d series does not show variable oxidation states?
    3. Why do transition metals and their compounds show catalytic activity?
    4. Why is Cu ion coloured while Znion is colourless in aqueous solutions?

30. Read the given passage and answer the questions number 1 to 6 that follow:

    The substitution reaction of alkyl halide mainly occurs by S_N1 or S_N2 mechanism. Whatever mechanism alkyl halides follow for the ubstitution reaction to occur, the polarity of the carbon halogen bond is responsible for these substitution reactions. The rate of S_N1 reactions are governed by the stability of carbocation whereas for S_N2 reactions steric factor is the deciding factor. If the starting material is a chiral compound, we may end up with an inverted product or racemic mixture depending upon the type of mechanism followed by alkyl halide. Cleavage of ethers with HI is also governed by steric factor and stability of carbocation, which indicates that in organic chemistry, these two major factors help us in deciding the kind of product formed.

1. Predict the stereochemistry of the product formed if an optically active alkyl halide undergoes substitution reaction by S_N1 mechanism.
2. Name the instrument used for measuring the angle by which the plane polarised light is rotated.
3. Predict the major product formed when 2-Bromopentane reacts with alcoholic KOH.
4. Give one use of CHI_3.

OR

Out of CH_3-Cl and CH_3-I, which is move reactive in S_N1 reaction?

SECTION E

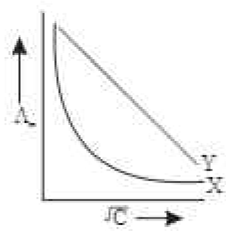
31. (a) The standard Gibbs energy ($\Delta_r G°$) for the following cell reaction is 300 kJ mol^{-1}

$Zn(s) + 2Ag^+ (aq) \rightarrow Zn^{2+} (aq) + 2Ag(s)$

Calculate $E°_{cell}$ for the reaction. (Given: 1 F = 96500 mol^{-1})

(b) Calculate $\lambda°_m$ for $MgCl_2$ if $\lambda°$ values for Mg^{2+} ion and Cl^- ion are 106 S cm^2 mol^{-1} and 76.3 S cm mol^{-1} respectively.

(c) In the plot of molar conductivity (Λ_m) $\sqrt{C}$ /square root of concentration (C), following curves are obtained for two electrolytes X and Y:



Answer the following:

(i) Predict the nature of electrolyte X and Y

(ii) What happens on extrapolation of Λ_m to concentration approaching zero for electrolytes X and Y?

OR

(a) When a steady current of 2A was passed through two electrolytic cells A and B containing electrolytes $ZnSO_4$ and $CuSO_4$ connected in series, 2g of Cu were deposited at the cathode of cell B. How long did the current flow?

What mass of Zn was deposited at cathode of cell A?

[Atomic mass: Cu = 63.5 g mol^{-1}, Zn = 65g mol^{-1}; 1F 96500 C mol^{-1}]

(b) Explain the effect of dilution on the molar conduction of electrolytic solution.

32. (a) Describe the preparation of potassium dichromate from ion chromite ore.

(b) How does acidified $KMnO_4$ solution react with

(i) Fe^{2+} (b) I^- (c) Oxalic acid

OR

(a) Write the equations involved in the preparation of $KMnO_4$ from pysolusite ore (MnO_2)

(b) Account for the following

(i) Transition metal form complex compounds

(ii) Cu^+ ion is unstable in aqueouse solution

(iii) Zn has lowest enthalpy of atomization.

3. (a) An organic compound 'A' having molecular formula $C_5H_{10}O$ gives negative Tollen's test, forms n-pentane on Clemmensen reduction but doesn't give iodo-form test. Identify 'A' and give all the reactions involved.

(b) Carrying out the following conversions.

(i) Propanoic acid to 2-Bromopropanoic acid

(ii) Benzoyl chloride to benzaldehyde

(c) How will you distinguish between benzaldehyde and acetaldehyde?

OR

(a) Complete the following sequence of reactions?

$$CH_3COCH_3 \xrightleftharpoons{Ba(OH)_2} (A) \xrightarrow[-H_2O]{\Delta} (B) \xrightarrow{NaOH,\ I_2} (C) + (D)$$

(i) Identify (A) to (D)

(ii) Give the IUPAC name of (A).

(b) How can you distinguish between:

(i) Ethanol and Propanone

(ii) Benzoic acid and Phenol?

UNSOLVED SAMPLE PAPER-2

Maximum Marks: 70 **Time: 3 hours**

General Instructions:

Read the following instrurctions carefully and strictly follow them:

(a) There are 33 questions in this questions paper with internal choice.

(b) This question paper is divided into five Sections – A, B, C, D and E.

(c) Section A – Consists of 16 multiple choice (MCQ) type questions, carrying 1 mark each.

(d) Section B – Consists of 5 very short answer (VSA) type questions, carrying 2 marks each.

(e) Section C – Consists of 7 short answer (SA) type questions, carrying 3 marks each.

(f) Section D – Consists of 2 case based (CB) type questions carrying 4 marks each.

(g) Section E – Consists of 3 long answer (LA) type questions carrying 5 marks each.

(h) All questions are compulsory

(i) Use of calculators is not allowed.

SECTION A

The following questions are multiple choice questions with one correct answer. Each question carry one mark. There is no internal choice is this section.

1. The colligative property used for the determination of molar mass of polymers and proteins is:
   (a) Osmotic pressure
   (b) Depression in freezing point
   (c) Relative lowering in vapour pressure
   (d) Elevation is boiling point
2. Low concentration of oxygen in the blood and tissues of people living at high altitude is due to:
   (a) high atmospheric pressure
   (b) low temperature
   (c) low atmospheric pressure

(d) both low temperature and high atmospheric pressure

3. The correct cell to represent the following reaction is:

$Zn + 2Ag^{+} \longrightarrow Zn^{2+} + 2Ag$

(a) $2Ag \mid Ag^{+} \parallel Zn \mid Zn^{2+}$

(b) $Ag^{+} \mid Ag \parallel Zn^{2+} \mid Zn$

(c) $Ag \mid Ag^{+} \parallel Zn \mid Zn^{2+}$

(d) $Zn \mid Zn^{2+} \parallel Ag^{+} \mid Ag$

4. ΔG and E°_{cell} for a spontaneous reaction will be:

(a) positive, negative (b) negative, negative

(c) negative, positive (d) positive, positive

5. Which of the following is affected by catalyst?

(a) ΔH (b) ΔG

(c) E_a (d) ΔS

6. The order of the reaction

$H_2(g) + Cl_2(g) \xrightarrow{h\nu} 2HCl(g)$ is:

(a) 2 (b) 1

(c) 0 (d) 3

7. The compounds $[Co(SO_4)(NH_3)_5]Br$ and $[Co(Br)(NH_3)_5]SO_4$ represent:

(a) optical isomerism (b) linkage isomerism

(c) ionisation isomerism (d) coordination isomerism

8. In the reaction $R-OH + HCl \xrightarrow{ZnCl_2} RCl + H_2O$, what the correct order of reactivity of alcohol?

(a) $1° < 2° < 3°$ (b) $1° > 3° > 2°$

(c) $1° > 2° > 3°$ (d) $3° > 1° > 2°$

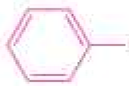
9. CH_3CONH_2 on reaction with NaOH and Br_2 in alcoholic medium gives:

(a) CH_3COONa (d) CH_3CH_2

(c) CH_3CH_2Br (d) $CH_3CH_2NH_2$

10. Which of the following is least basic?

(a) $(CH_3)_2NH$ (b) NH_3

(b)  NH_2 (d) $(CH_3)_3N$

11. The glycosidic linkage involved in linking the glucose units in amylase part of starch is:

(a) $C_1 - C_6$ α linkage (b) $C_1 - C_6$ β linkage

(b) $C_1 - C_4$ α linkage (d) $C_1 - C_4$ β linkage

12. An α-helix is a structural feature of:

(a) Sucrose (b) Starch

(c) Polypeptides (d) Nucleotides

For Questions number 13 to 16, two statements are given--one labelled as Assertion (A) and the other labelled as Reason (R). Select the correct answer to these questions from the codes (a), (b), (c) and (d) as given below.

(a) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of the Assertion (A).

(b) Both Assertion (A) and Reason (R) are true, but Reason (R) is not the correct explanation of the Assertion (A).

(c) Assertion (A) is true, but Reason (R) is false.

(d) Assertion (A) is false, but Reason (R) is true.

13. *Assertion (A):* — NH_2 group is o-and p-directing in electrophilic substitution reactions.

Reason (R): Aniline cannot undergo Friedel-Crafts reaction.

14. *Assertion (A):* Acetylation of aniline gives a monosubstituted product.

Reason (R): Activating effect of – $NHCOCH_3$ group is more than that of amino group.

15. *Assertion (A):* The molecularity of the reaction $H_2 + Br_2 \longrightarrow 2HBr$ appears to be 2.

Reason (R): Two molecules of the reactants are involved in the given elementary reaction.

16. *Assertion (A):* Low spin tetrahedral complexes are rarely observed.

Reason (R): Crystal field splitting energy is less than pairing energy for tetrahedral complexes.

SECTION B

This section contains 5 questions with internal choice in one question. The follwoing questions are very shrot answer the carry 2 mark each.

17. What is Henry's law? Give one application of it
18. On diluting two electrolytes 'A' and 'B', the Λ_m of 'A' increases 25 times while that of 'B' increases by 1.5 times. Which of the two electrolytes is strong? Justify your answer graphically.

OR

The electrical resistance of a column of 0.05 mol L^{-1} NaOH solution of diameter 1 cm and length 50 cm is $5{:}55 \times 10^3$ ohm. Calculate the conductivity.

19. Complete the following equations:
    (a) $2MnO_4^- + 5NO_2^- + 6H^+ \longrightarrow$
    (b) $Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow$
20. (a) $CH_3 - \underset{\displaystyle OH}{\underset{|}{CH}} - CH_3 \xrightarrow{PCl_5} 'A' \xrightarrow{AgCN} 'B'$

    (b) $CH_3CH_2CH_2Cl + KOH \xrightarrow{ethanol} 'A' \xrightarrow{HBr} 'B'$

    Identify 'A' and 'B' in the above reactions.
21. Account for the following:
    (i) Phenol is a stronger acid than an alcohol.
    (ii) The boiling point of alcohols decreases with increase branching of alkyl chain.

SECTION C

This section contains 7 questions with internal choice in one question. The following question are shot answer and carry 3 marks each.

22. (a) Differentiate between Ideal solution and Non-ideal solution.
    (b) 30 g of urea is dissolved in 846 g of water. Calculate the vapour pressure of water for this solution if vapour pressure of pure water at 298 K is 23.8 mm Hg.
23. Write main product formed when :
    (a) Methyl chloride is treated with NaI/Acetone.

(b) 2, 4, 6-trinitrochlorobenzene is subjected to hydrolysis.

(c) n-Butyl chloride is treated with alcoholic KOH

24. How do you convert the following:

(a) Phenol to picric acid

(b) Propanone to 2-Methylpropan-2-ol

(c) Phenol to anisole

25. Explain why:

(i) Carboxyl group in benzoic acid is meta directing.

(ii) Sodium bisulphite is used for the purification of aldehydes and ketones.

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

26. An organic compound 'A', having the molecular formula C_3H_8O on treatment with Cu at 573 K, gives 'B'. 'B' does not reduce Fehling's solution but gives a yellow precipitate of the compound "C" with $12/NaOH$. Deduce the structures of A, B and C

27. (a) What are the hydrolysis products of (i) Lactose, (ii) Maltose?

(b) Mention the basic structural difference between starch and cellulose.

28. Explain briefly:

(a) Carbylamine reaction

(b) Gabrial phthalimide reaction

(c) Swart Reaction

SECTION D

The following questions are case-based questions. Each questions has on internal choice. Read the case carefully and answer the questions that follow.

29. The rate of reaction is concerned with decrease in concentration of reactants or increase in the concentration of products per unit time. It can be expressed as instantaneous rate at a particular instant of time and average rate over a large interval of time. Mathematical representation of rate of reaction is given by rate law. Rate constant and order of a reaction can be determined from rate law or its integrated rate equation.

(i) What is average rate of reaction?

(ii) Write two factors that affect the rate of reaction.

(iii) (1) What happens to rate of reaction for zero order reaction?

(2) What is the unit of k for zero order reaction?

OR

(iii) (1) For a reaction P + 2Q $\longrightarrow$ Products

Rate = $k[P]^{1/2} (Q)^1$. What is the order of the reaction?

(2) Define pseudo first order reaction with an example.

30. In coordination compounds, metals show two types of linkages, primary and secondary. Primary valencies are ionisable and are satisfied by negatively charged ions. Secondary valencies are non-ionisable and are satisfied by neutral or negative ions having lone pair of electrons. Primary valencies are non-directional while secondary valencies decide the shape of the complexes.

(i) If $PtCl_2 2NH_3$ does not react with $AgNO_3$, what will be its formula?

(ii) What is the secondary valency of $[Co(en)_3]^{3+}$

(iii) (1) Write the formula of Iron(III)hexacyanidoferrate (II).

(2) Write the IUPAC name of $[Co(NH_3)_5]Cl_2$.

OR

(iii) Write the hybridization and magnetic behaviour of $[Ni(CN_4]^{2-}$

[Atomic number: Ni= 28]

SECTION E

The following questions are long answer type and carry 5 marks each. All questions have an internal choice.

31. (a) (i) State Kohlrausch's law of independent migration of ions. Write an expression for the limiting molar conductivity of acetic acid according to Kohlrausch's law.

(ii) Calculate the maximum work and log K_c for the given reaction at 298 K:

$$Ni\ (s) + 2Ag+\ (aq) \rightleftharpoons Ni^{2+}\ (aq) + 2Ag\ (s).$$

Given: $E°_{Ni}{}^{2+}/Ni = -0.25$ V, $E°_{Ag/Ag} = +0.80$ V, 1 F = 96500 C mol^{-1}

OR

(i) State Faraday's first law of electrolysis. How much charge, in terms of Faraday, is required for the reduction of 1 mol Cu^{2+} to Cu?

(ii) Calculate emf of the following cell at 298 K for

Mg (s) | Mg^{2+} (0.1 M) || Cu^{2+} (0.01 M) | Cu (s)

[$E°_{cell} = +2.71$ V, 1F = 96500 C mol^{-1} log 10 = 1]

32. Assign reason for each of the following:

(i) Manganese exhibits the highest oxidation state of +7 among the 3d""series of transition elements.

(ii) Transition metals and their compounds are generally found to be good catalysts in chemical reactions

(iii) Cr^{2+} is reducing in nature while with the same d-orbital configuration (d^4) Mn^{3+} is an oxidising agent.

(iv) Zn has lowest enthalpy of atomization.

(v) Cu^+ is unstable in an aqueous solution.

33. (a) (i) Carry out the following conversions:

(1) Ethanal to But-2-en-1-al

(2) Propanoic acid to 2-chloropropanoic acid

(ii) An alkene with molecular formula C_5H_{10} on ozonolysis gives a mixture of two compounds 'B' and 'C'. Compound 'B' gives positive Fehling test and also reacts with iodine and NaOH solution. Compound 'C' does not give Fehling solution test but forms iodoform. Identify the compounds 'A', 'B' and 'C'.

OR

(b) (i) Distinguish with a suitable chemical test:

(1) $CH_3COCH_2CH_3$ and $CH_3CH_2CH_2CHO$

(2) Ethanal and Ethanoic acid

(ii) Write the structure of oxime of acetone.

(iii) Identify A to D.