केंद्रीय विद्यालय संगठन

एरणाकुलम संभाग

KENDRIYA VIDYALAYA SANGATHAN

ERNAKULAM REGION

STUDENT SUPPORT MATERIAL

CLASS XII

SESSION 2022-23

आर सेन्दिल कुमार
उपायुक्त
R. Senthil Kumar
Deputy Commissioner

केन्द्रीय विद्यालय संगठन

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MESSAGE FROM DEPUTY COMMISSIONER

It gives me immense pleasure to publish the support material of Class XII (Chemistry). I am sure that the support material will definitely be of great help to the class XII students of all Kendriya Vidyalayas of our region.

Getting acquainted with the latest changes will help students to prepare well for the board examination and enable students to face Case Based and Multiple Choice Questions with confidence. This support material has been prepared by a team of dedicated and veteran teachers with expertise in their respective subjects

The Support material contains all the important aspects required by the students the design of question paper, term wise split up syllabus, summary of all the chapters, important formulae, sample question papers, problem solving and case study questions.

I would like to express my sincere gratitude to the In-charge principal and all the teachers who have relentlessly worked for the preparation of this study material. Their sincere contribution in making this project successful & praiseworthy will help the students to reach the pinnacle of success

With Best Wishes.

(R SENTHIL KUMAR)
DEPUTY COMMISSIONER

STUDENT SUPPORT MATERIAL

CHEMISTRY

OUR PATRON

Shri. R Senthil Kumar
Deputy Commissioner
KVS RO, Ernakulam Region

OUR MENTORS

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Assistant Commissioner
KVS RO, Ernakulam

CO-ORDINATOR

Shri. G Sasikumar

Principal, Kendriya Vidyalaya Kollam

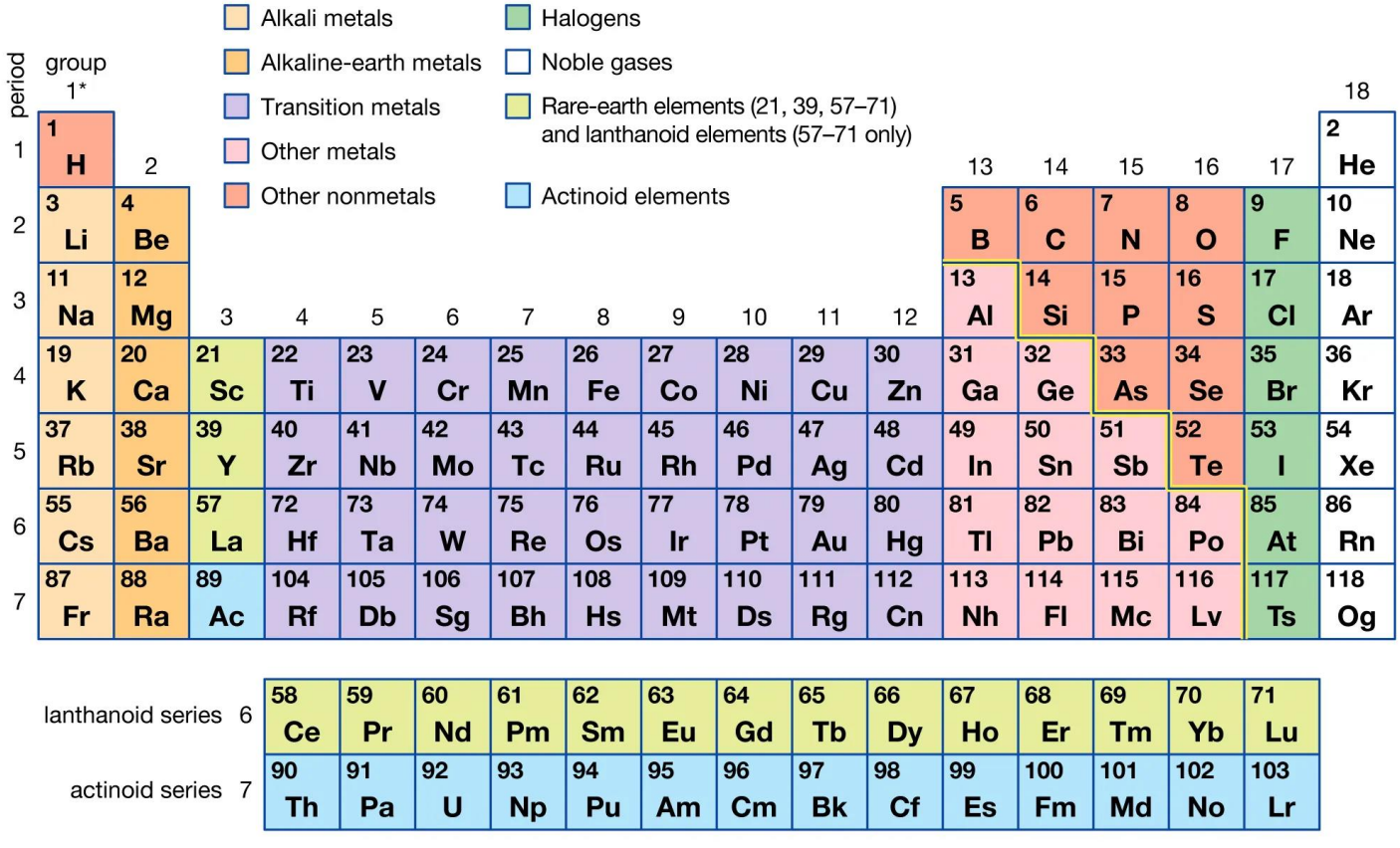
CONTENT DEVELOPMENT TEAM

S No	Name of the teacher	Name of the KV	Chapters
1	Mr Suma P	KV No.1 Calicut	Solutions
2	Ms Anitha K George	KV Keltron Nagar	
3	Mr Vinu T Rao	KV Pattom (Shift-1)	
4	Mr Sajimon K Paul	KV INS Dronacharya	Electrochemistry
5	Ms Geetha K G	KV Ramavarmapuram	
6	Ms Pameela Pavithran	KV AFS Akkulam	
7	Mr Sajeesh Kumar T V	KV Payyannur	Chemical Kinetics
8	Ms Daisy Joseph	KV No.1 Kochi	
9	Mr Pratheesh N	KV SAP Peroorkada	
10	Ms Usha Sethunath	KV NTPC Kayamkulam	d & f- Block Elements
11	Ms Nisy Sebastian P	KV Thrissur	
12	Mr N Kaladharan	KV Ottappalam	
13	Ms Jaya B	KV Ottappalam	Coordination Compounds
14	Ms Lakshmisree M	KV Kanjikode	
15	Ms Marriette P Sebastian	KV RB Kottayam	
16	Ms Ajitha A M	KV Kannur	Haloalkanes & Haloarenes
17	Ms M C Sandhya	KV Kanjikode	
18	Ms Swapna Sathees	KV Pattom (Shift-1)	
19	Mr Satheesh Kumar T T V	KV Ezhimala	Alcohols & Phenols
20	Ms Santha D	KV Pattom (Shift-2)	
21	Ms Daisy Joseph	KV RB Kottayam	
22	Ms Bindu T P	KV Malappuram	Aldehydes, Ketones & Carboxylic Acids
23	Ms Deepa C K	KV SAP Peroorkada	
24	Ms Raseena M	KV Kalpetta	
25	Ms Meena S Nair	KV Thrissur	Amines
26	Ms Biji K	KV Keltron Nagar	
27	Ms Sabitha N	KV Ernakulam	
28	Ms Seenath M S	KV Adoor (Shift-1)	Biomolecules
29	Mr Bromly Thomas	KV Pattom (Shift-2)	
30	Mr Sibu John	KV Kollam	

CONTENT REVIEW TEAM

S No	Name of the teacher	Designation	Name of the KV
1	Ms Shyla P	PGT Chemistry	KV Port Trust
2	Mr Sumesh M S	PGT Chemistry	KV Port Trust
3	Ms Raji K J	PGT Chemistry	KV Port Trust
4	Mr Sibu John	PGT Chemistry	KV Kollam

Periodic table of the elements



CHEMISTRY (Code No. 043) (2022-2023)

Higher Secondary is the most crucial stage of school education because specialized discipline-based, content-oriented courses are introduced at this juncture. Students reach this stage after 10 years of general education and opt for Chemistry to pursue their career in basic sciences or professional courses like medicine, engineering, technology and study courses in applied areas of science and technology at the tertiary level. Therefore, there is a need to provide learners with sufficient conceptual background in Chemistry, which will make them competent to meet the challenges of academic and professional courses after the senior secondary stage.

The new and updated curriculum is based on a disciplinary approach with rigour and depth taking care that the syllabus is not heavy and at the same time it is comparable to the international level. The knowledge related to the subject of Chemistry has undergone tremendous changes during the past decade. Many new areas like synthetic materials, biomolecules, natural resources, and industrial chemistry are coming in a big way and deserve to be an integral part of the chemistry syllabus at the senior secondary stage. At the international level, new formulations and nomenclature of elements and compounds, symbols and units of physical quantities floated by scientific bodies like IUPAC and CGPM are of immense importance and need to be incorporated into the updated syllabus. The revised syllabus takes care of all these aspects. Greater emphasis has been laid on the use of new nomenclature, symbols and formulations, the teaching of fundamental concepts, application of concepts in chemistry to industry/ technology, logical sequencing of units, removal of obsolete content and repetition, etc.

OBJECTIVES

The curriculum of Chemistry at Senior Secondary Stage aims to:

- promote understanding of basic facts and concepts in chemistry while retaining the excitement of chemistry.
- make students capable of studying chemistry in academic and professional courses (such as medicine, engineering, technology) at tertiary level.
- expose the students to various emerging new areas of chemistry and apprise them with their relevance in future studies and their application in various spheres of chemical sciences and technology.
- equip students to face various challenges related to health, nutrition, environment, population, weather, industries and agriculture.
- develop problem solving skills in students.
- expose the students to different processes used in industries and their technological applications.
- apprise students with interface of chemistry with other disciplines of science such as physics, biology, geology, engineering etc.
- acquaint students with different aspects of chemistry used in daily life.
- develop an interest in students to study chemistry as a discipline.
- integrate life skills and values in the context of chemistry.

COURSE STRUCTURE

CLASS–XI (THEORY) (2022-23)

Time:3Hours **Total Marks70**

S.NO	UNIT	PERIODS	MARKS
1	Some Basic Concepts of Chemistry	18	7
2	Structure of Atom	20	9
3	Classification of Elements and Periodicity in Properties	12	6
4	Chemical Bonding and Molecular Structure	20	7
5	Chemical Thermodynamics	23	9
6	Equilibrium	20	7
7	Redox Reactions	9	4
8	Organic Chemistry: Some basic Principles and Techniques	20	11
9	Hydrocarbons	18	10
	TOTAL	**160**	**70**

Unit I: Some Basic Concepts of Chemistry **18 Periods**

General Introduction: Importance and scope of Chemistry. Nature of matter, laws of chemical combination, Dalton's atomic theory: concept of elements, atoms and molecules. Atomic and molecular masses, mole concept and molar mass, percentage composition, empirical and molecular formula, chemical reactions, stoichiometry and calculations based on stoichiometry.

Unit II: Structure of Atom **20 Periods**

Discovery of Electron, Proton and Neutron, atomic number, isotopes and isobars. Thomson's model and its limitations. Rutherford's model and its limitations, Bohr's model and its limitations, concept of shells and subshells, dual nature of matter and light, de Broglie's relationship, Heisenberg uncertainty principle, concept of orbitals, quantum numbers, shapes of s, p and d orbitals, rules for filling electrons in orbitals - Aufbau principle, Pauli's exclusion principle and Hund's rule, electronic configuration of atoms, stability of half-filled and completely filled orbitals.

Unit III: Classification of Elements and Periodicity in Properties **12 Periods**

Significance of classification, brief history of the development of periodic table, modern periodic law and the present form of periodic table, periodic trends in properties of elements -atomic radii, ionic radii, inert gas radii, Ionization enthalpy, electron gain enthalpy, electronegativity, valency. Nomenclature of elements with atomic number greater than 100.

Unit IV: Chemical Bonding and Molecular Structure **20 Periods**

Valence electrons, ionic bond, covalent bond, bond parameters, Lewis's structure, polar character of covalent bond, covalent character of ionic bond, valence bond theory, resonance, geometry of covalent molecules, VSEPR theory, concept of hybridization,

involving s, p and d orbitals and shapes of some simple molecules, molecular orbital theory of homonuclear diatomic molecules (qualitative idea only), Hydrogen bond.

Unit VI: Chemical Thermodynamics 23 Periods

Concepts of System and types of systems, surroundings, work, heat, energy, extensive and intensive properties, state functions. First law of thermodynamics -internal energy and enthalpy, heat capacity and specific heat, measurement of ΔU and ΔH, Hess's law of constant heat summation, enthalpy of bond dissociation, combustion, formation, atomization, sublimation, phase transition, ionization, solution and dilution. Second law of Thermodynamics (brief introduction) Introduction of entropy as a state function, Gibb's energy change for spontaneous and non- spontaneous processes, criteria for equilibrium. Third law of thermodynamics (brief introduction).

Unit VII: Equilibrium 20 Periods

Equilibrium in physical and chemical processes, dynamic nature of equilibrium, law of mass action, equilibrium constant, factors affecting equilibrium - Le Chatelier's principle, ionic equilibrium- ionization of acids and bases, strong and weak electrolytes, degree of ionization, ionization of poly basic acids, acid strength, concept of pH, hydrolysis of salts (elementary idea), buffer solution, Henderson Equation, solubility product, common ion effect (with illustrative examples).

Unit VIII: Redox Reactions 09 Periods

Concept of oxidation and reduction, redox reactions, oxidation number, balancing redox reactions, in terms of loss and gain of electrons and change in oxidation number, applications of redox reactions.

Unit XII: Organic Chemistry -Some Basic Principles and Techniques 20 Periods

General introduction, methods of purification, qualitative and quantitative analysis, classification and IUPAC nomenclature of organic compounds. Electronic displacements in a covalent bond: inductive effect, electromeric effect, resonance and hyper conjugation. Homolytic and heterolytic fission of a covalent bond: free radicals, carbocations, carbanions, electrophiles and nucleophiles, types of organic reactions.

Unit XIII: Hydrocarbons 18 Periods

Classification of Hydrocarbons

Aliphatic Hydrocarbons:

Alkanes - Nomenclature, isomerism, conformation (ethane only), physical properties, chemical reactions including free radical mechanism of halogenation, combustion and pyrolysis.

Alkenes - Nomenclature, the structure of double bond (ethene), geometrical isomerism, physical properties, methods of preparation, chemical reactions: addition of hydrogen, halogen, water, hydrogen halides (Markovnikov's addition and peroxide effect), ozonolysis, oxidation, mechanism of electrophilic addition.

Alkynes - Nomenclature, the structure of triple bond (ethyne), physical properties, methods of preparation, chemical reactions: acidic character of alkynes, addition reaction of - hydrogen, halogens, hydrogen halides and water.

Aromatic Hydrocarbons:
Introduction, IUPAC nomenclature, benzene: resonance, aromaticity, chemical properties: mechanism of electrophilic substitution. Nitration, sulphonation, halogenation, Friedel Craft's alkylation and acylation, directive influence of the functional group in monosubstituted benzene. Carcinogenicity and toxicity.

PRACTICALS

3 HOURS/ 30 Marks

Evaluation Scheme for Examination	Marks
Volumetric Analysis	08
Salt Analysis	08
Content Based Experiment	06
Project Work	04
Class record and viva	04
Total	**30**

PRACTICAL SYLLABUS **Total Periods: 60**

Micro-chemical methods are available for several of the practical experiments, wherever possible such techniques should be used.

A. Basic Laboratory Techniques

1. Cutting glass tube and glass rod
2. Bending a glass tube
3. Drawing out a glass jet
4. Boring a cork

B. Characterization and Purification of Chemical Substances

1. Determination of melting point of an organic compound.
2. Determination of boiling point of an organic compound.
3. Crystallization of impure sample of any one of the following: Alum, Copper Sulphate, Benzoic Acid.

C. Experiments based on pH

1. Any one of the following experiments:

- Determination of pH of some solutions obtained from fruit juices, solution of known and varied concentrations of acids, bases and salts using pH paper or universal indicator.

- Comparing the pH of solutions of strong and weak acids of same concentration. Study the pH change in the titration of a strong base using universal indicator.

2. Study the pH change by common-ion in case of weak acids and weak bases.

D. Chemical Equilibrium

One of the following experiments:

1. Study the shift in equilibrium between ferric ions and thiocyanate ions by increasing/decreasing the concentration of either of the ions.
2. Study the shift in equilibrium between $[Co(H_2O)_6]^{2+}$ and chloride ions by changing the concentration of either of the ions.

E. Quantitative Estimation

1. Using a mechanical balance/electronic balance.
2. Preparation of standard solution of Oxalic acid.
3. Determination of strength of a given solution of Sodium hydroxide by titrating it against standard solution of Oxalic acid.
4. Preparation of standard solution of Sodium carbonate.
5. Determination of strength of a given solution of hydrochloric acid by titrating it against standard Sodium Carbonate solution.

F. Qualitative Analysis

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

Cation:

Pb^{2+}, Cu^{2+} As^{3+}, $A\ell^{3+}$, Fe^{3+}, Mn^{2+}, Zn^{2+}, Ni^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Mg^{2+}, NH_4^+

Anions:

$(CO_3)^{2-}$, S^{2-}, $(SO_3)^{2-}$, $(NO_2)^-$, $(SO_4)^{2-}$, $C\ell^-$, Br^-, I^-, $(PO_4)^{3-}$, $(C_2O_4)^{2-}$, CH_3COO^-, NO_3^-

(Note: Insoluble salts excluded)

2. Detection of -Nitrogen, Sulphur, Chlorine in organic compounds.

G. PROJECTS

Scientific investigations involving laboratory testing and collecting information from other sources.

A few suggested Projects

- Checking the bacterial contamination in drinking water by testing sulphide ion
- Study of the methods of purification of water
- Testing the hardness, presence of Iron, Fluoride, Chloride, etc., depending upon the regional variation in drinking water and study of causes of presence of these ions above permissible limit (if any).
- Investigation of the foaming capacity of different washing soaps and the effect of addition of Sodium carbonate on it
- Study the acidity of different samples of tea leaves.
- Determination of the rate of evaporation of different liquids.
- Study the effect of acids and bases on the tensile strength of fibers.

- Study of acidity of fruit and vegetable juices.

Note: Any other investigatory project, which involves about 10 periods of work, can be chosen with the approval of the teacher.

PRACTICAL EXAMINATION FOR VISUALLY IMPAIRED STUDENTS

Note: Same Evaluation scheme and general guidelines for visually impaired students as given for Class XII may be followed.

A. **List of apparatus for identification for assessment in practical (All experiments)**

Beaker, tripod stand, wire gauze, glass rod, funnel, filter paper, Bunsen burner, test-tube, test-tube stand, dropper, test tube holder, ignition tube, china dish, tongs, standard flask, pipette, burette, conical flask, clamp stand, dropper, wash bottle

- Odour detection in qualitative analysis
- Procedure/Setup of the apparatus

B. **List of Experiments A. Characterization and Purification of Chemical Substances**

1. Crystallization of an impure sample of any one of the following: copper sulphate, benzoic acid

C. **Experiments based on pH**

1. Determination of pH of some solutions obtained from fruit juices, solutions of known and varied concentrations of acids, bases and salts using pH paper
2. Comparing the pH of solutions of strong and weak acids of same concentration.

D. **Chemical Equilibrium**

1. Study the shift in equilibrium between ferric ions and thiocyanate ions by increasing/decreasing the concentration of either ions.
2. Study the shift in equilibrium between $[Co(H_2O)_6]^{2+}$ and chloride ions by changing the concentration of either of the ions.

E. **Quantitative estimation**

1. Preparation of standard solution of oxalic acid.
2. Determination of molarity of a given solution of sodium hydroxide by titrating it against standard solution of oxalic acid.

F. **Qualitative Analysis**

1. Determination of one anion and one cation in a given salt
2. Cations - NH_4^+

Anions – $(CO_3)^{2-}$, S^{2-}, $(SO_3)^{2-}$, Cl^-, CH_3COO^-
(Note: insoluble salts excluded)

3. Detection of Nitrogen in the given organic compound.
4. Detection of Halogen in the given organic compound.

Note: The above practical may be carried out in an experiential manner rather than recording observations.

PRESCRIBED BOOKS:

1. Chemistry Part – I, Class-XI, Published by NCERT.
2. Chemistry Part – II, Class-XI, Published by NCERT.
3. Laboratory Manual of Chemistry, Class XI Published by NCERT
4. Other related books and manuals of NCERT including multimedia and online sources

Note:

The content indicated in NCERT textbooks as excluded for the year 2022-23 is not to be tested by schools.

CLASS XII (2022-23) (THEORY)

Time: 3 Hours **70 Marks**

S.No.	Title	No. of Periods	Marks
1	Solutions	15	7
2	Electrochemistry	18	9
3	Chemical Kinetics	15	7
4	d -and f -Block Elements	18	7
5	Coordination Compounds	18	7
6	Haloalkanes and Haloarenes	15	6
7	Alcohols, Phenols and Ethers	14	6
8	Aldehydes, Ketones and Carboxylic Acids	15	8
9	Amines	14	6
10	Biomolecules	18	7
	Total	**160**	**70**

Unit II: Solutions **15 Periods**

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 **18 Periods**

Redox reactions, EMF of a cell, standard electrode potential, Nernst equation and its application to chemical cells, Relation between Gibbs energy change and EMF of a cell, conductance in electrolytic solutions, specific and molar conductivity, variations of conductivity with concentration, Kohlrausch's Law, electrolysis and law of electrolysis (elementary idea), dry cell-electrolytic cells and Galvanic cells, lead accumulator, fuel cells, corrosion.

Unit IV: Chemical Kinetics **15 Periods**

Rate of a reaction (Average and instantaneous), factors affecting rate of reaction: concentration, temperature, catalyst; order and molecularity of a reaction, rate law and specific rate constant, integrated rate equations and half-life (only for zero and first order reactions), concept of collision theory (elementary idea, no mathematical treatment), activation energy, Arrhenius equation.

Unit VIII: d and f Block Elements **18 Periods**

General introduction, electronic configuration, occurrence and characteristics of transition metals, general trends in properties of the first-row transition metals – metallic character, ionization enthalpy, oxidation states, ionic radii, 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 **18 Periods**

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. **15 Periods**

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 **14 Periods**

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**

Amines: 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.

Note:

The content indicated in NCERT textbooks as excluded for the year 2022-23 is not to be tested by schools.

PRACTICALS
3 HOURS/ 30 MARKS

Evaluation Scheme for Examination	**Marks**
Volumetric Analysis	08
Salt Analysis	08
Content Based Experiment	06
Project Work	04
Class record and viva	04
Total	**30**

PRACTICAL SYLLABUS **60 Periods**

Micro-chemical methods are available for several of practical experiments.

Wherever possible, such techniques should be used.

A. Surface Chemistry

(a) Preparation of one lyophilic and one lyophobic sol

Lyophilic sol - starch, egg albumin and gum

Lyophobic sol - aluminium hydroxide, ferric hydroxide, arsenous sulphide.

(b) Dialysis of sol-prepared in (a) above.

(c) Study of the role of emulsifying agents in stabilizing the emulsion of different oils.

B. Chemical Kinetics

(a) Effect of concentration and temperature on the rate of reaction between Sodium Thiosulphate and Hydrochloric acid.

(b) Study of reaction rates of any one of the following:

(i) Reaction of Iodide ion with Hydrogen Peroxide at room temperature using different concentrations of Iodide ions.

(ii) Reaction between Potassium Iodate, (KIO_3) and Sodium Sulphite: (Na_2SO_3) using starch solution as an indicator (clock reaction).

C. Thermochemistry

Any one of the following experiments

(a) Enthalpy of dissolution of Copper Sulphate or Potassium Nitrate.

(b) Enthalpy of neutralization of strong acid (HCl) and strong base (NaOH).

(c) Determination of enthaply change during interaction (Hydrogen bond formation) between Acetone and Chloroform.

D. Electrochemistry

Variation of cell potential in $Zn/Zn^{2+}||\ Cu^{2+}/Cu$ with change in concentration of electrolytes ($CuSO_4$ or $ZnSO_4$) at room temperature.

E. Chromatography

(a) Separation of pigments from extracts of leaves and flowers by paper chromatography and determination of Rf values.

(b) Separation of constituents present in an inorganic mixture containing two cations only (constituents having large difference in Rf values to be provided).

F. Preparation of Inorganic Compounds

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

G. Preparation of Organic Compounds

Preparation of any one of the following compounds

i) Acetanilide ii) Di -benzalAcetone iii) p-Nitroacetanilide iv) Aniline yellow or 2 -Naphthol Anilinedye.

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

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

I. Characteristic tests of carbohydrates, fats and proteins in pure samples and their detection in given foodstuffs.

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

(a) Oxalic acid,

(b) Ferrous Ammonium Sulphate

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

K. Qualitative analysis

Determination of one anion and one cation in a given salt

Cation:

Pb^{2+}, Cu^{2+} As^{3+}, $A\ell^{3+}$, Fe^{3+}, Mn^{2+}, Zn^{2+}, Ni^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Mg^{2+}, NH_4^+

Anions:

$(CO_3)^{2-}$, S^{2-}, $(SO_3)^{2-}$, $(NO_2)^-$, $(SO_4)^{2-}$, Cl^-, Br^-, I^-, $(PO_4)^{3-}$, $(C_2O_4)^{2-}$, CH_3COO^-, NO_3^-
(Note: Insoluble salts excluded)

INVESTIGATORY PROJECT

Scientific investigations involving laboratory testing and collecting information from other sources A few suggested Projects.

- Study of the presence of oxalate ions in guava fruit at different stages of ripening.
- Study the quantity of casein present in different samples of milk.
- Preparation of soybean milk and its comparison with natural milk with respect to curd formation, the effect of temperature, etc.
- Study of the effect of Potassium Bisulphate as a food preservative under various conditions (temperature, concentration, time, etc.)
- Study of digestion of starch by salivary amylase and effect of pH and temperature on it.
- Comparative study of the rate of fermentation of the following materials: wheat flour, gram flour, potato juice, carrot juice, etc.
- Extraction of essential oils present in Saunf (aniseed), Ajwain (carum), Illaichi (cardamom).
- Study of common food adulterants in fat, oil, butter, sugar, turmeric power, chilli powder and pepper.

Note: Any other investigatory project, which involves about 10 periods of work, can be chosen with the approval of the teacher.

Practical Examination for Visually Impaired Students of Classes XI and XII
Evaluation Scheme

Time Allowed: Two hours **Max. Marks:30**

Topic	**Marks**
Identification/Familiarity with the apparatus	5
Written test (based on given/prescribed practicals)	10
Practical Record	5
Viva	10
Total	**30**

General Guidelines

- The practical examination will be of two hours duration.
- A separate list of ten experiments is included here.
- The written examination in practicals for these students will be conducted at the time of the practical examination of all other students.
- The written test will be of 30 minutes duration.
- The question paper given to the students should be legibly typed. It should contain a total of 15 practical skill-based very short answer type questions. A student would be required to answer any 10 questions.
- A writer may be allowed to such students as per CBSE examination rules.

- All questions included in the question papers should be related to the listed practical. Every question should require about two minutes to be answered.
- These students are also required to maintain a practical file. A student is expected to record at least five of the listed experiments as per the specific instructions for each subject. These practicals should be duly checked and signed by the internal examiner.
- The format of writing any experiment in the practical file should include aim, apparatus required, simple theory, procedure, related practical skills, precautions etc.
- Questions may be generated jointly by the external/internal examiners and used for assessment.
- The viva questions may include questions based on basic theory/principle/concept, apparatus/materials/ chemicals required, procedure, precautions, sources of error etc.

1. Items for Identification/Familiarity of the apparatus for assessment in practical (All experiments)

Beaker, glass rod, tripod stand, wire gauze, Bunsen burner, Whatman filter paper, gas jar, capillary tube, pestle and mortar, test tubes, tongs, test tube holder, test tube stand, burette, pipette, conical flask, standard flask, clamp stand, funnel, filter paper

Hands-on Assessment

- Identification/familiarity with the apparatus
- Odour detection in qualitative analysis

2. List of Practicals

The experiments have been divided into two sections:

Section A and Section B.

The experiments mentioned in Section B are mandatory.

SECTION- A

A **Surface Chemistry**

1 Preparation of one lyophilic and one lyophobic sol - starch, egg albumin and gum
2 Preparation of one lyophobic sol– Ferric hydroxide

B **Chromatography**

Separation of pigments from extracts of leaves and flowers by paper chromatography and determination of R_f values (distance values may be provided).

C **Tests for the functional groups present in organic compounds**:

(1) Alcoholic and Carboxylic groups.
(2) Aldehydic and Ketonic

D Characteristic tests of carbohydrates and proteins in the given foodstuffs.

E Preparation of Inorganic Compounds- Potash Alum

SECTION-B (Mandatory)

F Quantitative analysis

(1) (a) Preparation of the standard solution of Oxalic acid of a given volume

(b) Determination of molarity of $KMnO_4$ solution by titrating it against a standard solution of Oxalic acid.

(2) The above exercise [F 1 (a) and (b)] to be conducted using Ferrous ammonium sulphate (Mohr's salt)

G Qualitative analysis:

(1) Determination of one cation and one anion in a given salt. Cation $–NH_4^+$

Anions – CO_3^{2-}, S^{2-}, SO_3^{2-}, Cl^-, CH_3COO^-

(Note: Insoluble salts excluded)

Note: The above practical may be carried out in an experiential manner rather than recording observations.

PRESCRIBED BOOKS

1. Chemistry Part -I, Class-XII, Published by NCERT.
2. Chemistry Part -II, Class-XII, Published by NCERT.
3. Laboratory Manual of Chemistry, Class XI Published by NCERT
4. Other related books and manuals of NCERT including multimedia and online sources

QUESTION PAPER DESIGN CLASSES –XI and XII (2022-23)

S.No	Domains	Marks	%
1	**Remembering and Understanding:** Exhibit memory of previously learned material by recalling facts, terms, basic concepts and answers. Demonstrate understanding of facts and ideas by organizing, comparing, translating, interpreting, giving descriptions and stating main ideas.	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

For more details kindly refer to Sample Question Paper of class XII for the year 2022-23 to be published by CBSE at its website.

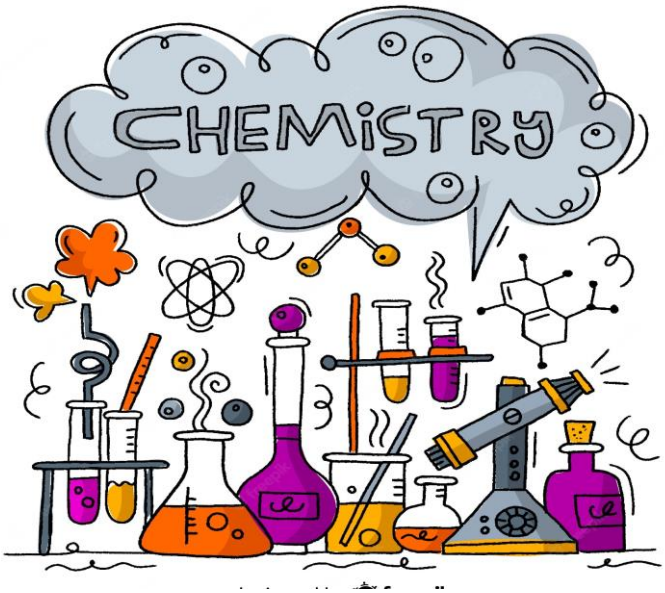
KENDRIYA VIDYALAYA SANGATHAN ERNAKULAM REGION
SPLIT UP SYLLABUS FOR CHEMISTRY (043) CLASS XII -2022-2023

MONTH	UNIT	NAME OF CHAPTER	NO OF PERIODS
APRIL	1	SOLUTIONS	15
	2	ELECTROCHEMISTRY (till and including 3.3.2 Nernst equation)	9
JUNE	2	ELECTROCHEMISTRY (from 3.4 Measurement of Conductivity)	9
JULY	3	CHEMICAL KINETICS	15
	4	d-AND f-BLOCK ELEMENTS (d Block elements)	13
AUGUST	4	d-AND f-BLOCK ELEMENTS (from 8.5 f block elements)	5
	5	COORDINATION COMPOUNDS	18
	6	HALO ALKANES AND HALO ARENES (till and including 10.6.1 Reactions of Halo Alkanes)	7
SEPTEMBER	6	HALO ALKANES AND HALO ARENES (From 10.6.2 Reactions of Halo Arenes)	08
	7	ALCOHOLS	14
OCTOBER	8	ALDEHYDES, KETONES AND CARBOXYLIC ACIDS	15
		REVISION & HALF YEARLY EXAMINATION	
NOVEMBER	9	AMINES	14
	10	BIOMOLECULES	18
DECEMBER		REVISION & PB-1	
JANUARY		REVISION & PB-2	

SPLIT UP SYLLABUS FOR PRACTICAL CHEMISTRY (043) CLASS XII

MONTH	SI	EXPERIMENTS
JUNE/JULY	1	Volumetric Analysis
AUGUST / SEPTEMBER	2	Qualitative Analysis
OCTOBER /NOVEMBER	3	Core experiments and Investigatory project

INDEX



CHAPTER 2

SOLUTIONS

GIST OF THE LESSON

- **Solution:** A homogeneous mixture of two or more chemically non-reactive substances whose concentration can be varied within certain limits.
- **Solubility:** The amount of the solute present in 100g of the solvent in a saturated solution at a given temperature**.**
- **Saturated Solution:** A solution which cannot dissolve any more of the solute at a particular temperature.
- **Unsaturated Solution**: A solution in which more of the solute can be dissolved at a particular temperature.
- **Super Saturated Solution:** A solution in which the amount of solute present in 100g of the solvent at a particular temperature is more than its normal solubility at that temperature.

- **Mass Percent:** Mass of solute per 100g of solution**.**
- **Molarity:** Number of moles of solute per litre of solution.
- **Molality:** Number of moles of solute per kilogram of solvent.
- **Mole Fraction:** Ratio of number of moles of component to total number moles.
- **Parts per million:** The number of parts by mass of solute per million parts by mass of solution.

Gas in Liquid solution:

- Solubility of gas in liquid decreases with rise in temperature
- Henry's law: At a given temperature, mole fraction of a gas is proportional to the partial pressure of the gas over the solution.
- $p = K_H \chi$
- **K_H α Temperature, K_H α 1/Solubility**

Liquid in Liquid solution:

- **Vapour Pressure:** The pressure developed above the liquid at particular temperature at the equilibrium point.
- **Raoult's Law:** In solution of volatile liquids, the partial vapour pressure of each component is directly proportional to its mole fraction**.**

$$p_A = p^0_A \chi_A \quad , pB = p^0_B \chi_B \quad ,\text{Total pressure } p = p_A + p_B$$

- **Ideal Solution:** The liquid-liquid solution which obey Raoult's law at all concentrations**.**
  Forces of attraction between A-A, B-B is similar to A-B

$$p_{total} = p_A + p_B, \ \Delta H_{mix} = 0; \ \Delta V_{mix} = 0.$$

- **Non−Ideal Solution:** The liquid-liquid solution which do not obey Raoult's law. Show positive or negative deviations from Raoult's law.

- **Azeotrope:** The mixture of liquids which boils at constant temperature like pure liquid and has same composition of component in liquid as well as vapour phase**.**

- **Types of azeotropes**:

  (i) Minimum boiling azeotrope: The solutions which show a large positive deviation from Raoult's law form minimum boiling azeotrope. Eg: ethanol-water mixture

  (ii) Maximum boiling azeotrope: The solutions that show large negative deviation from Raoult's law form maximum boiling azeotrope at a specific composition. Eg: Nitric acid and water mixture.

- **Colligative Properties:** The properties of the solution which are independent of nature of solute but depend upon the concentration of solute particles.
  - **Lowering of Vapour Pressure:** It is the difference in the vapour pressure of the pure solvent and that of solution which are added with non-volatile solute**.**
  - **Relative Lowering of Vapour Pressure:** The ratio of the lowering of vapour pressure to the vapour pressure of pure solvent**.**
  - **Molal Elevation Constant (Kb):** The elevation in the boiling point of the solution when its molality is unity. It is also called molal ebullioscopic constant**.**
  - **Molal Depression Constant (Kf):** The depression in the freezing point when the molality of the solution is unity. It is also called molal cryoscopic constant.
  - **Osmosis Pressure:** The excess pressure that must be applied to the solution side to prevent the flow of solvent into solution through a semi−permeable membrane**.**
  - **Isotonic Solutions:** Two solutions having same osmotic pressure at a given temperature are called isotonic solutions. They have same molar concentration. When such solutions are separated by semipermeable membrane no osmosis occurs between them.
  - Osmotic pressure associated with the fluid inside the blood cell is equivalent to that of 0.9% (mass/ volume) sodium chloride solution, called normal saline solution and it is safe to inject intravenously. On the other hand, if we place the cells in a solution containing more than 0.9% (mass/volume) sodium chloride, water will flow out of the cells and they would shrink. Such a solution is called hypertonic. If the salt concentration is less than 0.9% (mass/volume), the solution is said to be hypotonic. In this case, water will flow into the cells if placed in this solution and they would swell.
  - **Reverse Osmosis**: If the pressure applied on the solution side is more than osmotic pressure of the solution then the solvent particles will move from solution to solvent side. This process is reverse osmosis. Reverse osmosis is used in desalination of sea water. Cellulose acetate is permeable to water but impermeable to impurities and ions present in sea water.
  - Molar masses that are lower or higher than expected values when calculated (generally using colligative properties) are called abnormal molar masses.

Association of molecules leads to decrease in the number of particles in the solution resulting in a decrease in the value of colligative property. Colligative property is inversely related to the molecular mass.

Dissociation leads to increase in the number of solute particles in the solution resulting in an increase in the value of colligative property.

$$i = \frac{\text{Normal molar mass}}{\text{Abnormal molar mass}}$$

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

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

In the case of dissociation $i < 1$

And in the case of association $i > 1.$

Thus, equations for colligative properties can be modified as follows after inclusion of Van't Hoff factors.

Relative lowering of vapour pressure of solvent

$$\frac{p_1^0 - p_1}{p_1^0} = i \,.\frac{n_2}{n_1}$$

Elevation of boiling point

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

Depression of Freezing point,

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

Osmotic pressure of solutions,

$$\pi = i\, n_2\, RT/V$$

(1) Mass Percentage:

$$\text{Mass \% of component} = \frac{\text{Mass of component in solution}}{\text{Total mass of the solution}} \times 100$$

(2) **Volume Percentage:**

$$\text{Volume \% of component} = \frac{\text{Volume of component}}{\text{Total volume of the component}} \times 100$$

(3) **Parts Per million:**

$$\text{ppm} = \frac{\text{Mass of component}}{\text{Total mass of solution}} \times 10^6$$

(4) **Molarity (M)**

$$\text{Molarity} = \frac{\text{Moles of solute}}{\text{Volume of solutoin (in litre)}}$$

$$\text{moles}(n) = \frac{\text{weight}}{\text{Molecular weight}}$$

If volume of solution is in ml then divide it by 1000 to change into liters

$$\text{Molarity} = \frac{\text{Moles of solute}}{\frac{\text{volume of solution (in ml)}}{1000}}$$

(5) **Molality (m)**

$$\text{Molality}(m) = \frac{\text{moles of solute}}{\text{weight of solvent}(kg)}$$

(6) **Mole fraction**

$$\text{Mole fraction } (x) = \frac{\text{Number of moles of component}}{\text{Total number of moles of all component}}$$

(7) **Henry's law**

$$p = k_H x \qquad \text{OR} \qquad m = k_H p$$

(8) **Roult's law**

$$p_A = p_A^\circ x_A$$
$$p_B = p_B^\circ x_B$$

p_A = Vapour pressure of component in solution

p_A° = Vapour pressure of pure component

x_A = Mole fraction of component

(9) **Relative lowering of vapour pressure**

$$\frac{p_A^\circ - p_A}{p_A^\circ} = x_B \qquad (x_B = \text{mole fraction of solute})$$

OR

$$\frac{p_A^\circ - p_A}{P_A^\circ} = \frac{n_B}{n_A + n_B}$$

(10) **Elevation in Boiling Point**

$$\Delta T_b = k_b m \qquad (m = \text{molality})$$

$$\Delta T_b = \frac{k_b \; w_B \times 1000}{M_B \times w_A} \quad (k_b = \text{constant})$$

$$\Delta T_b = T_b - T_b^\circ$$

(11) **Depression in freezing point**

$$\Delta T_f = k_f m \qquad (T_f = \text{freezing point of solution})$$

$$\Delta T_f = T_f^\circ - T_f \qquad (T_f^\circ = \text{freezing point of pure solvent})$$

$$\Delta T_f = \frac{k_f \; W_B \times 1000}{M_B \times W_A}$$

(12) **Osmotic pressure**

$$\pi v = nRT$$

$$\pi = \frac{n}{v} RT = \frac{w_B RT}{v_{MB}} \quad (\pi = \text{osmotic pressure})$$

$$\pi = CRT$$

(13) **Vant Hoff Factor (i)**

$$i = \frac{\text{Normal molar mass}}{\text{Observed molar mass}(\text{abnormal})}$$

(14) **Degree of association/dissociation**

$$(\alpha) = \frac{\text{No. of moles of substance associated/dissociated}}{\text{Total number of moles of the substance taken}}$$

Ex – **In case of Association**

$$2\,CH_3COOH \rightarrow (CH_3COOH)_2$$

$\rightarrow$ initial moles = 1 0

$\rightarrow$ After association = $1-\alpha$ $\frac{\alpha}{n}$

$$i = \frac{1 - \alpha + \frac{\alpha}{n}}{1}$$

Ex. **In case of Dissociation**

$$\begin{array}{lccc} & kCl & \rightarrow k^{+} & + \quad Cl^{-} \\ \rightarrow \text{initially} = & 1 & 0 & 0 \\ \rightarrow \text{After dissociation} = & 1-\alpha & \alpha & \alpha \end{array}$$

$$i = \frac{1-\alpha+n\alpha}{1}$$

MULTIPLE CHOICE QUESTIONS

1. **Osmotic pressure of a solution is 0.0821 atm at a temperature of 300 K. The concentration in moles/lit will be:**
   (a) 0.33
   (b) 0.666
   (c) 0.0033
   (d) 3

2. **The value of Henry's Law constant is:**
   (a) larger for gases with higher solubility
   (b) larger for gases with lower solubility
   (c) constant for all gases
   (d) not related to the solubility of gases

3. **The elevation in boiling point of 0.01 M $BaCl_2$ solution is about than that of 0.01 M solution of glucose.**
   (a) Same
   (b) two times
   (c) three times
   (d) four times

4. **Considering the formation, breaking and strength of Hydrogen bond, predict which of the following mixtures will show a positive deviation from Roult's law?**
   (a) Methanol and Acetone
   (b) Chloroform and Acetone
   (c) Nitric Acid and Water
   (d) Phenol and Aniline

5. **If a molecule AB undergoes dimerization in Benzene, its Van't Hoff factor is found to be 0.60. The degree of dissociation of AB is**
   (a) 20%
   (b) 60%
   (c) 80%
   (d) 50%

6. **Density of a 2.05 M solution of acetic acid in water is 1.02 g/mL. The molality of the solution is**
   (a) 3.28 mol kg^{-1}
   (b) 2.28 mol kg^{-1}

(c) 0.44 mol kg^{-1}
(d) 1.14 mol kg^{-1}

7. **At certain temperature, a 5.12% solution of cane sugar is isotonic with a 0.9% solution of an unknown solute. The molar mass of solute is**
   (a) 60
   (b) 46.67
   (c) 120
   (d) 90

8. **Which is not a colligative property?**
   (a) Osmotic pressure
   (b) Lowering of vapour pressure
   (c) Depression in freezing point
   (d) Molal elevation constant

9. **12g of Urea is dissolved in 1L of water and 68.4g sucrose is dissolved in 1L of water. Relative lowering of vapour pressure of Urea solution is:**
   (a) Greater than sucrose solution
   (b) Less than sucrose solution
   (c) Double that of sucrose solution
   (d) Equal to that of sucrose solution

10. **Ethylene glycol is used as an antifreeze in a cold climate. Mass of Ethylene glycol which should be added to 4kg water to prevent it from freezing at -6^0C will be (K_f for water = 1.86Kkg/mol^{-1}, Molar mass of Ethylene glycol = 62g/mol)**
    (a) 204.30g
    (b) 800g
    (c) 304.60g
    (d) 400g

11. **The depression in freezing point for 1M Urea, 1M Glucose and 1M NaCl are in the ratio**
    (a) 1:1:2
    (b) 3:2:2
    (c) 1:2:3
    (d) None of these

12. **The solution that forms maximum boiling azeotropes is**
    (a) Carbon disulphide – Acetone
    (b) Benzene - Toluene
    (c) Acetone – Chloroform
    (d) n-Hexane – n-Hectane.

13. **The type of intermolecular interaction present in a solution of n- Hexane and n-Octane is:**
    (a) London dispersion forces
    (b) Dipole-dipole interaction
    (c) Hydrogen bonding
    (d) Ion-dipole interaction

14. Which among the following is least soluble in water?

(a) Phenol
(b) Toluene
(c) Ethylene glycol
(d) Pentanol

15. Which of the following is dependent on temperature?

(a) Molality
(b) Molarity
(c) Mole Fraction
(d) Mass percentage

ANSWER KEY

1. c	2. b	3. c	4. a	5. c
6. b	7. a	8. d	9. d	10. b
11. a	12. c	13. a	14. b	15. b

ASSERTION -REASON TYPE QUESTIONS

In the following questions, two statements (Assertion) A and Reason (R) are given.

Mark

(a) If A and R both are correct and R is the correct explanation of A
(b) If A and R both are correct 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

1. **Assertion**: When a blood cell is placed in hypertonic solution, it shrinks.
Reason: Blood is isotonic with 0.9% NaCl solution.

2. **Assertion**: The aquatic species feel more comfortable in winter than summer
Reason: Solubility of gases increases with increase of temperature.

3. **Assertion**: Azeotropic mixture are formed only by non-ideal solutions.
Reason: Boiling point of an azeotropic is either higher than both the components or lower than both the components.

4. **Assertion**: Soft drink and soda water bottles are sealed under high pressure.
Reason: The dissolution of gas in liquid is an endothermic process.

5. **Assertion**: On adding non-volatile solute to water its vapour pressure increases.
Reason: Relative lowering of vapour pressure is a colligative property

6. **Assertion**: Addition of ethylene glycol to water lowers the freezing point of water, therefore, used as antifreeze.
Reason: 1, 2-Ethanediol is soluble in water because it can form H-bond with water, therefore vapour pressure of solution is lowered.

7. **Assertion**: In an ideal solution, ΔH_{mix} is zero.
Reason: In an ideal solution, A – B interactions are lower than A-A and B-B interactions.

8. **Assertion**: Mixture of ethanol and cyclohexane forms a solution with negative deviation from Raoult's law.
Reason: When ethanol mixes in cyclohexane, it reduces the intermolecular force between ethanol molecules.

9. **Assertion**: Van't Hoff factor for Benzoic acid in Benzene is less than 1
Reason: Benzoic acid dimerizes in Benzene.

10. **Assertion**: Larger the value of cryoscopic constant of the solvent, lesser will be the freezing point of solution.
Reason: Depression in freezing point depends on the nature of the solvent.

11. **Assertion**: An aqueous solution of NaCl freezes below 273 K.
Reason: Vapour pressure of the solution is less than that of the pure solvent.

12. **Assertion**: The sum of mole fractions of all components of a solution is unity.
Reason: Mole fraction is independent of temperature.

13. **Assertion**: Osmosis involves movement of solvent molecules from its lower concentration to its higher concentration.
Reason: Solution having the same osmotic pressure are called isotonic solution.

14. **Assertion**: When blood cell is placed in a solution containing 1.5 % NaCl, it willshrink.

Reason: Blood is isotonic with 1.5% NaCl solution.

15. **Assertion**: Molarity of a solution in liquid state changes with temperature.
Reason: The volume of a solution changes with change in temperature.

ANSWER KEY

1. b	2. c	3. b	4. c	5. d
6. a	7. c	8. d	9. a	10. c
11. a	12. b	13. b	14. c	15. a

SHORT ANSWER QUESTIONS

1**. How does sprinkling of salt help in clearing the snow-covered roads in hilly areas? Explain the phenomenon involved in the process.**

Ans: The phenomenon involved in the melting of snow in snow covered roads is the depression in freezing point which caused by the addition of non-volatile impurities to a liquid. Addition

of salt (sodium chloride) lowers the freezing point temperature of water and thus, helps in the melting of snow.

2. What is "semi permeable membrane"?

Ans: The membranes which allow only the movement of the solvent molecules through them is called semi permeable membrane. The membranes appear to be continues sheet or flims. here only the molecules of the solvent can pass while those of the solute which are of bigger size, are not in a position to pass through.

3. Give an example of a material used for making semipermeable membrane for carrying out reverse osmosis.

Ans: Polymer cellulose acetate is used for making semipermeable membrane for carrying out reverse osmosis.

4.**Distinction between molarity and molality.**
Ans: Molarity: It is the number of moles of solute dissolved in 1 litre of solution. It is temperature dependent.
Molality : It is the number of moles of solute dissolved in 1 kg of the solvent and independent of temperature.

5.Define an ideal solution and write one of its characteristics.
Ans: An ideal solution may be defined as the solution which obeys Raoult's law exactly over the entire range of temperature and pressure. For ideal solution Heat of mixing is zero
Volume change of mixing is zero.

6. (i) Write the colligative property which is used to find the molecular mass of macromolecules.
(ii) In non-ideal solution, what type of deviation shows the formation of minimum boiling azeotropes?
Ans (i) Osmotic pressure
(ii) Minimum boiling azeotropes show positive deviation from Raoult's law.

7.Explain why on addition of 1 mol of NaCl to 1 litre of water, the boiling point of water increases, while addition of 1 mol of methyl alcohol to one litre of water decreases its boiling point.

Ans: Sodium chloride (NaCl) is a non-volatile solute. When added to water taken in a beaker, the solute occupies some surface area. As a result, the vapour pressure decreases and the boiling point of solution increases. On the other hand, methyl alcohol is more volatile than water. The addition of methyl alcohol to water increases the total vapour pressure of the solution. The boiling point of the solution decreases.

8.What type of intermolecular attractive interaction exists in the pair of methanol and acetone?

Ans: Solute-solvent dipolar interactions exist in the pair of methanol and acetone.
9. 1.00 molal aqueous solution of trichloroacetic acid (CCl_3COOH) is heated to its boiling point. The solution has the boiling point of 100.18°C. Determine the van't Hoff factor for trichloroacetic acid. (K_b for water = 0.512 K kg mol^{-1})
Answer:
As $\Delta T_b = iK_bm$

(100.18 – 100) °C = i × 0.512 K kg mol^{-1} × 1 m
0.18 K = i × 0.512 K kg mol^{-1} × 1 m
∴ i = 0.3

10.At 300 K ,30g of glucose present per litre in its solution has an osmotic pressure of 4.98 bar.If the osmotic pressure of another glucose solution is 1.52 bar at the same temperature ,calculate the concentration of other solution

$\pi = W_2RT/M_2V = CRT$

4.98=30XRX300/180X1=50R

1.52=CXRX300=300CR

300CR/50R=1.52/4.98=0.051M

11.Calculate the mass of NaCl (molarmass=58.5g/mol) to be dissolved in 37.2 g of water to lower the freezing point by 2 degree assuming that NaCl undergoes complete dissociation.

I=2

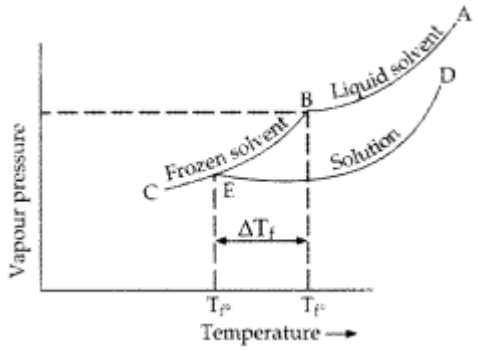
$W_2 = \Delta Tf \times M_2 \times W_1 / i \times Kf \times 1000$

W2=2x58.5x37.2/2x1.86x1000=1.17g

12. **What is the significance of Henry's Law constant K_H ?**

Solution: Henry's Law constant (K_H) helps in comparing the relative solubilities of different gases in the same solvent (e.g. water). In general, lesser the value of K_H, more is the solubility of a gas

13.An aqueous solution of sodium chloride freezes below 273 K. Explain the lowering in freezing points of water with the help of a suitable diagram.
An aqueous solution of sodium chloride freezes below 273 K because vapour pressure g of the solution is g less than that of the pure solvent.



14. On mixing liquid X and liquid 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?
(ii) What happens when we place the blood cell in water (hypotonic solution)? Give reason.
Answer:
(i) Volume decreases by mixing X and Y. It shows negative deviations from Raoult's law. There will be rise in temperature. ($\Delta H_{mix} < 0$)
(ii) Blood cell will swell due to osmosis as water enters the cell.

15. A solution is prepared by dissolving 10 g of non-volatile solute in 200 g of water. It has a vapour pressure of 31.84 mm Hg at 308 K. Calculate the molar mass of the solute. (Vapour pressure of pure water at 308 K = 32 mm Hg) (All India 2015)
Answer:

$$\frac{P^0_{solvent} - P_{solvent}}{P^0_{solvent}} = \frac{W_{solute}}{M_{solute}} \times \frac{M_{solvent}}{W_{solvent}}$$

$$\frac{32.00 - 31.84}{32} = \frac{10}{M_{solute}} \times \frac{18}{200} = \frac{0.16}{32} = \frac{9}{10M_{solute}}$$

$$M_{solute} = \frac{32 \times 9}{1.6} = \mathbf{180\ g/mol}$$

LONG ANSWER QUESTIONS

1.a) **Why is the mass determined by measuring a colligative property in case of some solutes is abnormal? Discuss it with the help of the Van't Hoff factor.**

Certain solutes do not behave normally in solution in the sense that they may either undergo dissociation or association. As a result, the number of solute particles in solution changes.

Since the colligative properties are linked with the number of particles, they show abnormal results. In the same way, the molecular masses of these solutes also show abnormal results.

The exact behavior of the solute in solution and the extent of association or dissociation can be expressed in terms of Van't Hoff factor (i).

i = Normal/ calculated molecular mass/ Observed molecular mass.

or i = Observed colligative properties/ Normal colligative properties.

- If i = 1 , solute behave normally in the solution
- If i > 1 , solute undergo dissociation in solution
- If i < 1 , solute undergo association in solution

b) **Calculate the mass of compound (molar mass = 256 g mol^{-1}) to be dissolved in 75 g of benzene to lower its freezing point by 0.48 K (K_f = 5.12 K kg mol^{-1}). (Delhi 2014)**
Answer:
Given: ΔT_f =0.48K,W_1 =75g,M_2 =256gmol^{-1} W_2 =?

Usingformula,W_2 = M2×W1×ΔTf1000×Kf
= 256×75×0.481000×5.12 = 1.8 g

2.a) Explain the following phenomena with the help of Henry's law.

- **(i) Painful condition known as bends.**
- **(ii) Feeling of weakness and discomfort in breathing at high altitude.**
- **(b) Why soda water bottle kept at room temperature fizzes on opening?**

(i) When scuba divers go deep in the sea, solubility of atmospheric gases increases in blood. When the divers come up, there is release of dissolved gases and it leads to the formation of bubbles of nitrogen in our blood capillaries and hence there is painful sensation called bends. To avoid bends; the tanks of scuba divers are filled with He,N_2 and oxygen.

- (ii) At high altitude, partial pressure of oxygen is low, it leads to low concentration of oxygen in blood of people living there. Low concentration of oxygen develops anoxia, i.e., unable to think and act properly.
- (b) In order to increase the solubility of CO_2 gas in soft drinks and soda water, the bottles are normally sealed under high pressure. Increase in pressure increases the solubility of a gas in a solvent according to Henry's Law. If the bottle is opened by removing the stopper or seal, the pressure on the surface of the gas will suddenly decrease. This will cause a decrease in the solubility of the gas in the liquid. As a result, it will rush out of the bottle producing a hissing noise or with a fiz.

b)A solution prepared by dissolving 1.25 g of oil of winter green (methyl salicylate) in 99.0 g of benzene has a boiling point of 80.31°C. Determine the molar mass of this compound. (B.P. of pure benzene = 80.10°C and Kb for benzene = 2.53°C kg mol-1)

Answer:

Given : W_2 = 1.25 g, W_1 = 99 g

ΔTb = 80.31 – 80.10°C = 0.21°C

Kb = 2.53°C kg mol-1

According to the formula :

M_2 = 1000Kb W_2 /W_1 ΔTb

Substituting these values in the formula, we get

M2 = 1000×2.53×1.25 /99×0.21

= 152 g mol-1

3. a) 18 g of glucose, $C_6H_{12}O_6$ (Molar mass – 180 g mol^{-1}) is dissolved in 1 kg of water in a sauce pan. At what temperature will this solution boil? (K_b for water = 0.52 K kg mol^{-1}, boiling point of pure water = 373.15 K) (Delhi 2013)
Answer:

We know that :
Elevation of boiling point ΔT_b
WBMB×100×Kbwt. of solvent
Given: W_B = 18 g
M_B = Formula of glucose is $C_6H_{12}O_6$
= 6 × 12 + 12 + 6 × 16 = 180
Wt. of solvent = 1 kg or 1000 g,
K_b = 0.52 K kg mol^{-1}
Hence, ΔT_b = 18g180×1000×0.521000g = 0.52 K ∴B.P of the solution = 373.15 + 0.052 =373.202 K
b) Define osmotic pressure of a solution.?How is the osmotic pressure related to the concentration of a solute in a solution?
Answer:
Osmotic pressure : It is the external pressure which is applied on the side solution which is sufficient to prevent the entry of the solvent through semi-permeable membrane.
According to the Boyle-van't Hoff Law, the osmotic pressure (π) of a dilute solution is directly proportional to its molar concentration provided temperature is constant.
$\pi \propto C$ (At constant temperature)
$\pi \propto CT$ (At constant concentration)
$\pi = CRT$ (R = Solution constant)

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

Answer:(a) Since $MgCl_2$ is an ionic compound, so it undergoes complete dissociation.

$$MgCl_2 \longrightarrow Mg^{2+} + 2Cl^-$$

	$MgCl_2$	Mg^{2+}	$2Cl^-$
Initial moles	1	0	0
After dissociation	0	1	2

∴ Total number of moles = 1 + 2 = 3

Thus, $i = \frac{3}{1} = 3$

Using formula,

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

$$\Delta T_f = 3 \times 1.86 \times \frac{1.9 \times 1000}{95 \times 50} \quad \left(\because m = \frac{w_b \times 1000}{M_b \times w_a}\right)$$

$$\therefore \Delta T_f = \frac{10602}{4750} = 2.232 \text{ K}$$

Also, $T_f = T°_f - \Delta T_f$ = 273.15 K – 2.233 K

∴ **T_f = 270.92 K**

b(i) 2M glucose will have a higher boiling point than 1M glucose because elevation in boiling point is a colligative property which depends upon the number of particles in the solution

which is more in the case of 2M glucose solution.
(ii) When the external pressure applied becomes more than the osmotic pressure of the solution, then the solvent will flow from the solution into the pure solvent through the semi-permeable membrane. The process is called reverse osmosis.

5. 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?
(iii)Define ideal solution?
Answer:
(a) Given: w_b = 2.56 g w_a = 100 g = 0.1 kg
ΔT_f = 0.383 K K_f= 3.83 K kg mol^{-1}
Atomic mass of sulphur = 32 g mol^{-1}
M_b = ?
Using formula,

$$M_b = \frac{K_f \times w_b}{\Delta T_f \times w_a} = \frac{3.83 \times 2.56}{0.383 \times 0.1}$$

$$\left[\because \Delta T_f = \frac{K_f \times w_b}{M_b \times w_a} \times 1000\right]$$

$\therefore M_b$ = 256 g mol^{-1}
Hence the no. of atoms present in one molecule of sulphur = 256/32 = 8
$\therefore$ the formula is S_8.
(b) (i) If RBCs are placed in contact with 1.2% NaCl solution, then the osmotic pressure of 1.2% NaCl becomes higher than that of RBCs due to which water present inside the cells moves into the NaCl solution which results in shrinkage of RBCs.
(ii) Reverse process will take place if RBCs are kept in contact with 0.4% NaCl solution which has less osmotic pressure ' due to which water moves into RBCs and th**ey will swell.**

(iii)Ideal solution : The solutions which obey Raoult's law over the entire range of concentration are known as ideal solutions.

CASE BASED QUESTIONS

1. Read the following paragraph and answer the questions:

An ideal solution of two liquids is a solution in which each component obeys Raoult's law which states that the vapour pressure of any component in the solution depends on the mole fraction of that component in the solution and the vapour pressure of that component in the pure state. However, there are many solutions which do not obey Raoult's law. In other words, they show deviations from ideal behaviour which may be positive or negative. However, in either case, corresponding to a particular composition, they form a constant boiling mixtures called azeotropes.

(i) The mole fraction of Ethyl alcohol in its solution with Methyl alcohol is 0.80. The vapour pressure of pure Ethyl alcohol at this temperature is 40mm of Mercury. What is its vapour pressure in the solution if the solution is ideal?

(ii) Why do a solution of Phenol and Aniline exhibit negative deviation from ideal behaviour?

(iii) Write and example for maximum boiling azeotrope.

(iv) Why pure Ethyl alcohol cannot be obtained from rectified spirit even by fractional distillation?

(v) When two liquids A & B are mixed the volume of the resulting solution is found to be slightly greater than sum of the volumes of A & B. Identify the type of deviation exhibited by the solution.

2. Read the following paragraph and answer the questions:

Colligative properties of a solution depend upon the number of moles of the solute dissolved and do not depend upon the nature of the solute. However, they are applicable only to dilute solutions in which the solutes do not undergo any association or dissociation. For solutes undergoing such changes, Van't Hoff introduced a factor, called Van't Hoff factor (i). This has helped not only to explain the abnormal molecular masses of such solutes in the solution but has also helped to calculate the degree of association or dissociation.

(i) What is Van't Hoff factor (i) for a compound undergoing tertramerization in an organic solvent?

(ii) Arrange the following in the increasing order of freezing point
0.1M $Al_2(SO_4)_3$, 0.1M KCl, 0.1M Glucose, 0.1M K_2SO_4

(iii) The molar mass of Sodium Chloride determined by elevation of boiling point method is found to be abnormal. Why?

(iv) What is the elevation of boiling point of a solution of 13.44g of $CuCl_2$ in 1kg of water? (K_b for water = 0.52Kkg/mol^{-1}, molar mass of $CuCl_2$ = 134.4g/mol)

(v) Equimolal solutions of NaCl and $BaCl_2$ are prepared in water. Freezing pint of NaCl is found to be -2^0C. What freezing point do you expect for $BaCl_2$ solution?

ANSWER KEY

1. (i) $P_{C2H5OH} = x_{C2H5OH} \times P^0_{C2H5OH}$
= 0.80 x 40mm
= 32 mm of Mercury

(ii) The Hydrogen bond formed between Phenolic proton and lone pairs of electron of Aniline is stronger than the interactions existing in pure Phenol and in pure Aniline.

(iii) Mixture of water and Nitric acid.

(iv) Because a mixture of 95.4% alcohol and 4.6% of water forms an azeotrope.

(vi) Positive deviation.

2. (i) i= ¼ = 0.25

(ii) 0.1M $Al_2(SO_4)_3$, 0.1M K2SO4, 0.1M KCl, 0.1M Glucose

(iii) Elevation of boiling point is a colligative property. Since Sodium chloride dissociates in the solution we get abnormal molecular mass.

(iv) $\Delta T_b = iK_bm$
$= 3 \times 0.52 \times 0.1$
$= 1.56$ K

(v) i for NaCl = 2, i for $BaCl_2 = 3$
$\frac{\Delta T_f \text{ NaCl}}{\Delta T_f \text{ } BaCl_2} = \frac{2}{3}$
Hence T_f for $BaCl_2 = -3^0C$

CBSE BOARD QUESTIONS

1) What type of intermolecular attractive interaction exists in the pair of methanol and acetone?
Ans: - Solute-solvent dipolar interactions exist in the pair of methanol and acetone

2) What mass of NaCl must be dissolved in 65g of water to lower the freezing point of water by 7.50°C? The freezing point depression constant (K_f) for water is 1.86°C/m.Assume van't Hoff factor for NaCl is 1.87(Molar mass of NaCl =58.5g)?
Ans: - $\Delta T = ixK_fxw_Bx1000/m_BxW_A$
$\Delta T=7.5$, $i=1.87$, $Kf=1.86 km^{-1}$, $w_A=65g$, $m_B=58.5g/mol$, $w_B=?$
Putting the values, we get,
$7.5=1.87x1.86xw_Bx1000/58.5x65$
$w_B=8.2g$

3) Out of $BaCl_2$ and KCl, which one is more effective in causing coagulation of a negatively charged colloidal Sol? Give reason?
Ans: - $BaCl_2$ is more effective in causing coagulation because it has double +ve charge than K+.

4) A 1.00 molal aqueous solution of trichloroacetic acid (CCl_3COOH) is heated to its boiling point. The solution has the boiling point of 100.18°C. Determine the van't Hoff factor for trichloroacetic acid. (K_b for water = 0.512 K kg mol^{-1})
Ans: - $\Delta T_b = iK_bm$
$(100.18 - 100)$ °C $= i \times 0.512$ K kg $mol^{-1} \times 1$ m
0.18 K $= i \times 0.512$ K kg $mol^{-1} \times 1$ m
$\therefore i = 0.3$

5) Explain why aquatic species are more comfortable in cold water rather than in warm water?
Ans: - Aquatic species need dissolved oxygen for breathing. As solubility of gases decreases with increase of temperature, less oxygen is available in summer in the lake. Hence the aquatic species feel more comfortable in winter (low temperature) when the solubility of oxygen is higher.

6) **18 g of glucose, $C_6H_{12}O_6$ (Molar mass – 180 g mol^{-1}) is dissolved in 1 kg of water in a sauce pan. At what temperature will this solution boil? (K_b for water = 0.52 K kg mol^{-1}, boiling point of pure water = 373.15 K)?**

Ans: - We know that:

Elevation of boiling point ΔT_b,

$\Delta T_b = K_b x m$ (m-molality)

Hence, $\Delta T_b = 18 \times 1000 \times 0.52/180 = 0.52$ K

$\therefore$B.P of the solution = 373.15 + 0.052

= 373.202 K

7) **What is meant by 'reverse osmosis'?**

Ans: - If a pressure higher than the osmotic pressure is applied on the solution, the solvent will flow from the solution into the pure solvent through semipermeable membrane. This process is called reverse osmosis.

8) **How is the vapour pressure of a solvent affected when a non-volatile solute is dissolved in it?**

Ans: - The vapour pressure of a solvent decreases when a non-volatile solute is dissolved in it because some solvent molecules are replaced by the molecules of solute

9) **At 25°C, the vapour pressure of pure water is 23.76mm of Hg and that of an aqueous solution of urea is 22.98mm of Hg. Calculate the molality of the solution?**

Ans: - We know that,

P^o-P/Po=X_B=Mole fraction of solute

23.76-22.98/23.76=X_B

X_B=0.0328

molality of the solution 'm' =X_Bx1000/ (1-0.0328) x18=1.88

10) **A solution is prepared by dissolving 10 g of non-volatile solute in 200 g of water. It has a vapour pressure of 31.84 mm Hg at 308 K. Calculate the molar mass of the solute. (Vapour pressure of pure water at 308 K = 32 mm Hg)?**

Ans: -

$$\frac{P^0_{solvent} - P_{solvent}}{P^0_{solvent}} = \frac{W_{solute}}{M_{solute}} \times \frac{M_{solvent}}{W_{solvent}}$$

$$\frac{32.00 - 31.84}{32} = \frac{10}{M_{solute}} \times \frac{18}{200} = \frac{0.16}{32} = \frac{9}{10M_{solute}}$$

$$M_{solute} = \frac{32 \times 9}{1.6} = \mathbf{180\ g/mol}$$

11) **Define the terms osmosis and osmotic pressure. Is the osmotic pressure of a solution a colligative property? Explain?**

Ans:- **Osmosis :** The net spontaneous flow of the solvent molecules from the solvent to the solution or from a less concentrated solution to a more concentrated solution through a semipermeable membrane is called osmosis.

Osmotic pressure : The minimum excess pressure that has to be applied on the solution to

prevent the entry of the solvent into the solution through the semipermeable membrane is called the osmotic pressure.

The osmotic pressure method has the advantage that it uses molarities instead of molalities and it can be measured at room temperature.

12)(a) State the following:

(i) Henry's law about partial pressure of a gas in a mixture.

(ii) Raoult's law in its general form in reference to solutions?

Ans: - Henry's law: "The solubility of a gas in a liquid at a particular temperature is directly proportional to the pressure of the gas in equilibrium with the liquid at that temperature."

Applications of Henry's law:

• In the production of carbonated beverages which are prepared under high pressure.

• Deep sea divers depend upon compressed air for their oxygen supply.

(ii) 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.

$P = P°x$

Non-ideal solution shows positive and negative deviations from Raoult's law.

13) Define the following terms:

(i) Ideal solution (ii) Azeotrope?

Ans: - Ideal solution**:** An ideal solution is that which obeys Raoult's law and in which the intermolecular interactions between the different components are of same magnitude as that is found in pure components.

(ii) Azeotrope: It is a type of liquid mixture having a definite composition and boiling like a pure liquid, (distils without change in compositions)

14) a) What type of deviation is shown by a mixture of ethanol and acetone? Give reason.

(b) A solution of glucose (molar mass = 180 g mol^{-1}) in water is labelled as 10% (by mass). What would be the molality and molarity of the solution?

(Density of solution = 1.2 g mL^{-1})?

Ans: - (a) Since acetone is nearly non-polar in nature and ethanol is polar in nature therefore, no interaction occurs between acetone and ethanol, the number of molecules increases, which shows positive deviation.

(b) 10% glucose means 10 g in 100 g solution or, 90 g of water = 0.090 kg of water

$$\therefore \text{ Molality} = \frac{10}{180 \times 0.090} = 0.617 \text{ m}$$

$$100 \text{ g of solution} = \frac{100}{1.2} \text{ mL}$$

$$= 83.33 \text{ mL} = 0.08333 \text{ L}$$

$$\therefore \text{ Molarity} = \frac{10}{180 \times 0.0833} = 0.067 \text{ M}$$

CHAPTER 3

ELECTROCHEMISTRY

GIST OF THE LESSON

- **In an electrochemical cell:**
  1. The half-cell in which oxidation takes place is known as oxidation half-cell
  2. The half-cell in which reduction takes place is known as reduction half-cell.
  3. Oxidation takes place at anode which is negatively charged and reduction takes place at cathode which is positively charged.
  4. A salt bridge is a U shaped tube containing an inert electrolyte in agar-agar and gelatine.
- **Salt bridge:** A salt bridge maintains electrical neutrality and allows the flow of electric current by completing the electrical circuit.
- **Representation of an electrochemical cell:**
  1. Anode is written on the left while the cathode is written on the right.
  2. Anode represents the oxidation half-cell and is written as: Metal/Metal ion (Concentration)
  3. Cathode represents the reduction half-cell and is written as: Metal ion (Concentration)/Metal
  4. Salt bridge is indicated by placing double vertical lines between the anode and the cathode
  5. Standard electrode potential: When the concentration of all the species involved in a half cell is unity, then the electrode potential is known as standard electrode potential. It is denoted as E^0.
- **Types of electrode potential:** There are 2 types of electrode potentials namely,
  1. Oxidation potential
  2. Reduction potential
- **Oxidation potential:** It is the tendency of an electrode to lose electrons or get oxidized.
- **Reduction potential:** It is the tendency of an electrode to gain electrons or get reduced. Oxidation potential is the reverse of reduction potential.
- The standard electrode potential of an electrode cannot be measured in isolation.
- According to convention, the Standard Hydrogen Electrode is taken as a reference electrode and it is assigned a zero potential at all temperatures.
- **SHE:** Standard hydrogen electrode consists of a platinum wire sealed in a glass tube and carrying a platinum foil at one end. The electrode is placed in a beaker containing an aqueous solution of an acid having 1 Molar concentration of hydrogen ions. Hydrogen gas at 1 bar pressure is continuously bubbled through the solution at 298 K. The oxidation or reduction takes place at the Platinum foil. The standard hydrogen electrode can act as both anode and cathode.
- If the standard hydrogen electrode acts as an anode:
  $H_2(g) \rightarrow 2H + (aq) + 2e^-$
  If the standard hydrogen electrode acts as a cathode:
  $2H + (aq) + 2e \rightarrow H_2(g)$
- In the electrochemical series, various elements are arranged as per their standard reduction potential values.
- A substance with higher reduction potential value means that it has a higher tendency to get reduced. So, it acts as a good oxidising agent.
- A substance with lower reduction potential value means that it has a higher tendency to get oxidised. So, it acts as a good reducing agent.

- The electrode with higher reduction potential acts as a cathode while the electrode with a lower reduction potential acts as an anode.
- The potential difference between the 2 electrodes of a galvanic cell is called cell potential and is measured in Volts.
- The cell potential is the difference between the reduction potential of cathode and anode.
  E cell = E cathode – E anode
- Cell potential is called the electromotive force of the cell (EMF) when no current is drawn through the cell.
- Nernst formulated a relationship between standard electrode potential EΘ and electrode potential E.

$$E = E^0 - \frac{2.303RT}{nF} \log \frac{1}{[M^{n+}]}$$

$$E = E^0 - \frac{0.059}{n} \log \frac{1}{[M^{n+}]} (At\ 298\text{k})$$

- Electrode potential increases with increase in the concentration of the electrolyte and decrease in temperature.
- Nernst equation when applied to a cell, it helps in calculating the cell potential.

$$E_{cell} = {E_{cell}}^0 - \frac{2.303RT}{nF} \log \frac{[Anode\ \text{ion}]}{[Cathode\ \text{ion}]}$$

- At equilibrium, cell potential E_{cell} becomes zero.

$${E_{cell}}^0 = \frac{0.059}{n} \log K_c (At 298K)$$

- Work done by an electrochemical cell is equal to the decrease in Gibbs energy

$$\Delta G^0 = -nF{E^0}_{cell}$$

- Every conducting material offers some obstruction to the flow of electricity which is called resistance. It is denoted by R and is measured in ohm.
- The resistance of any object is directly proportional to its length l and inversely proportional to its area of cross section A.

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

  Where ρ is called specific resistance or resistivity.
- The SI unit of specific resistivity is ohm metre.
- The inverse of resistance is known as conductance, G
- Unit of conductance is ohm^{-1} or mho. It is also expressed in Siemens denoted by S.
- The inverse of resistivity is known as conductivity. It is represented by the symbol **κ**.
- The SI unit of conductivity is S/m. But it is also expressed in S/cm.
- Conductivity = Conductance × Cell constant
- A conductivity cell consists of 2 Pt electrodes coated with Pt black. They have area of cross section A and are separated by a distance '*l*'. Resistance of such a column of solution is given by the equation:
- $$R = \rho \frac{l}{A} = \frac{1}{k} \frac{l}{A}$$

  Where $\frac{l}{A}$ is called cell constant and is denoted by the symbol G^*
- **Molar conductivity of a solution:** It is defined as the conducting power of all the ions produced by dissolving 1 mole of an electrolyte in solution.

  Molar conductivity $\wedge_m = \frac{k \text{ x } 1000}{M}$

  Where **κ**= Conductivity and M is the molarity Unit of Molar conductivity is $Scm^2\ mol^{-1}$

- **Equivalent conductivity:** It is the conductivity of all the ions produced by dissolving one gram equivalent of an electrolyte in solution. Unit of equivalent conductivity is S cm^2 (eq) $^{-1}$
  Equivalent conductivity: $\wedge_e = \frac{k \text{ x } 1000}{N}$
- **Kohlrausch's Law of independent migration of ions:** According to this law, molar conductivity of an electrolyte, at infinite dilution, can be expressed as the sum of individual contributions from its individual ions.
- If the limiting molar conductivity of the cations is denoted by λ^0_+ and that of the anions by λ^0_-, then the limiting molar conductivity of electrolyte is:
  $\wedge^0_m = v_+\lambda^0_+ + v_-\lambda^0_-$
  Where v+ and v- are the number of cations and anions per formula of electrolyte
- **Degree of dissociation:** It is ratio of molar conductivity at a specific concentration 'c' to the molar conductivity at infinite dilution.
  $a = \frac{\wedge^c_m}{\wedge^0_m}$
- **Dissociation constant:** $k_a = \frac{ca^2}{1-a}$ Where Ka is acid dissociation constant, 'c' is concentration of electrolyte, α is degree of ionization.
- **Faraday constant:** It is equal to charge on 1 mol of electrons. It is equal to 96487 C mol^{-1} or approximately equal to 96500 C mol^{-1}.
- **Faraday's first law of electrolysis:** The amount of substance deposited during electrolysis is directly proportional to quantity of electricity passed.
- **Faraday's second law of electrolysis:** If same charge is passed through different electrolytes, the mass of substance deposited will be proportional to their equivalent weights.
- **Products of electrolysis:** The products of electrolysis depend upon
- The nature of electrolyte being electrolyzed and the nature of electrodes. If electrode is inert like platinum or gold, they do not take part in chemical reaction i.e. they neither lose nor gain electrons. If the electrodes are reactive then they will take part in chemical reaction and products will be different as compared to inert electrodes.
- **Primary cells:** A primary cell is a cell in which electrical energy is produced by the reaction occurring in the cell, e.g. Daniel cell, dry cell, mercury cell. It cannot be recharged.
- **Dry Cell:**
  At anode $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$
  At cathode $MnO_2(s) + NH_4^+(aq) + e^- \rightarrow MnO(OH) + NH_3$
  The net reaction: $Zn + NH_4^+(aq) + MnO_2(s) \rightarrow Zn^{2+} + MnO(OH) + NH_3$
- **Mercury Cell:** The electrolyte is a paste of KOH and ZnO.
  At Anode: $Zn(Hg) + 2OH^- \rightarrow ZnO(s) + H_2O + 2e^-$
  At cathode: $HgO(s) + H_2O + 2e^- \rightarrow Hg(l) + 2OH^-$
  The net reaction: $Zn(Hg) + HgO(s) \rightarrow ZnO(s) + Hg(l)$
- **Secondary cells:** Those cells which are used for storing electricity, e.g., lead storage battery, nickel – cadmium cell. They can be recharged.
- **Lead storage battery:**
  Anode: $Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$
  Cathode: $PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$
  The overall cell reaction consisting of cathode and anode reactions is:
  $Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$
  On recharging the battery, the reaction is reversed.

- **Nickel cadmium cell:** It is another type of secondary cell which has longer life than lead storage cell but more expensive to manufacture.
  The overall reaction during discharge is
  $Cd(s) + 2Ni(OH)_3(s) \rightarrow CdO(s) + 2Ni(OH)_2(s) + H_2O(l)$
- **Fuel cells:**
  At Anode: $2H_2(g) + 4OH^-(aq) \rightarrow 4H_2O(l) + 4e^-$
  At cathode: $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$
- **Overall reaction:**
  $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$
- **Corrosion:**
  Oxidation: $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$
  Reduction: $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$
- **Galvanization:** It is a process of coating zinc over iron so as to protect it from rusting.
- **Cathodic protection:** Instead of coating more reactive metal on iron, the use of such metal is made as sacrificial anode.

MULTIPLE CHOICE QUESTIONS

1. **Which of the following is a secondary cell?**
   (a) Leclanche cell
   (b) Lead storage battery
   (c) Concentration cell
   (d) All of these

Answer: (b) Lead storage battery

2. **If 96500 coulomb electricity is passed through $CuSO_4$ solution, it will liberate**
   (a) 63.5 gm of Cu
   (b) 31.76 gm of Cu
   (c) 96500 gm of Cu
   (d) 100 gm of Cu

Answer: (b) 31.76 gm of Cu

3. **Fused NaCl on electrolysis gives …….. on cathode.**
   (a) Chlroine
   (b) Sodium
   (c) Sodium amalgam
   (d) Hydrogen

Ans. (b) Sodium

4. **Molar conductivity of 0.15 M solution of KCl at 298 K, if its conductivity of 0.0152 S cm^{-1} will be**
   (a) 124 Ω^{-1} cm^2 mol^{-1}
   (b) 204 Ω^{-1} cm^2 mol^{-1}
   (c) 101 Ω^{-1} cm^2 mol^{-1}
   (d) 300 Ω^{-1} cm^2 mol^{-1}

Answer: (c) 101 Ω^{-1} cm^2 mol^{-1}

5. **The molar conductivity is maximum for the solution of concentration**
   (a) 0.004 M
   (b) 0.002 M
   (c)0.005 M

(d) 0.001 M
Answer: (d) 0.001 M

6. How long would it take to deposit 50 g of Al from an electrolytic cell containing Al_2O_3 using a current of 105 amperes?
(a) 1.54 h
(b) 1.42 h
(c) 1.32 h
(d) 2.15 h
Answer: (b) 1.42 h

7. **How many coulombs of electricity is required to reduce 1 mole of $Cr_2O_7^{2-}$ in acidic medium?**
(a) 4 × 96500 C
(b) 6 × 96500 C
(c) 2 × 96500 C
(d) 1 × 96500 C
Answer: (b) 6 × 96500 C

8. **When heating one end of a metal plate, the other end gets hot because of**
a. the resistance of the metal
b. mobility of atoms in the metal
c. energised electrons moving to the other end
d. minor perturbation in the energy of atoms.
Answer: (c)

9. **The equivalent conductance of Ba^{2+} and Cl^- are respectively 127 and 76 ohm^{-1} cm^{-1} eq^{-1} at infinite dilution. The equivalent conductance of $BaCl_2$ at infinite dilution will be**
a. 139.5
b. 203
c. 279
d. 101.5
Answer: (a)

10. **Standard solution of KNO_3 is used to make a salt bridge because**
(a) Velocity of K^+ is greater than that of NO^{-3}.
(b) Velocity of NO^{-3} is greater than that of K^+.
(c) Velocity of both K^+ and NO^{-3} are nearly same
(d) KNO_3 is highly soluble in water.
Answer: (c) Velocity of both K^+ and NO^{-3} are nearly same

11. **The amount of electricity required to deposit 1 mol of aluminium from a solution of $AlCl_3$ will be**
(a) 0.33 F
(b) 1 F
(c) 3 F
(d) 1 ampere
Answer: (c) 3 F

12. **Which of the following is supplied to the cathode of a fuel cell?**
a) Hydrogen
b) Nitrogen

c) Oxygen
d) Chlorine
Ans. c

13. **If limiting molar conductivity of Ca^{2+} and Cl^- are 119.0 and 76.3 S cm^2 mol^{-1}, then the value of limiting molar conductivity of $CaCl_2$ will be**
(a) 195.3 S cm^2 mol^{-1}
(b) 271.6 S cm^2 mol^{-1}
(c) 43.3 S cm^2 mol^{-1}
(d) 314.3 S cm^2 mol^{-1}.
Answer: b

14. **The reaction, $3ClO^-$ (aq) → ClO_3 (aq) + $2Cl^-$ (aq) is an example of**
(a) Oxidation reaction
(b) Reduction reaction
(c) Disproportionation reaction
(d) Decomposition reaction
Answer: c

15. **Without losing its concentration $ZnCl_2$ solution cannot be kept in contact with**
a. Au
b. Al
c. Pb
d. Ag
Answer: b

ASSERTION REASON TYPE OF QUESTIONS

The question given below consist of an assertion and a reason use the following key to choose appropriate answer

a) Both assertion and reason are correct and reason is the correct explanation of the assertion
b) Both assertion and reason are correct and reason is not the correct explanation of the assertion
c) Assertion is correct but reason is incorrect
d) Assertion is wrong Reason is correct.

1) **Assertion**: The electrode potential of SHE is zero

Reason: In SHE HCl 1M and H_2 gas at one bar pressure is taken

2) **Assertion**: H^+ ion cannot oxidize copper

Reason: Reduction potential of Cu^{2+} / Cu is greater than H^+/H

3) **Assertion**: The reduction potential of F^-/F is highest among all electrodes

Reason: Fluorine is the strongest oxidising agent

4) **Assertion**: Electronic conduction decreases with temperature

Reason: The flow of electrons hindered on increasing the temperature

5) **Assertion**: conductivity decreases with increasing dilution

Reason: No of ions increases per unit volume increases with dilution.

6) **Assertion**: Electrolytic conduction increases with temperature

Reason: On increasing the temperature mobility of ion increases

7) **Assertion**: Molar conductivity of electrolytes decreases with dilution

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

8) **Assertion:** It is difficult to measure the conductivity of ionic solutions

Reason: Electrolytes conduct electricity and undergoes chemical change.

9) **Assertion:** Molar conductivity of strong electrolytes increases with dilution

Reason: On dilution inter ionic interaction increases.

10) **Assertion**: Molar conductivity of acetic acid increases sharply with dilution

Reason: Degree of dissociation of acetic acid decreases with dilution

11)**Assertion**:An external potential of 1.1V is passed through Danielcell, no current flow through it.
Reason: Standard emf of galvanic cell is 1.1 volt.

12) **Assertion**: Out of Li and K Potassium is the strongest reducing agent

Reason: Reduction potential of K is greater than that of Li

13) **Assertion**: Electrolytic conduction of electrolytes depends on size of ions

Reason: Larger the size of ion lesser will be the mobility of ions.

14) **Assertion**: Limiting molar conductivity of weak electrolytes can be obtained graphically

Reason: Limiting molar conductivity of weak electrolytes increases with dilution

15) **Assertion:** Electrolysis of aqueous NaCl produces Oxygen at the anode

Reason: Oxidation potential of Oxygen is lower than chlorine.

ANSWER KEY

1)b	2) a	3) b	4) a	5) c	6) a	7) d	8) a
9) c	10) c	11) b	12) d	13) a	14) b	15) d	

SHORT ANSWER TYPE QUESTIONS

1. **The chemistry of corrosion of iron is essentially an electrochemical phenomenon. Explain the reactions occurring during the corrosion of iron in the atmosphere.**

   The redox reaction involves
   At anode : $Fe(S) \rightarrow Fe^{2+}(aq) + 2e^-$
   At cathode : $H_2O + CO_2 \rightleftharpoons H_2CO_3$ (Carbonic acid)
   $H_2CO_3 \rightleftharpoons 2H^+ + CO_2^{2-}$
   $H^+ + e^- \rightarrow H$
   $4H + O_2 \rightarrow 2H_2O$
   Then net resultant Redox reaction is
   $2Fe(s) + O_2(g) + 4H^+ \rightarrow 2Fe^{2+} + 2H_2O$

2. **Determine the values of equilibrium constant (K_c) and $\Delta G°$ for the following reaction at 298K. $Ni(s) + 2Ag^+(aq) \rightarrow Ni^{2+}(aq) + 2Ag(s)$,**
   $E° = 1.05$ V , 1F = 96500 C/ mol

$\Delta G^\circ = -nFE^\circ = -2 \times 96500 \times 1.05$

$\Delta G^\circ = -202650$ J /mol

R = 8.314 J/Mol/K, T = 298 K

$$\log K = \frac{\Delta G^\circ}{2.303\,RT}$$

$$\text{or } \log K = \frac{-202650}{2.303 \times 8.314 \times 298}$$

$$\log K = \frac{-202650}{5705.84831} = 35.52$$

K = Antilog of 35.52 $\therefore$ **$K = 0.35 \times 10^7$**

3. **A zinc rod is dipped in 0.1 M solution of $ZnSO_4$. The salt is 95% dissociated at this dilution at 298 K. Calculate the electrode potential. [$E^\circ_{Zn^{2+}}/Zn = -0.76$ V]**

The electrode reaction is given as

$Zn^{+2} + 2e \rightarrow Zn$

Using Nernst Equation

$$E_{Zn^{+2}/Zn} = E^\circ_{Zn^{2+}/Zn} - \frac{0.0591}{2} \log \frac{1}{[Zn^{+2}]}$$

$$[Zn^{+2}] = \frac{95}{100} \times 0.1 = 0.095$$

$$E_{Zn^{+2}/Zn} = -0.76 - 0.0295 \log \frac{1}{0.095}$$

$$= -0.76 - 0.0295\,[\log 1000 - \log 95]$$

$$= -0.76 - 0.0295\,[3 - 1.9777]$$

$$= -0.76 - 0.03016 = \mathbf{-0.79\ volt}$$

4. **Write the reactions taking place at cathode and anode in lead storage battery when the battery is in use. What happens on charging the battery?**

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

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

On charging the battery, the reaction is reversed and $PbSO_4$ on anode and cathode is converted into Pb and PbO_2 respectively.

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

The limiting molar conductivity of an electrolyte is the sum of the limiting ionic conductivities of the cation and the anion each multiplied with the number of ions present in one formula unit of the electrolyte

$\Lambda^\circ m$ for $A_xB_y = x\lambda^\circ_+ + y\lambda^\circ_-$

For acetic acid Λ° (CH_3COOH) = $\lambda^\circ_{CH3}COO^- + \lambda^\circ_{H^+}$

$\Lambda^\circ(CH_3COOH) = \Lambda^\circ\,(CH_3COOK) + \Lambda^\circ\,(HCl) - \Lambda^\circ\,(KCl)$

6. **Define the following terms : (i) Molar conductivity (Λ_m) (ii) Secondary batteries**

Molar conductivity of a solution at a given concentration is the conductance of the volume 'V' of a solution containing one mole of electrolyte kept between two electrodes with area of cross section 'A' and distance of unit length. It is represented by Λ_m. Unit of Λ_m is S cm^2 mol^{-1}

$\Lambda_m = k_c$ x 1000/Molarity

Secondary batteries are those batteries which can be recharged by passing an electric current through them and can be used again and again are called secondary batteries.

7. **Calculate the time to deposit 1.27 g of copper at cathode when a current of 2A was passed through the solution of $CuSO_4$. (Molar mass of Cu = 63.5 g mol^{-1},1 F = 96500 C mol^{-1})**
   $CuSO_4 \rightarrow Cu+ + SO_4^{2-}$
   $Cu^{2+} + 2e^- \rightarrow Cu$
   63.5 gram of copper is deposited = 2 × 96500 C
   1.27 gram of Cu is deposited =(2×96500/63.5) × 1.27
   = 3860
   $Q = I \times t$
   3860 = 2 x t
   t = 3860/2 = 1930 seconds

8. **Calculate the degree of dissociation of acetic acid if its molar conductivity (Λ_m) is 39.05 S cm^2 mol^{-1}. Given: $\lambda°(H^+)$ = 349.6 S cm^2 mol^{-1} and $\lambda°(CH3COO^-)$ = 40.9 S cm^2 mol^{-1}**
   $\lambda°_{CH3}COOH = \lambda°_{H^+} + \lambda°_{CH3}COO^-$
   = 349.6 S cm^2 mol^{-1} + 40.9 S cm^2 mol^{-1}
   = 390.5 S cm^2 mol^{-1}

$$\alpha = \frac{\Lambda_m}{\Lambda_m^0} = \frac{39.05\,cm^2\,mol^{-1}}{390.05\,cm^2\,mol^{-1}} = \mathbf{0.1}$$

9. **Write the name of the cell which is generally used in transistors. Write the reactions taking place at the anode and the cathode of this cell**.
   Leclanche cell is used in transistors.
   Reaction at Anode:
   $Zn(s) \rightarrow Zn^{2+} + 2e^-$
   At Cathode:
   $MnO_2 + NH_4^+ + e^- \rightarrow MnO(OH) + NH_3$

10. **What are fuel cells? Explain the electrode reactions involved in the working of H_2-O_2 fuel cell**.
    Fuel cells are the devices which convert the energy produced during combustion of fuels like H_2, CH_4, etc. directly into electrical energy.
    The electrode reaction for $H_2 – O_2$ fuel cell :

$$\textit{At anode}: 2H_2(g) + 4OH^-(aq) \longrightarrow 4H_2O(l) + 4e^-$$
$$\textit{At cathode}: O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$$
$$\textit{Overall reaction}: \quad 2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$$

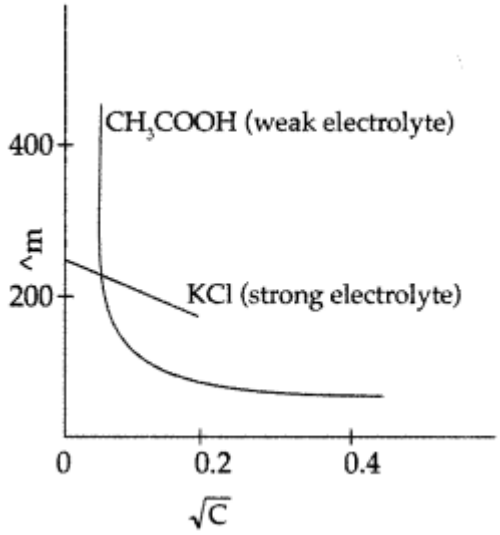
11. **Describe how for weak and strong electrolytes, molar conductivity changes with concentration of solute. How is such change explained?**

    In the case of strong electrolytes there is a small increase in conductance with dilution because a

strong electrolyte is completely dissociated in solution and the number of ions remains constant. Moreover there will be greater inter-ionic attractions at higher concentrations which retards the motion of ions and conductance decreases.

In case of weak electrolytes there is increase in conductance with decrease in concentration due to the increase in the number of ions in the solution and increase in mobility.

The graph between Λ_m and concentration also rectifies the above statement.



12. **Write the name of the cell which Is generally used in hearing aids. Write the reactions taking place at the anode and the cathode of this cell**

Mercury cell

$$\text{At Anode: } Zn\,(Hg) + 2OH^- \longrightarrow ZnO + H_2O + 2e^-$$
(Amalgam)

At Cathode: $HgO + H_2O + 2e^- \rightarrow Hg\,(I) + 2OH^-$

13. **Using the E° values of A and B, predict which one is better for coating the surface of iron [$E^\circ_{(Fe^{2+}/Fe)} = -0.44V$] to prevent corrosion and why?**

Given: $E^\circ_{(A^{2+}|A)} = -2.37$ V and $E^\circ_{(B^{2+}|B)} = -0.14$ V (CBSE Al 2016)

Answer: 'A' will prevent iron from rusting. So, we can coat the iron surface with metal A because it has more negative value.

14. **Express the relation among the cell constant, the resistance of the solution in the cell and the conductivity of the solution. How is molar conductivity of a solution related to its conductivity?**

$\kappa = \frac{1}{R} \times \frac{l}{A}$, where κ is the conductivity of solution, R is resistance, $\frac{l}{A}$ is cell constant. 'l' is distance between electrodes, a is area of cross-section.

$\Lambda_m = \frac{1000\,\kappa}{M}$ where 'κ' is conductivity in S cm^{-1} and M is the molarity of solution.

Λ_m is molar conductivity in S cm^2 mol^{-1}.

15. **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 X 10^3 ohm. Calculate its resistivity, conductivity and molar conductivity.**

$$A = \pi r^2 = 3.14 \times (0.5)^2 \text{ cm}^2 = 0.785 \text{ cm}^2$$

$$\rho \text{ (resistivity)} = \frac{R \times A}{l} = \frac{5.55 \times 10^3\ \Omega \times 0.785 \text{ cm}^2}{50 \text{ cm}} = 87.135\ \Omega \text{ cm}.$$

$$\kappa = \frac{1}{\rho} = \frac{1}{87.135\ \Omega \text{ cm}} = 0.01148 \text{ S cm}^{-1}$$

$$\Lambda_m = \frac{\kappa \times 1000}{\text{M}} = \frac{0.01148 \times 1000}{0.05 \text{ M}} = 229.6 \text{ S cm}^2 \text{ mol}^{-1}$$

LONG ANSWER TYPE QUESTIONS

1. **A voltaic cell is set up at 25°C with the following half cells :**
   Al/Al^{3+} (0.001 M) and Ni/Ni^{2+} (0.50 M)
   Write an equation for the reaction that occurs when the cell generates an electric current and determine the cell potential.
   $E^oNi^{2+}/Ni = -0.25V$ and $E0Al^{3+}/Al = -1.66V$
   (Log $8 \times 10^{-6} = -0.54$)

   Half cell reactions and overall cell reaction are

$$\text{Al} \rightarrow \text{Al}^{+3} + 3\text{e}] \times 2$$
$$\text{Ni}^{+2} + 2\text{e} \rightarrow \text{Ni}] \times 3$$
$$2\text{Al} + 3\text{Ni}^{+2} \rightarrow 2\,\text{Al}^{+3} + 3\text{Ni} \qquad n = 6$$

$$E^0_{\text{cell}} = E^0_{\text{Cathod}} - E^0_{\text{Anode}}$$

$$\Rightarrow E^0_{\text{cell}} = -0.25 - (-1.66) = 1.41 \text{ V}$$

$$E_{M^{n+}/M} = E^0_{\text{cell}} - \frac{0.0591}{6} \log \frac{[\text{Al}^{+3}]^2}{[\text{Ni}^{+2}]^3}$$

$$\therefore E^0_{M^{n+}/M} = 1.41 - \frac{0.0591}{6} \log \frac{(1 \times 10^{-3})^2}{(5 \times 10^{-1})^3}$$

$$= 1.41 - 0.00985 \log \frac{10^{-6}}{125 \times 10^{-3}}$$

$$= 1.41 - 0.00985 \quad (-\log 10^{-3} - \log 125)$$

$$= 1.41 + 0.0985 \times 5.0970$$

$$= 1.41 + 0.05 = \textbf{1.46 volts}$$

2. **(a) Write the anode and cathode reactions and the overall reaction occuring in a lead storage battery.**
   (b) A copper-silver cell is set up. The copper ion concentration is 0.10 M. The concentration of silver ion is not known. The cell potential when measured was 0.422 V. Determine the concentration of silver ions in the cell.

   (Given : $E^0_{Ag^+/Ag} = +0.80$ V,

   $E^0_{Cu^{2+}/Cu} = +0.34$ V).

(a) ***At anode :***

$$Pb + SO_4^{2-} \rightarrow PbSO_4 + 2e^- \text{ (oxidation)}$$

At cathode :

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

Overall reaction :

$$Pb + PbO_2 + 4H^+ + 2SO_4^{2-} \rightarrow 2PbSO_4 + 2H_2O$$

(b) The reaction takes place at anode and cathode in the following ways :

At anode (oxidation) :

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

At cathode (reduction) :

$Cu(s) + 2Ag^{2+}(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$

The complete cell reaction is

$$Cu(s) \mid Cu^{2+}(aq) \parallel Ag^+(aq) \mid Ag(s)$$

$\because \quad E^0_{cell} = E^0_{cathode} - E^0_{anode}$

or $\quad E^0_{cell} = + 0.80 - (+ 0.34)$

or $\quad E^0_{cell} = 0.80 - 0.34 = 0.46 \text{ V}$

Using *Nernst equation*

$$E_{cell} = E^0_{cell} - \frac{0.059}{2} \log \frac{[Cu^{2+}(aq)]}{[Ag^+(aq)]^2}$$

$$0.422 = 0.46 - \frac{0.059}{2} \log \frac{(0.1)}{[Ag^+]^2}$$

$$0.422 - 0.46 = - \frac{0.059}{2} \log \frac{10^{-1}}{[Ag^+]^2}$$

$$-0.038 = -0.0295 \, [\log 10^{-1} - \log [Ag^+]^2]$$

$$-0.038 = -0.0295 \, [-1 - 2 \log [Ag^+]]$$

$$-0.038 = 0.0295 + 0.059 \log [Ag^+]$$

or $\quad -0.059 \log [Ag^+] = 0.038 + 0.0295$

or $\quad -0.059 \log [Ag^+] = 0.0675$

or $\quad -\log [Ag^+] = \frac{0.0675}{-0.059}$

or $\quad \log [Ag^+] = 1.14407$

or $\quad [Ag^+] = \text{Antilog } 1.14407$

$\therefore \quad [Ag^+] = \mathbf{13.93 \text{ M}}$

3. **Explain the following:**

(a) CO_2 is always present in natural water. Explain its effect (increases, stops or no effect) on rusting of iron.

(b) Rusting of iron is quicker in saline water than in ordinary water. Explain.

(c) Discuss electrical protection for preventing rusting of iron pipes in underground water.

(a) Presence of CO_2 in natural water increases rusting of iron. It dissolves in water to form H_2CO_3 which gives H^+ ions. The H^+ ions accelerate the process of corrosion.

In rusting of iron, Fe oxidises to Fe^{2+} ions

$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$ (anode)

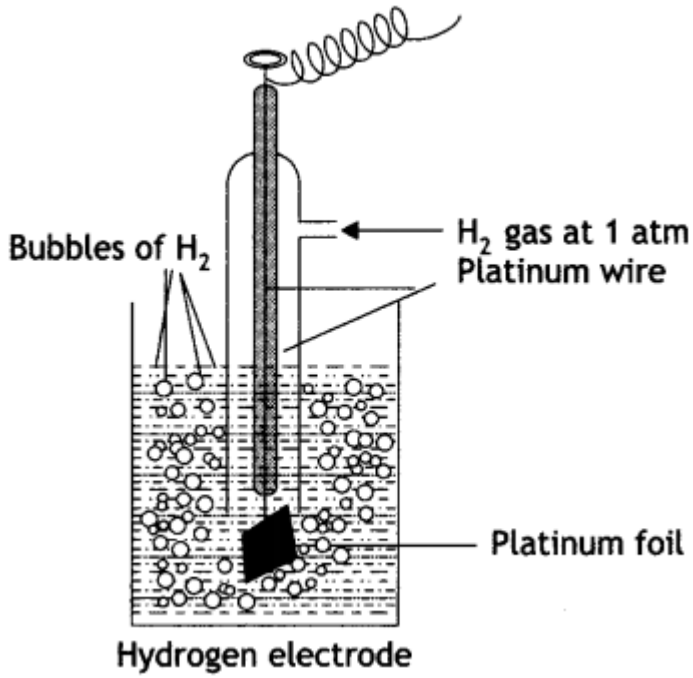
The released electrons go to the cathode and reduce oxygen in the presence of H^+ ions (obtained from H_2CO_3). The reaction occurs at cathode. Thus, CO_2 increases rusting.
O_2 (g) + $4H^+$(aq) + $4e^- \rightarrow 2H_2O$ (l)

(b) Rusting of iron is quicker in saline water (salt water) than in ordinary water. This is mainly due to the fact that saline water increases the electrical conduction of electrolyte solution formed on the metal surface. Therefore, rusting becomes more serious problem where salt water is present.

(c) In this method iron articles which are in contact with water such as underground water pipes are protected from rusting. The article of iron is connected with more active metals like magnesium or zinc. This prevents its tendency to lose electrons and therefore, corrosion is prevented. The cathodes of magnesium of zinc can be fixed to the surface of iron or burned in sub-soil water near by the pipes.

4. **Give the construction and working of Standard Hydrogen Electrode ?**

The standard hydrogen electrode consists of platinum wire sealed in a glass tube and has a platinum foil attached to it. The foil is coated with finely divided platinum and acts as platinum electrode. It is dipped into an acid solution containing H^+ ions in 1 M concentration (1 M HCl). Pure hydrogen gas at 1 atmosphere pressure is constantly bubbled into the solution at constant temperature of 298 K. The surface of the foil acts as a site for the reaction. This is shown in figure.
The following reactions occur in this half cell depending upon whether it acts as an anode or as a cathode:



If S.H.E. acts as anode:
$H_2(g) \rightarrow 2H^+ + 2e^-$
If S.H.E. acts as cathode:
$2H^+ + 2e^- \rightarrow H_2(g)$
The electrode potential of an electrode can be determined by connecting this half cell with a standard hydrogen electrode. The electrode potential of the standard hydrogen electrode is taken as zero.

Measurement of the standard electrode potential (E°): The standard electrode potential of a metal electrode is measured with respect to a standard hydrogen electrode. A cell is prepared in which the metal electrode constitutes one half cell and the S.H.E. as the other half cell (anode). The electrons released by the metal in the oxidation half cell are accepted by the H+ ions of the acid in the reduction half cell.
The cell may be represented as:
$Pt(s) \mid H_2(g, 1\ atm) \mid H^+ (aq, 1\ M) \parallel M^{n+} (aq, 1M) \mid M$
Now, e.m.f. of cell
$e.m.f. = E_R - E_L$
Since the potential of S.H.E. has been fixed to be zero, i.e. $E_L = 0$ so that
$e.m.f. = E_R - 0$
or E_R = e.m.f.
From the knowledge of e.m.f. of the cell, the electrode potential of the electrode can be calculated. For example, if we wish to determine the electrode potential of zinc electrode in 1 M solution of $ZnSO_4$, it is combined with S.H.E. The e.m.f. of the cell is found to be – 0.76 V so that
$e.m.f. = E_L - E_L$
$-0.76 = E_R - 0$
or $E_R = -0.76$ V.

5. **The chemistry of corrosion of iron is essentially an electrochemical phenomenon. Explain the reactions occurring during the corrosion of iron in the atmosphere.**

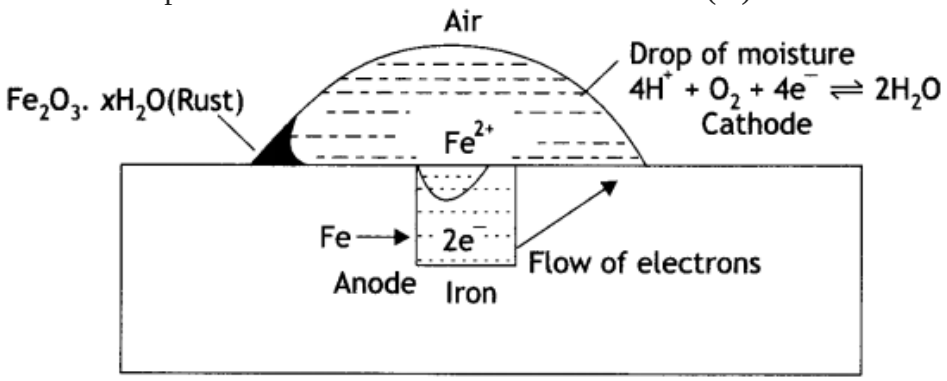
The chemistry of corrosion of iron is an electrochemical theory which involves oxidation and reduction reactions. According to this theory it is believed that non-uniform surface of metal or impurities present in iron behave like small electric cells (called corrosion couples) in the presence of water containing dissolved oxygen or carbon dioxide. A film of moisture with dissolved CO_2 acts as electrolytic solution covering the metal surface at various places. This is shown in Fig. In these small electrolytic cells, pure iron acts as anode while cathodes are impure portions. The overall rusting involves the following steps:
Oxidation occurs at the anode of each electrochemical cell. Therefore, at each anode iron is oxidised to Fe^{2+} ions.

At anode:
$Fe\ (s) \rightarrow Fe^{2+}\ (aq) + 2e^-$ …… (i)
Thus, the metal atoms in the lattice pass into the solution as ions, leaving electrons on the metal itself. These electrons move towards the cathode region through the metal.

At the cathode of each cell, the electrons are taken up by hydrogen ions (reduction takes place). The H^+ ions are obtained either from water or from acidic substance in water:
$H_2O \rightleftharpoons H^+ + OH^-$ …… (ii)
or $CO_2 + H_2O \rightarrow H^+ + H^+CO_3^-$ …… (iii)

At cathode:
$H^+ + e^- \rightarrow H+$ …… (iV)
Thus, hydrogen atoms on the iron surface reduce dissolved oxygen.
$4H + O_2 \rightarrow 2H_2O$ ……..(v)
Therefore, the overall reaction at cathode of different electrochemical cells may be written as:
$4H^+(aq) + O_2\ (g) + 4e^- \rightarrow 2H_2O\ (l)$ ……. (vi)
The overall redox reaction may be written by multiplying reaction at anode Eq. (i) by 2 and adding reaction at cathode Eq. (iv) to equalise number of electrons lost and gained, i.e. Oxidation half

reaction:
$Fe\ (s) \rightarrow Fe^{2+}\ (aq) + 2e^- \times 2$
Reduction half reaction:
$4H^+(aq) + O_2\ (g) + 4e^- \rightarrow 2H_2O\ (l)$
Overall cell reaction:
$2Fe\ (s) + 4H^+(aq) + O_2\ (g) \rightarrow 2Fe^{2+}(aq) + 2H_2O\ (l)$
The ferrous ions are oxidised further by atmospheric oxygen to Fe^{3+} (as Fe_2O_3) and form rust
$4Fe^{2+} + O_2\ (g) + 4H_2O \rightarrow 2Fe_2O_3 + 8H^+$
and $Fe_2O_3 + xH_2O \rightarrow Fe_2O_3.\ xH_2O$
The H^+ ions produced above are also used for reaction (iv).



Mechanism of rusting of air.

6. **(a) Calculate the emf for the given cell at 25 °C:**
Cr | Cr^{3+} (0.1 M)|| Fe^{2+} (0.01 M) | Fe
[Given:$E^0_{Cr3+/Cr}$= -0.74 V, $E^0_{Fe2+/Fe}$ = -0. 44 V]
(b) Calculate the strength of the current required to deposit 1.2<g of magnesium from molten $MgCl_2$ in 1 hour.
[1 F = 96,500 C mol^{-1}; Atomic mass: Mg = 24.0]

(*a*)
$$2Cr(s) \longrightarrow 2Cr^{3+}(aq) + 6e^-$$
$$3Fe^{2+}(aq) + 6e^- \longrightarrow 3Fe(s)$$
$$2Cr(s) + 3Fe^{2+}(aq) \longrightarrow 2Cr^{3+}(aq) + 3Fe(s) \qquad n = 6$$

$$\therefore \quad E_{cell} = E^\circ_{Fe^{2+}/Fe} - E^\circ_{Cr^{3+}/Cr} - \frac{0.0591}{6} \log \frac{[Cr^{3+}]^2}{[Fe^{2+}]^3}$$

$$= -0.44\ V - (-0.74\ V) - \frac{0.0591}{6} \log \frac{(0.1)^2}{(0.01)^3}$$

$$= +\ 0.30\ V - \frac{0.0591}{6} \times \log 10^4$$

$$= +\ 0.30\ V - \frac{0.0591}{6} \times 4$$

$$= +0.30\ V - \frac{0.2364}{6}$$

$$= +\ 0.30 - 0.0394 = +\ 0.2606\ V$$

(*b*) $I = ?,\ m = Z \times I \times t$

$$1.2\ g = \frac{12}{96500} \times I \times 60 \times 60$$

$$\Rightarrow \quad I = \frac{1.2 \times 96500}{12 \times 60 \times 60} = \frac{965}{360} = 2.68\ A.$$

CASE BASED QUESTIONS

1. **Read the given passage and answer the questions 1 to 5 that follow**:

"Car battery is the most important type of secondary cell having a lead anode and a grid of Lead packed with PbO_2 as cathode. It is also called lead storage battery. It contains 40% solution of sulphuric acid (Density = 1.294 gmL^{-1}) as electrolyte. The battery holds 3.5 L of the acid. During the discharge of the battery, the density of H_2SO_4 falls to 1.139 gmL^{-1} (20% H_2SO_4 by mass)"

1. Write the reaction taking place at the cathode when the battery is in use.
2. How much electricity in terms of Faraday is required to carry out the reduction of one mole of PbO_2
3. What is the molarity of sulphuric acid before discharge?
4. Why is lead storage battery considered a secondary cell?
5. Write the products of electrolysis when dilute sulphuric acid is electrolysed using platinum electrodes.

Answers

1. Cathode reaction is
   $PbO_2 + SO_2 + 4H^+ + 2e^- \rightarrow 2PbSO_4 + 2H_2O$
2. 2F
3. Molarity = (% ×10 ×d) ÷ (Molarity of H_2SO_4) = (40 x 10 x 1.294) ÷ 98 = 5.28 mol L^{-1}
4. It can be recharged again and again.
5. H_2 at cathode and O_2 at anode.

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

The potential difference between the two electrodes of a galvanic cell is called the cell potential and is measured in volts. The cell potential is the difference between the electrode potentials (reduction potentials) of the cathode and anode. It is called the cell electromotive force (emf) of the cell when no current is drawn through the cell. It is now an accepted convention that we keep the anode on the left and the cathode on the right while representing the galvanic cell. A galvanic cell is generally represented by putting a vertical line between metal and electrolyte solution and putting a double vertical line between the two electrolytes connected by a salt bridge.

In a galvanic cell, the following cell reaction occurs:
$Zn(s) + 2Ag^+(aq) \rightarrow Zn^{2+}(aq) + 2Ag(s)$
$E^\circ_{cell} = +1.56$ V

(i) **What is the direction of the flow of electrons?**

(a) First from silver to zinc, then the direction reverses
(b) Silver to zinc
(c) First from zinc to silver, then the direction reverses
(d) Zinc to silver

(ii) **How will concentration of Zn^{2+} ions and Ag^+ ions be affected when the cell functions?**

(a) Concentration of both Zn and Ag^+ ions increase
(b) Concentration of Zn^{2+}increases and Ag^+ ions decreases
(c) Concentration of Zn^{2+} decreases and Ag^+ ions increases
(d) Concentration of both Zn^{2+} and Ag^+ ions decreases

(iii) **Name the cell which is generally used in inverters?**

(a) Mercury cell
(b) Leclanche cell
(c) Lead storage battery
(d) Lithium ion battery

(iv) **Which cell used in hearing aids?**

(a) Mercury cell
(b) Leclanche cell
(c) Dry cell
(d) Nickel Cadmium cell

(v) **The standard electrode potential for Daniell cell is 1.1V. Calculate the standard Gibbs energy for the reaction:**

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

(a) 215.36 kJ mol^{-1}
(b) -212. 27 kJ mol^{-1}
(b) 212.27 kJ mol^{-1}
(d) -218 kJ mol^{-1}

Answers

(i) d
(ii) b
(iii) c
(iv) a
(v) b

CBSE BOARD QUESTIONS

1.**From the given cells : Lead storage cell, Mercury cell, Fuel cell and Dry cell Answer the following :**

(i)Which cell is used in hearing aids ?
(ii) Which cell was used in Apollo Space Programme ?
(iii) Which cell is used in automobiles and inverters ?
(iv) Which cell does not have long life ? (2)

ANS:(i) Mercury cell (ii) Fuel cell (iii) Lead storage battery (iv)Dry cell

2.**Calculate e.m.f of the following cell at 298 K :** (3)

$2Cr(s) + 3Fe^{2+}(0.1M) \rightarrow 2Cr^{3+}(0.01M) + 3\,Fe(s)$

Given : $E°(Cr^{3+} | Cr) = -0.74$ V $E°(Fe^{2+} | Fe) = -0.44$ V

(i) $E^0_{cell} = E^0_c - E^0_a$
$= (-0.44)-(-0.74)$ V
$= 0.30$V

$$E_{cell} = E^0_{cell} - \frac{0.059}{n} \log \frac{[Cr^{3+}]^2}{[Fe^{2+}]^3}$$

$$E_{cell} = E^0_{cell} - \frac{0.059}{6} \log \frac{[0.01]^2}{[0.1]^3}$$

$= 0.30-(-0.059/6)$
$= 0.3098$V

3.Write the name of the cell which is generally used in hearing aids. Write the reactions taking place at the anode and the cathode of this cell. (3)

Ans:Mercury cell, Anode : $Zn(Hg)+2OH^- \rightarrow ZnO(s)+H_2O+2e^-$

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

4. **(a) The cell in which the following reaction occurs :$2 Fe^{3+}(aq) + 2I^- (aq) \longrightarrow 2Fe^{2+}(aq)+I_2(s)$ has E^0cell = 0·236 V at 298 K. Calculate the standard Gibbs energy of the cell reaction. (Given : 1 F = 96,500 C mol–1)** (2)

(b) How many electrons flow through a metallic wire if a current of 0·5 A is passed for 2 hours ? (Given : 1 F = 96,500 C mol–1) (3)

Ans: (a)$\Delta G^0 = -nFE^0$ cell

n= 2 ,$\Delta G^0 = - 2 \times 96500$ C /mol x 0.236 V

$= - 45548$ J/mol

$= -45.548$ kJ/mol

(b) Q= I t = 0.5 x 2 x 60 x 60

= 3600 C

96500 C = 6.023×10^{23} electrons

so 3600 C = 2.25×10^{22} electrons

5.**A current of 1.50 A was passed through an electrolytic cell containing $AgNO_3$ solution with inert electrodes. The weight of silver deposited was 1.50 g. How long did the current flow ? (Molar mass of Ag = 108 g mol–1, 1F = 96500 C mol–1).** (3)

Ans: $Ag^+ + 1e \rightarrow Ag$

96500C depositing 108 g of Ag

Quantity of electricity required for depositing

1.5g of Ag= 96500x1.5/108 =1340.27C

Q=Ixt so t=Q/I t=1340.27/1.5=893.5s.

6.**The conductivity of a 0.01 M solution of acetic acid at 298 K is $1.65 \times 10–4$ S cm^{-1} . Calculate molar conductivity (Λm) of the solution.** (2)

Ans: $\Lambda m = 1000k/c$, $\Lambda m = 1000x1.65x10^{-4}/ 10^{-2} = 16.5 Scm^2mol^{-1}$

7.**Consider the following reaction : $Cu(s) + 2Ag^+ (aq) \rightarrow 2Ag(s) + Cu^{2+}(aq)$**

(i) Depict the galvanic cell in which the given reaction takes place.

(ii) Give the direction of flow of current. (iii) Write the half-cell reactions taking place at cathode and anode. (3)

Ans: (i) $Cu_{(s)}|Cu^{2+}_{(aq)}||Ag^+_{(aq)}|Ag_{(s)}$

(ii)Silver electrode to Copper electrode

(iii) Anode, $Cu \rightarrow Cu^{2+} + 2e$

Cathode, $Ag^+ + 1e \rightarrow Ag$

8. **E° cell for the given redox reaction is 2.71 V**

$Mg(s) + Cu^{2+} (0.01 M) \longrightarrow Mg^{2+} (0.001 M) + Cu_{(s)}$

(a)Calculate E_{cell} for the reaction.(b) Write the direction of flow of current when an external opposite potential applied is

(i) less than 2.71 V and (ii) greater than 2.71 V (3+2)

Ans: (a) E cell = E^0 cell - $\frac{0.059}{n} \log K_c$

$= E^o_{cell} - \frac{0.059}{} \log(\frac{10^{-3}}{})$

$$2 \qquad \frac{(10^{-2})}{}$$

$= 2.71 + 0.0295$

$E_{cell} = 2.7395$ V

(b) i)Cu to Mg / Cathode to anode / Same direction

ii)Mg to Cu / Anode to cathode / Opposite direction

9.**A steady current of 2 amperes was passed through two electrolytic cells X and Y connected in series containing electrolytes $FeSO_4$ and $ZnSO_4$ until 2.8g of Fe deposited at the cathode of cell X. How long did the current flow ? Calculate the mass of Zn deposited at the cathode of cell Y. (Molar mass : Fe = 56 g mol^{-1} Zn = 65.3 g mol^{-1}, 1F = 96500 C mol^{-1})**

(a) $m = z\ I\ t$

2.8 g = $\frac{56 \times 2 \times t}{2 \times 96500}$

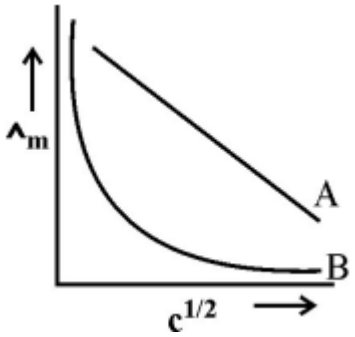
t= 4825 s 0r 80.417 min

$m1 / m2 = E1 / E2$

$2.8 / mZn = (56 / 2)\ X(\ 2 / 65.3)$

mZn = 3.265 g

10.**In the plot of molar conductivity (Λm) vs square root of concentration ($C^{1/2}$), following curves are obtained for two electrolytes A and B :**



Answer the following :

(1)Predict the nature of electrolytes A and B. (2)

(2)What happens on extrapolation of Λm to concentration approaching zero for electrolytes A & B

Ans: i)A- strong electrolyte , B-Weak electrolyte

ii)Λ^0m for weak electrolytes cannot be obtained by extrapolation while Λ^0m for strong electrolytes can be obtained as intercept.

11.**(a)Calculate ΔG° for the reaction**

$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$. 3

Given : E° for Zn2+/Zn = – 0·76 V and E° for Cu2+/Cu =+0·34V R = 8·314 JK–1 mol–1 F = 96500 C mol–1.

(b)Give two advantages of fuel cells. (3+2)

Ans: (a) E^0 cell = $E^oC - E^oA = 0.34 - (-0.76) = 1.10$V

$\Delta G^o = -nFE^oCell = -2 \times 1.10 \times 96500$

$= -212300$ J/mol or -212.3 kJ/mol

(b) (i) Pollution free (ii) High efficiency.

12.**(a) Out of the following pairs, predict with reason which pair will allow greater conduction of electricity :**

(i) Silver wire at 30°C or silver wire at 60°C.

(ii) 0·1M CH_3COOH solution or 1M CH_3COOH solution.

(iii) KCl solution at 20°C or KCl solution at 50°C.

(b)Give two points of differences between

electrochemical and electrolytic cells. (3+2)

Ans:(a) (i) Silver wire at 30^0C because as temperature decreases, resistance decreases so conduction increases.

(ii) 0.1 M CH_3COOH, because on dilution degree of ionization increases hence conduction increases.

(iii)KCl solution at 50^0C, because at high temperature mobility of ions increases and hence conductance increases

(b) Electrochemical cell

(1) Anode -ve Cathode +ve

(2) Convert chemical Energy to electrical energy

Electrolytic cell

(1) Anode +ve ,Cathode -ve

(2) Convert electrical Energy to chemical energy (or any other correct differences)

13. a) Write the Nernst equation for the following cell reaction: $Zn_{(s)}+Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)}+Cu_{(s)}$

b) How will the E_{cell} be affected when concentration of

(i)Cu^{2+} ions is increased and (ii) Zn^{2+} ions is increased ?(3)

Ans: a) $Zn_{(s)}|Zn^{2+}_{(aq)}||\ Cu^{2+}_{(aq)}|Cu_{(s)}$

b) (i) $E_{(cell)}$ increases (ii) $E_{(cell)}$ decreases

14. (a) The standard Gibbs energy (Δ_rG^0) for the following cell reaction is -300 kJ mol^{-1}:

$Zn(s) + 2Ag^+(aq) \rightarrow Zn^{2+}(aq) + 2Ag(s)$ (3)

Calculate E^0 cell for the reaction. (Given: lF = 96500 moI^{-1})

Ans: $\Delta_rG^0 = -nFE^0_{(cell)}$

$-300x1000j/mol=-2x96500xE^0_{(cell)}$

$E^0_{(cell)}=300000/2x96500=1.55v$

15. Calculat λ^0_m for $MgCl_2$ if λ^0 values for Mg^{2+} ion and Cl^- ion are 106 S cm^2mol^{-1} and 76.3 S cm^2mol^{--1}respectively.(2)

Ans: $\Lambda^0m\ MgCl_2 = \lambda^0Mg^{2+}+ \lambda^02Cl^-$

$= 106\ Scm^2mol^{—1}+76.3x2\ Scm^2mol^{—1}$

$= 258.6\ Scm^2mol^{—1}$

CHAPTER 4

CHEMICAL KINETICS

GIST OF THE LESSON

- **Rate of a Chemical Reaction**: It is the change in concentration of a reactant or product in unit time (or) itis the rate of change of concentration of reacting species.

  Consider a reaction, $R \rightarrow P$

  Rate of a Chemical Reaction $= \frac{\Delta [P]}{\Delta t} = \frac{-\Delta [R]}{\Delta t}$

Rate of reaction always expressed for every one mole.
Consider a general reaction: $a\ A + b\ B \rightarrow c\ C + d\ D$, then

Rate of reaction $= -\frac{1}{a}$ [Rate of disappearance of A] $= -\frac{1}{b}$ [Rate of disappearance of B]
$= \frac{1}{c}$ [Rate of disappearance of C] $= \frac{1}{d}$ [Rate of disappearance of D]

- **Units of rate of a reaction:** $mol\ L^{-1}s^{-1}$.

Average Rate	Instantaneous Rate
It is the change in concentration of reactants in agiven interval of time	It is the change in concentration of reactants at amoment of time

- **Rate Law Expression:** It is a mathematical expression in which rate of reaction is expressed in terms of molar concentration of reactants with each term raised to power, which may or may not be equal to the stoichiometric coefficient of the reacting species in a balanced chemical equation.

Consider a general reaction:
$a\ A + b\ B \rightarrow c\ C + dD$, then,
Rate Law = $k [A]^x [B]^y$, where,
'x' may/ may not be equal to 'a' and 'y' may/ may not be equal to 'b'

- **Order of a Reaction:** It is the sum of powers of concentrations of reactants expressed in rate law.Consider a general reaction: $a\ A + b\ B \rightarrow c\ C + d\ D$, then
  Rate Law = $k [A]^x [B]^y$, overall order of reaction = (x+y) and x and y represent the order with respect tothe reactants A and B respectively.

- **Units of rate constant (k) for n^{th} order of reaction:** $\mathbf{mol^{(1-n)}L^{(n-1)}S^{-1}}$

  To know the order of reaction when unit of rate constant is given, then just add 1 to the number given in power of litre factor.

- **Molecularity of a Reaction**: The number of reacting species (atoms, ions or molecules) taking part

in an elementary reaction, which must collide simultaneously in order to bring about a chemical reaction is calledmolecularity of a reaction.

- Difference between order of reaction and molecularity of reaction:

	Order of reaction	**Molecularity of reaction**
1	It is the sum of powers of concentrations of reactants expressed in rate law.	The number of reacting species (atoms, ions or molecules) taking part in an elementary reaction, which must collide simultaneously in order to bring about a chemical reaction
2	Order of a reaction is anexperimental quantity.	Molecularity of a reaction is a theoretical quantity.
3	It can be zero and even a fraction	Molecularity cannot be zero or a non-integer.
4	Order is applicable to elementary as well as complex reactions	Molecularity is applicable only for elementary reactions.

- **Elementary reactions**: The reactions taking place in one step are called Elementary Reactions
- **Complex reactions**: The reactions taking place in more than one step are called complex reactions.
- **INTEGRATED RATE LAW EQUATIONS**:

a) Zero order reaction: $k = \frac{[R_0] - [R]}{T}$

b) First order reaction: $k = \frac{2.303}{t} \log([R_0]/[R])$

c) Integrated rate equation for first order gas phase reaction , $A(g) \rightarrow B(g) + C(g)$ or $A(g) \rightarrow 2B(g)$

$k = \frac{2.303}{t} \log (P_i / 2P_i - P_t)$ where P_i- Initial pressure & P_t – Total pressure at time t.

- **Half-Life of a Reaction:** It is the time required to reduce the concentration of reactant to half of its initial concentration.

Case 1: For a zero order reaction, rate constant is given by equation

$$k = \frac{[R_0 - R]}{t}$$

when $t = t_{½}$, then $[R] = ½ [R_0]$

$$t_{½} = \frac{[R_0]}{2k}$$

$t_{½}$ for a zero order reaction is directly proportional to the initial concentration of the reactants and inverselyproportional to the rate constant.

Case 2: For the first order reaction,

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

At $t = t_{½}$, then $[R] = ½ [R_0] \Rightarrow$

$$k = \frac{2.303}{t_{½}} \log \frac{[Ro]}{[R_0]/2}$$

$$k = \frac{2.303}{t_{½}} \log 2 \qquad t_{½} = \frac{0.693}{k}$$

For a first order reaction, half-life period is constant, i.e., it is independent of initial concentration of thereacting species.

For zero order reaction $t_{½} \alpha [R]_0$.

For first order reaction $t_{½}$ is independent of $[R]_0$. In general for n th order, $t_{½} \alpha [R_0]^{(1-n)}$

- **Pseudo First Order Reaction:** A reaction which appear to follow higher order but follows first order kinetics. In this type of reaction one of the reactant is present in large excess i.e. the concentration does not get altered much during the course of the reaction. e.g.

a) Acid catalyzed hydrolysis of ester: $CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$,
Rate = $k[CH_3COOC_2H_5]$

b) Inversion of cane sugar is another pseudo first order reaction

- **Dependence of temperature on rate of a reaction – Arrhenius Equation**
  - $k = A\, e^{-Ea / RT}$
    $e^{-Ea / RT}$ represents the fraction of molecules with energies equal to or greater than Ea
  - $\log k = \log A - Ea / 2.303RT$
  - Let k_1 & k_2 be the rate constant for a reaction at temperature T_1 & T_2, then
    $\log (k_2/ k_1) = [Ea/2.303R][(T_2-T_1)/T_1T_2]$
  - Threshold Energy: The minimum energy that a reacting species must possess in order to undergo effective collisions
  - Activated Complex: The highly energetic arrangement of atoms formed during the course of reaction which corresponds to the peak of curve in the energy profile diagram for the progress of the reaction.
  - Activation Energy (E_a): The additional energy required by reacting species over and above their average PE to enable them to cross the energy barrier between reactants and products.

- **Effect of Catalyst on rate of reaction**:
  - Substances which alter the rate of a chemical reaction without itself undergoing any permanent chemical change are known as catalysts.
  - Catalyst provides an alternate pathway or reaction mechanism by reducing the activation energy and hence lowering the potential energy barrier. Lower the value of activation energy faster will be the rate of a reaction.
  - A catalyst does not alter Gibbs energy, ΔG of a reaction.
  - A catalyst does not change the equilibrium constant of a reaction rather it helps in attaining the

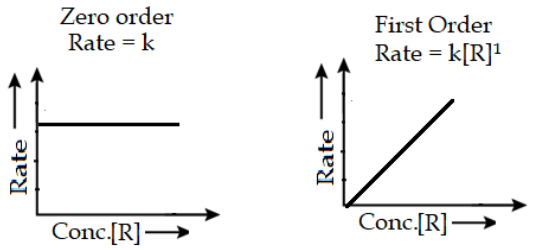
equilibrium faster.

➢ **Collision theory**:

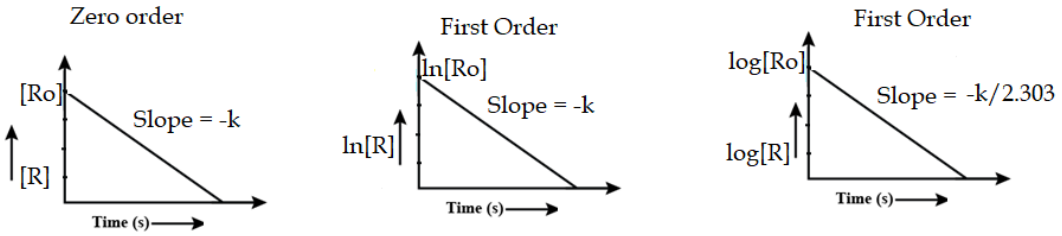
- According to collision theory rate of reaction depends on the collision frequency and effective collisions.
- Collision frequency (Z): The number of collisions per second per unit volume of the reaction mixture.
- Effective collisions: The collisions in which molecules collide with sufficient kinetic energy (Threshold energy) and proper orientation so as to facilitate breaking of bonds between reacting species and formation of new bonds to form products.
- Rate = $PZ_{AB}\ e^{-Ea / RT}$

Graphical representation of Zero order and First order reactions:

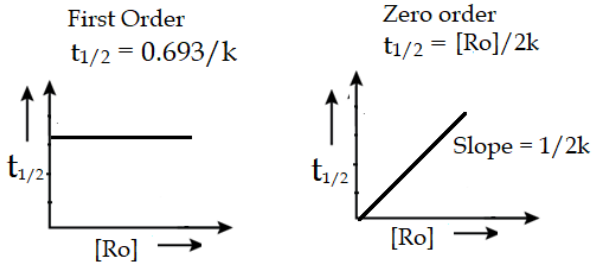
a) Rate vs Concentration of reactant



b) Concentration of reactant vs Time



c) Half life vs Initial concentration of reactant



MULTIPLE CHOICE QUESTIONS

1. For a reaction P + Q → 2 R + S , the incorrect statement is

(a) Rate of disappearance of P = Rate of appearance of S
(b) Rate of disappearance of Q = 2 x Rate of appearance of R
(c) Rate of disappearance of Q = Rate of disappearance of P
(d) Rate of disappearance of Q = ½ x Rate of appearance of R

2. The reaction $NO_2 + CO \rightarrow NO + CO_2$ takes place in two steps.

$2NO_2 \rightarrow NO + NO_3$ (k_1) – slow

$NO_3 + CO \rightarrow CO_2 + NO_2$ (k_2) – fast

The rate law is

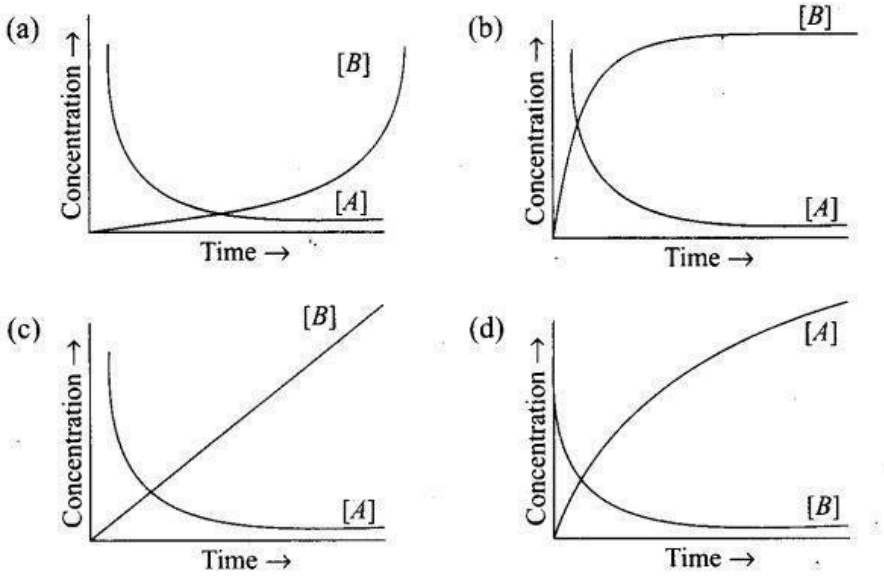
a) $R = k_1 [NO_2]^3$

b) $R = k_2 [NO_3] [CO]$

c) $R = k_1 [NO_2]^2$

d) $R = k_1 [NO_2]$

3.Consider the reaction A —> B. The concentration of both the reactants and the products variesexponentially with time. Which of the following figures correctly describes the change in concentration of reactants and products with time?



4. In a reaction, $2X \rightarrow Y$, the concentration of X decreases from 0.50 M to 0.38 M in 10 min. Whatis the rate of reaction in Ms^{-1} during this interval ?

(a) 2×10^{-4}

(b) 4×10^{-2}

(c) 2×10^{-2}

(d) 1×10^{-2}

5. A first order reaction takes 40 min for 30% decomposition. $t^{1/2}$ will be

(a) 77.7 min

(b) 52.5 min

(c) 46.2 min

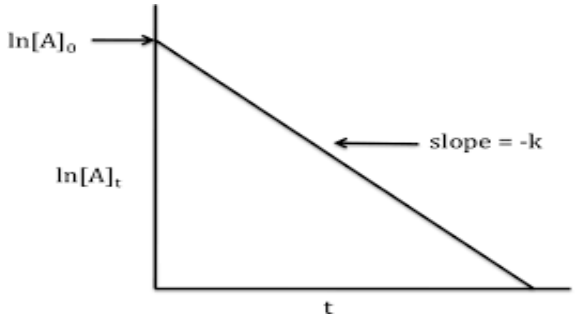
(d) 22.7 min

6. If the initial concentration of reactant is doubled, $t^{1/2}$ is also doubled, the order of reaction is

a) 1/2

b) 1
c) 2
d) 0

7. A plot is shown below between concentration and time *t*. Which of the given orders is indicated by the graph



(a) Zero Order
(b) Second Order
(c) First Order
(d) Fractional Order

8. In the reaction 2 A + B → A_2B , if the concentration of A is doubled and that of B is halved , the rate of it reaction will

(a) Increase by 4 times
(b) Increase by 2 times
(c) Decrease by 2 times
(d) Remains the same

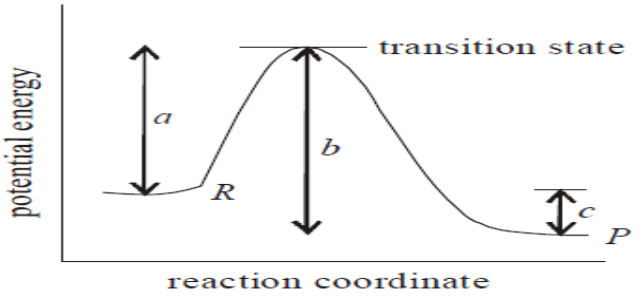
9. On increasing the temperature by 10 K , the rate of reaction becomes almost double. The most appropriate reason is

(a) Increase in the number of collisions
(b) Decrease in activation energy
(c) Increase in the energy of collisions
(d) Almost double the number of molecules crossing the energy barrier

10. The potential Energy diagram for a reaction , R → P is shown below

Enthalpy change of the reaction corresponds to ----

(a) a (b) a + b (c) c (d) b



11. A first order reaction has a rate constant $1.15 \times 10^{-3}\ s^{-1}$. Time taken for 5 g of this reactant to reduce to 3 g is

(a) 444 s
(b) 400 s
(c) 528 s
(d) 669 s

12. Compounds A **and** B **react according to the following chemical equation.**

A(g)+2B(g)→2C(g) **Concentration of either 'A' or 'B ' were changed keeping the concentrations of one of the reactantsconstant and rates were measured as a function of initial concentration. Following results were obtained. Choose the correct option for the rate equations for this reaction.**

Expt	[A]	**[B]**	**Initial Rate (mol L^{-1} s^{-1})**
I	**0.01**	**0.01**	**0.005**
II	**0.02**	**0.01**	**0.020**
III	**0.02**	**0.03**	**0.060**

(a) Rate= k[A] [B]
(b) Rate= k$[A]^{1}$ $[B]^{2}$
(c) Rate= k$[A]^{2}[B]^{2}$
(d) Rate= k$[A]^{2}$[B]

ANSWER KEY

1 . b	**2.** c	3.b	4. a
5 a	6. d	7.c	8 .b
9 .d	10 c	11 a	12 d

ASSERTION-REASON TYPE QUESTIONS

A statement of assertion is followed by a statement of a reason. Mark the correctchoice from the options given below:
a) Both assertion and reason are true and reason is the correct explanation of assertion.
b) Both assertion and reason are true but reason is not the correct explanation ofassertion.
c) Assertion is true but reason is false.
d)Assertion is false and reason is true

1. **Assertion**: Rate constant of a zero-order reaction has same units as the rate of reaction.
Reason: Rate constant of a zero-order reaction does not depend upon the concentration of reactant.
2. **Assertion :** The molecularity of the reaction , $H_2 + Br_2 \rightarrow 2\,HBr$ is 2
Reason : The order of the reaction can be determined only experimentally.

3. Assertion: All collision of reactant molecules lead to product formation.
Reason: Only those collisions in which molecules have correct orientation and sufficient kinetic energy lead to compound formation

4. **Assertion** : Half-life period is always independent of initial concentration .
Reason : Half-life Period is inversely proportional to rate constant.

5. **Assertion:** Diamond shall convert to graphite.
Reason: The rate is so slow that the change is not perceptible at all.

6. **Assertion:** A catalyst does not alter the free energy change of a reaction.
Reason: A catalyst lowers the activation energy of a process.

7. **Assertion:** According to collision theory the rate of reaction does not depend on collision frequency.
Reason: The collisions in which molecules collide with sufficient kinetic energy and proper orientation are called effective collisions.

8. **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.

9. **Assertion:** Hydrolysis of methyl ethanoate is a pseudo first order reaction.
Reason: Water is present in large excess and therefore its concentration remained Constant throughout the reaction.

10. Assertion: The order for a reaction with rate constant $k=3x10^4s^{-1}$ is 1.
Reason: Order of a reaction is the sum of the powers to which concentration terms are raised to in the rate law

11.Assertion : Rate constant of a zero order reaction has the same units as the rate of reaction .
Reason : Rate of a zero order reaction does not depend on the concentration..

12. Assertion: 50% of a reaction is completed in 50 sec, 75% of the reaction will becompleted in 75 sec.
Reason: The rate constant of a zero-order reaction depends upon time.

13.Assertion: The thermal decomposition of HI on gold is a zero-order reaction.
Reason: The thermal decomposition of HI on gold depends on the initial concentration

14.Assertion: The reaction X→Y follows second order kinetics. If concentration of X increased 3 times rate become 3 times.
Reason: The rate of a reaction is directly proportional to the concentration ofreactants

15.**Assertion:** The enthalpy of reaction remains constant in the presence of a catalyst**.**
Reason: A catalyst participating in the reaction, forms different activated complex andlowers down the activation energy but the difference in energy of reactant and product remains the same**.**

ANSWERS

1 c	2 b	3 d	4 c	5 a
6 b	7 d	8 c	9 a	10 b

11 b	12 c	13 c	14 d	15 a

SHORT ANSWER QUESTIONS

1. **Define rate of a reaction? What is the SI Unit of rate of reaction?** (2)

   Ans: Change in molar concentration of reactant or product in per unit time is called rate of reaction. Unit of rate: $MolL^{-1}S^{-1}$

2. **(i) State rate law?** **(2)**

   (ii) For a reaction in 10 minutes concentration of reactant reduced from 0.12µg to 0.06 µg and in next 10 minutes it becomes 0.03 µg. find the order of this reaction.

   Ans. (i) Expression in which reaction rate is given in terms of molar conc. of reactants with each term rise to some power which may or may not be same as the stoichiometric coefficient of the reacting species in a balanced chemical equation.

   (ii) Since in every 10 minutes concentration becomes half. Half-life is independent of concentration for first order reaction. So it is a first order reaction

3. **The kinetic of the reaction $2NO + 2H_2 \rightarrow N_2 + 2H_2O$ is explained by the following steps:** **(2)**

   (i) $2NO + H_2 \rightarrow N_2 + H_2O_2$ **…… slow**

   (ii) $H_2O_2 + H_2 \rightarrow 2H_2O$ **……. fast**

   What is the rate law for the reaction?

   Ans: Slow reaction is the rate determining step.

   Rate law, rate = $k[NO]^2[H_2]$

4. **For a reaction $A + B \rightarrow P$, the rate is given by Rate = $k[A][B]^2$** **(2)**

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

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

   Ans. a) Rate will increase 4 times of the actual rate of reaction

   b) 2^{nd} order

5. **A) What are complex reactions?** **(2)**

   B) What is the order of reaction whose unit of rate constant and rate of reaction are same?

   Ans. i) Reactions taking place in more than one step are called complex reaction.

   ii) Zero order

6. **When ammonia and oxygen react at high temperature nitrogen (II) oxide and water are formed. In an experiment the rate of formation of NO was found to be $3.2x10^{-3}molL^{-1}s^{-1}$. Compute the rate of disappearance of ammonia and rate of formation of water. The reaction**

is $4NH_3 + 5O_2 \rightarrow 4NO + 6\ H_2O$ **(2)**

Ans: For the given reaction general rate is

$$\text{Rate} = -\frac{\Delta[NH_3]}{4\Delta t} = -\frac{\Delta[O_2]}{5\,\Delta t} = \frac{\Delta[NO]}{4\Delta t} = \frac{\Delta[H_2O]}{6\Delta t}$$

Rate of disappearance of ammonia = Rate of formation of NO = $3.2\times10^{-3}molL^{-1}s^{-1}$

Rate of formation of water = 6/4 * Rate of formation of NO = $6\times3.2\times10^{-3}/4 = 4.8\times10^{-3}molL^{-1}s^{-1}$

7.**The rate constant for a first order reaction is $60s^{-1}$. How much time will it take to reduce 1g of the reactant to 0.0625 g?** (2)

Ans:

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

$$t = \frac{2.303}{60}\log\frac{1}{0.0625}$$

$$t = 0.0462\ s$$

8.**i) Identify the reaction order from the rate constant $k=2.3\times10^{-5}\ mol^{-1}\ Ls^{-1}$** **(2)**

ii) Define molecularity of a reaction.

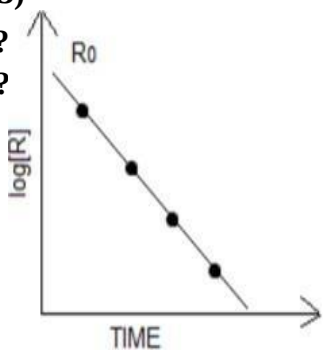
Ans i) 2

ii) The number of reacting species taking part in an elementary reaction which must colloid simultaneously in order to bring about a chemical reaction is called molecularity of reaction.

9. **Observe the graph in diagram and answer the following questions.** **(3)**

(i) If slope is equal to $-2.0\times10\text{-}6\ S^{-1}$, what will be the value of rate constant?

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



Ans: i) Slope = -k

$-2.0\times10^{-6}\ sec^{-1} = -k$

Hence k = $2.0\times10^{-6}\ sec^{-1}$

ii) $t_{½} = R_0/2k$

10.A first order reaction is 40% complete in 80 minutes. Calculate the value of rate Constant (k). In what time will the reaction be 90% completed? (3)

[Given: log 2 = 0·3010, log 3 = 0·4771, log 4 = 0·6021, log 5 = 0·6771, log 6 = 0·7782]

Ans.

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

$$= \frac{2.303}{80}\log\frac{100}{60}$$

$$= \frac{2.303}{80}\ x\ (1 - 0.7782)$$

$$= 0.0064\ min^{-1}$$

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

$$= \frac{2.303}{0.0064}\log\frac{100}{10}$$

$$= 360\ min$$

11. **For the reaction A + B →products, the following initial rates were obtained at various given initial concentrations. Determine the half-life period.** (3)

S.No.	[A] mol / L	[B] mol / L	Initial rate M/s
1.	0.1	0.1	0.05
2.	0.2	0.1	0.10
3.	0.1	0.2	0.05

$$rate = k\,[A]^x\,[B]^y$$
$$0.05 = k[0.1]^x[0.1]^y \quad \ldots\ldots(i)$$
$$0.10 = k[0.2]^x[0.1]^y \quad \ldots\ldots(ii)$$
$$0.05 = k[0.1]^x[0.2]^y \quad \ldots\ldots(iii)$$
$$(ii) \div (i)$$
$$\frac{0.10}{0.05} = (2)^x$$
$$x = 1$$
$$(iii) \div (i)$$
$$\frac{0.05}{0.05} = (2)^y$$
$$y = 0$$
$$rate = k[A]^1[B]^0$$

It is a first order reaction.

$$k = \frac{rate}{[A]} = 0.5\,s^{-1}$$
$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.5}$$
$$t_{1/2} = 1.386\ s$$

12. The following data were obtained during the first order thermal decomposition of SO_2Cl_2 at a constant volume: (3)

$SO_2Cl_2\,(g) \rightarrow SO_2(g) + Cl_2\,(g)$

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

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

for first order reaction.

$$K = \frac{2.303}{t}\log\frac{P_0}{2P_0 - P_t}$$
$$= \frac{2.303}{100}\log\frac{0.4}{2\times0.4 - 0.7} = \frac{2.303}{100}\log\frac{0.4}{0.1}$$
$$K = \frac{2.303\times0.602}{100}$$
$$K = 1.386\times10^{-2}\,s^{-1}$$

13. Show that the time required for 99% completion of a first order reaction is

twice the timerequired for the completion of 90% of reaction. (3)

I set : $[R]_o$= 100, [R]=[100-90]=10 t=$t_{90\%}$
IIset : $[R]_o$= 100 [R]= [100-99]1 t=$t_{99\%}$
To be proved $t_{99\%}= 2t_{90\%}$

$$K= \frac{2.303}{t} \times \log \frac{[R]_o}{[R]}$$

Sub. I set values .

$$K= \frac{2.303}{t_{90\%}} \times \log \frac{100}{10}$$

$$K = \frac{2.303 \times \log 10}{t_{90\%}}$$

$$K= \frac{2.303 \times 1}{t_{90\%}} \quad -(1)$$

Substituting II set values

$$K= \frac{2.303}{t_{99\%}} \times \log \frac{100}{1}$$

$$K= \frac{2.303 \times 2}{t_{99\%}} \quad \text{----------(2)}$$

Comparing equations (1) & (2)

$$\frac{2.303 \times 1}{t_{90\%}} = \frac{2.303 \times 2}{t_{99\%}}$$

$$t_{99\%} = 2t_{90\%}$$

14. The decomposition of phosphine, PH_3, proceeds according to the following equation:

$4PH_3(g) \rightarrow P_4(g) + 6H_2(g)$ (3)

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

Rate =k[PH3]

The half-life of PH_3 is 37.9 s at 120°C

i) How much time is required for 3/4th of PH3 to decompose?

ii) What fraction of the original sample of PH3 remains behind after 1 minute?

Ans: i) This is a first order reaction.

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

k = 0.693/ 37.9 & [R] = ¼[Ro]

$$t = \frac{2.303}{0.693/37.9} \log [Ro]/ 1/4[Ro]$$

t = 2.303 x 37.9 x log 4 / 0.693

t = 75.82 s

(ii) $\log \frac{[Ro]}{[R]} = \frac{k \times 60}{2.303}$

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

$$\log \frac{[Ro]}{[R]} = \frac{60}{37.9} \log 2$$

$$\frac{[Ro]}{[R]} = 2.99$$

R/Ro = 0.334 = Fraction of PH_3 after 1 minute

15. For the zero order reaction A → 2B, the rate constant is 2 x 10^{-6}M min^{-1}. The reaction is started with 10M of A. (3)

i) What will be the concentration of A after 2 days?

ii) What is the initial half-life of the reaction?

iii) In what time, the reaction will complete?

Ans: i) $kt = [R_0] - [R]$, $[R] = [R_0] - kt$

$[R] = 10 - 2 \times 10^{-6} \times 2 \times 24 \times 60 = 9.994M$

ii) $t_{1/2} = [R_0]/2k = 10/ 2 \times 2 \times 10^{-6} = 2.5 \times 10^6$ min.

iv) When reaction is complete, $[R] = 0$

$t = [R_0] - [R] / k = [R_0]/k$

$t = 10/ 2 \times 10^{-6} = 5 \times 10^6$ min.

LONG ANSWER TYPE OF QUESTIONS

1. (i) Express the rate of the following reaction in terms of the formation of ammonia: (5)

$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

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

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

(iv) Define the following:

(a) Elementary step in a reaction

(b) Rate constant

Ans (i)

$$\frac{-d[N_2]}{dt} = \frac{-1}{3}\frac{d[H_2]}{dt} = +\frac{1}{2}\frac{d[NH_3]}{dt}$$

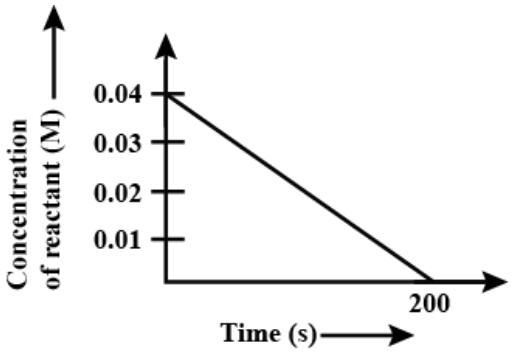
(ii) S^{-1} is the unit for rate constant of first order reaction.

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

(iv) (a) Elementary step in a reaction: Each step of a complex reaction is called the elementary step of the reaction.

(b) Rate constant is equal to the rate of reaction when molar concentration of reactant is unity.

2.a) Vijay plotted a graph between concentration of R and time for a reaction $R \rightarrow P$. On the basisof this graph, answer the following questions:



(i) Predict the order of reaction.

(ii) What does the slope of the line indicate?

(iii) What are the units of rate constant?

(b) **A first order reaction takes 25 minutes for 25% decomposition. Calculate $t_{1/2}$.**
[Given:log 2= 0·3010, log 3 = 0·4771, log 4 = 0·6021]

Ans:

(a) (i) zero order

(b) (ii) slope = - k

(c) (iii) $molL^{-1}$ s

(b) $k = 2.303/t \log [R_0]/[R]$

$= 2.303/25 \log 100/75$

$= 2.303/25 \log 4/3$

$= 2.303/25(0.6021 - 0.4771)$

$= 0.0115$ min-1

$t_{1/2} = 0.693/k = 0.693/0.0115$

$= 60.26$ min or 60.2 min

3. **a) Consider a certain reaction A → Products with $k = 2.0 \times 10^{-2}$ s^{-1}. Calculate the concentrationof a remaining after 100s if the initial concentration of A is 1.0 $molL^{-1}$.**
b) The half-life for radioactive decay of 14C is 5730 years. An archaeological artifact containing wood had only 80% of the 14C found in a living tree. Estimate the age of the sample. (3+2)

Ans a)

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

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

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

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

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

b)

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

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

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

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

4.**The rate constant for the first order decomposition of a certain reaction is described by the equation $\log k\ (s^{-1}) = 14.34 - 1.25 \times 10^4\ K / T$ (5)**

i) What is the pre-exponential factor and energy of activation for this reaction?

ii) At what temperature will its half-life period be 256min?

Ans: i) From Arrhenius equation, $k = Ae^{-Ea/RT}$

$\log k = \log A - Ea / 2.303RT$ -----(1)

$\log k(s^{-1}) = 14.34 - 1.25 \times 10^4 \text{ K} / T$ ---- (2)

Comparing (1) and (2), $\log A = 14.34$, $A = \text{Antilog}(14.34) = 2.188 \times 10^{14} s^{-1}$

$Ea / 2.303R = 1.25 \times 10^4$

$Ea = 1.25 \times 10^4 \times 2.303 \times 8.314 = 239.34 kJ/mol$

ii) For first order reaction, $t_{½} = 0.693/k$, $k = 0.693/ t_{½} = (0.693/256 \times 60)s^{-1}$

$\log (0.693/256 \times 60) = 14.34 - 1.25 \times 10^4 / T$

$T = 668.96K$

5.A) The rate constant for a first order reaction becomes eight times when the temperature is increased from 360K to 400K. Calculate the activation energy for the reaction.

B) For a reaction, the energy of activation is zero. What is the value of rate constant at 300K, if k= $1.6 \times 10^6 s^{-1}$ at 280K? R = $8.31 JK^{-1}mol^{-1}$

Ans: A) If rate constant at 360K is k, then at 400K it will be 8k

From Arrhenius equation,

$$\log k_2/ k_1 = Ea/2.303R(T_2-T_1/T_1T_2)$$

$$\log 8k/k = \frac{Ea}{2.303 \times 8.314} \frac{[400-360]}{400 \times 360}$$

$Ea = 62.24 kJ/mol$

B) From Arrhenius equation, we have

$$\log k2/ k1 = Ea/2.303R(T_2-T_1/T_1T_2)$$

When the energy of activation is zero, Ea = 0,

$\log k2/ k1 = 0$

$k2/ k1 = 1$

$k2 = k1 = 1.6 \times 10^6 s^{-1}$

The rate constant at 300K is same as the rate constant at 280K when Ea is zero

CASE BASED QUESTIONS

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

The rate of a reaction, which may also be called its velocity or speed, can be defined with relation to the concentration of any of the reacting substances, or to that of any product of the reaction. If the species chosen is a reactant which has a concentration cat time t the rate is -dc/dt, while the rate with reference to a product having a concentration x at time t is dx/dt. Any concentration units may be used for expressing the rate; thus, if moles per litre are employed for concentration and seconds for the time, the units for the rate aremoles $litre^{-1}$ sec^{-1}. For gas reactions pressure units are sometimes used in place of concentrations, so that legitimate units for the rate would be (mm. Hg) sec^{-1} and $atm.sec^{-1}$ The order of a reaction concerns the dependence of the rate upon

the concentrations of reacting substances; thus, if the rate is found experimentally to be proportional to the α^{th} power of the concentration of one of the reactants A, to the β^{th} power of the concentration of a second reactant B, and so forth, via., rate = k [A] $^{\alpha}$ [B] $^{\beta}$ (1)the over-all order of the reaction is simn = $\alpha + \beta +$ (2) Such a reaction is said to be of the α^{th} order with respect to the substance A, the β th order with respect to B and so on...*(Laidler, K. J., & Glasstone, S. (1948). Rate, order and molecularity in chemical kinetics. Journal of Chemical Education, 25(7), 383.)*

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 explanationfor 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:** Rate of reaction is a measure of decrease in concentration of reactantwith respect to time.
Reason: Rate of reaction is a measure of increase in concentration of product withrespect to time.

2. **Assertion:** For a reaction: P +2Q → Products,Rate = k $[P]^{1/2}[Q]^{1}$ so the order of reaction is 1.5
Reason: Order of reaction is the sum of stoichiometric coefficients of the reactants.

3. **Assertion:** The unit of k is independent of order of reaction.
Reason: The unit of k is moles L^{-1} s^{-1} for a zero order reaction

4. **Assertion:** Reactions can occur at different speeds.
Reason: Rate of reaction is also called speed of reaction.

5.Assertion : The rate of a chemical reaction is expressed in terms of Instantaneous rate rather than average rate.
Reason : The concentration of reactants continuously changes with time

II . Observe the table given showing volume of CO_2 obtained by reaction of $CaCO_3$ and dilute HCl after every minute. Answer the questions that follow:

Table showing volume of CO_2 at one minute interval by reaction of $CaCO_3$ with dilute HCl.

Time/mm	Volume of CO2/cm
0	0
1	24 cm3
2	34 cm3
3	38 cm
4	40 cm
5	40 cm
6	40 cm

(a)What happens to rate of reaction with time?
(b)Why does $CaCO_3$ powder react faster than marble chips?
(c)What happens to rate of reaction if concentrated HCl is used?
(d)In manufacture of NH_3, $N_2(g) + 3H_2(g) \rightarrow 2NH_3$ + heat, what is effect of catalyst on the rate of reaction?
(e) Why does rate of reaction becomes almost double for energy 10° rise in temperature?

ANSWERS

I - 1. b 2.c 3. d 4.b 5. A

II - 1. Rate first decreases with time and then becomes constant.
2. $CaCO_3$ has greater surface area.
3. Increases with increase in concentration
4. Equilibrium is attained faster.
5. No. of effective collisions become double

CBSE BOARD QUESTIONS

Question 1.
Define 'rate of a reaction'. (Delhi 2010)
Answer: **Rate of a reaction:** Either, The change in the concentration of any one of the reactants or products per unit time is called rate of a reaction. Or, The rate of a chemical reaction is the change in the molar concentration of the species taking part in a reaction per unit time.

Question 2.
Define 'order of a reaction'. (All India 2011)
Answer:
The sum of powers of the concentration of the reactants in the rate law expression is called the order of reaction.

Question 3.
Define 'activation energy' of a reaction. (All India 2011)
Answer:
The minimum extra amount of energy absorbed by the reactant molecules to form the activated complex is called activation energy.
The activation energy of the reaction decreases by the use of catalyst.

Question 4.
Express the rate of the following reaction in terms of the formation of ammonia :
$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ (Comptt. All India 2013)
Answer:

$$\frac{-d[N_2]}{dt} = \frac{-1}{3}\frac{d[H_2]}{dt} = +\frac{1}{2}\frac{d[NH_3]}{dt}$$

Question 5.
If the rate constant of a reaction is $k = 3 \times 10^{-4}\ s^{-1}$, then identify the order of the reaction. (Comptt. All India 2013)

Answer:
S^{-1} is the unit for rate constant of first order reaction.

Question 6.
Write the unit of rate constant for a zero order reaction. (Comptt. All India 2013)
Answer:
Mol L^{-1} S^{-1} is unit of rate constant for a zero order reaction.

Question 7.
Define rate of reaction. (Comptt. Delhi 2016)
Answer:
The change in concentration of reactant or product per unit time is called rate of reaction.

Question 8.
Define rate constant (K). (Comptt. All India 2016)
Answer:
Rate constant. It is defined as the rate of reaction when the concentration of reaction is taken as unity.

Question 9.
For a reaction R → P, half-life ($t_{1/2}$) is observed to be independent of the initial concentration of reactants. What is the order of reaction? (Delhi 2017)
Answer:
The $t_{1/2}$ of a first order reaction is independent of initial concentration of reactants.

Question 10
Define the following :
(i) Elementary step in a reaction
(ii) Rate of a reaction (All India 2009)
Answer:
(i) Elementary step in a reaction: Those reactions which take place in one step are called elementary reactions.
Example : Reaction between H_2, and I_2 to form 2HI
$H_2 + I_2 \rightarrow 2HI$
(ii) Rate of a reaction**:** The change in the concentration of any one of the reactants or products per unit time is called rate of reaction.

Question 11.
Define the following :
(i) Order of a reaction
(ii) Activation energy of a reaction (All India 2009)
Answer:
(i) Order of a reaction :
It is the sum of powers of molar concentrations of reacting species in the rate equation of the reaction.
It may be a whole number, zero, fractional, positive or negative.
(ii) Activation energy of a reaction: The minimum extra amount of energy absorbed by the reactant molecules to form the activated complex is called activation energy.

Question 12.
A reaction is of first order in reactant A and of second order in reactant B. How is the rate of this reaction affected when (i) the concentration of B alone is increased to three times (ii) the

concentrations of A as well as B are doubled? (Delhi 2010)
Answer:
$r = K[A]^1 [B]^2$
(i) When concentration of B increases to 3 times, the rate of reaction becomes 9 times
$r = KA(3B)^2 \therefore r = 9KAB^2 = 9$ times
(ii) $r = K(2A)(2B)^2 \therefore r = 8KAB^2 = 8$ times

Question 13.
The rate constant for a reaction of zero order in A is 0.0030 mol L^{-1} s^{-1}. How long will it take for the initial concentration of A to fall from 0.10 M to 0.075 M? (Delhi 2010)
Answer:
For a zero order reaction,

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

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

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

Question 14
Distinguish between 'rate expression' and 'rate constant' of a reaction. (Delhi 2011)
Answer:
Rate expression: The expression which expresses the rate of reaction in terms of molar concentrations of the reactants with each term raised to their power, which may or may not be same as the stoichiometric coefficient of that reactant in the balanced chemical equation.
Rate constant: The rate of reaction when the molar concentration of each reactant is taken as unity.

Question 15.
What do you understand by the rate law and rate constant of a reaction? Identify the order of a reaction if the units of its rate constant are : (i) L^{-1} mol s^{-1} (ii) L mol^{-1} s^{-1} (All India 2011)
Answer:
The rate of reaction is found to depend on α concentration of term of reactant A and β concentration term of reactant B
Then Rate of reaction $\propto [A]_\alpha [B]_\beta$
or Rate = $K [A]_\alpha [B]_\beta$
This expression is called Rate law.
'K' in this expression is called Rate constant. Rate constant's unit :
(i) Unit = L^{-1} mol s^{-1} → Zero order reaction
(ii) Unit = L mol^{-1} s^{-1} → Second order reaction.

Question 16.
The thermal decomposition of HCO_2H is a first order reaction with a rate constant of 2.4×10^{-3} s^{-1} at a certain temperature. Calculate how long will it take for three-fourths of initial quantity of HCO_2H to decompose. (log 0.25 = -0.6021) (All India 2011)
Answer:
Given : $K = 2.4 \times 10^{-3}$

According to the formula, where $\begin{cases} a = 1 \\ K = 2.4 \times 10^{-3} \\ x = \frac{3}{4} = 0.75 \end{cases}$

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

Putting these values in the above equation

$$t = \frac{2.303}{K} \log \frac{1}{1-0.75}$$

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

or $$t = \frac{2.303}{2.4 \times 10^{-3}} \times 0.6020$$

or $$t = \frac{1.386406}{2.4 \times 10^{-3}} = 577.6$$

∴ **Time taken, t = 577.6 sec.**

Question 17.

A reaction is of second order with respect to a reactant. How is the rate of reaction affected if the concentration of the reactant is reduced to half? What is the unit of rate constant for such a reaction? (All India 2011)

Answer:

Rate = K $[A]^2$ = Ka^2

If [A] = 1/2a Rate = K $(1/2a)^2$=1/4 Ka^2

∴ Rate = $1/4^{th}$ (one fourth of original rate)

The unit of rate constant is L mol^{-1} s^{-1}

Question 18.

What do you understand by the 'order of a reaction'? Identify the reaction order from each of the following units of reaction rate constant:

(i) L^{-1} mol s^{-1} (ii) L mol^{-1} s^{-1} (Delhi 2012)

Answer:

Order of reaction**:** The sum of powers of the concentration of the reactants in the rate law expression is called the order of that chemical reaction.

r = K$[A]^x[B]^y$ Order = x + y

(i) Zero order

(ii) Second order

Question 19.

A reaction is of second order with respect to a reactant. How is its rate affected if the concentration of the reactant is (i) doubled (ii) reduced to half? (All India 2012)

Answer:

As Formula, r = K$[R|^2$ …(Given)

(i) R' = 2R ⇒ r = K$[2R]^2$ = $4KR^2$

∴ Rate becomes 4 times than original rate

(*ii*) $R' = \frac{1}{2}R \quad \Rightarrow r = K\left[\frac{R}{2}\right]^2 = \frac{K}{4}R^2$

∴ *Rate becomes* $\frac{1}{4}$ *of the original rate*

Question 20.

What is meant by rate of a reaction? Differentiate between average rate and instantaneous

rate of a reaction. (Comptt. All India 2012)
Answer:
Rate of reaction**:** It is the change in concentration of the reactants or products in a unit time.
Average rate : Average rate depends upon the change in concentration of reactants or products and the time taken for the change to occur. R → P

$$\text{Average rate} = -\frac{\Delta[R]}{\Delta t}$$

$$\text{or} \quad \text{Average rate} = +\frac{\Delta[P]}{\Delta t}$$

Instantaneous rate: It is defined as the rate of change in concentration of any one of the reactant or product at a particular moment of time.

$$\lim_{\Delta t \to 0}\left[\frac{-\Delta[R]}{\Delta t}\right] = \frac{-d[R]}{dt}$$

Question 21
Rate constant k for a first order reaction has been found to be 2.54×10^{-3} sec^{-1}. Calculate its 3/4th life, (log 4 = 0.6020). (Comptt. India 2013)
Answer:
For first order reaction:

$$t_{3/4} = \frac{2.303}{k}\log 4$$

$$= \frac{2.303}{2.54\times10^{-3}\,\text{sec}^{-1}} \times 0.6020 = 545.8 \text{ sec.}$$

$$= \mathbf{9.09 \text{ min.}}$$

Question 22.
A first order gas phase reaction : $A_2B_2(g) \rightarrow 2A(g) + 2B(g)$ at the temperature 400°C has the rate constant $k = 2.0 \times 10^{-4}$ sec^{-1}. What percentage of A_2B_2 is decomposed on heating for 900 seconds? (Antilog 0.0781 = 1.197) (Comptt. All India 2013)
Answer: Since the reaction is of the first order

$$\therefore \quad k = \frac{2.303}{t}\log\frac{a}{a-x} \qquad \log\frac{100}{x} = 0.781$$

Given : $k = 2.0 \times 10^{-4}$ sec^{-1}, $t = 900$ sec
Substituting these values, we get

$$2.0 \times 10^{-4} = \frac{2.303}{900}\log\frac{a}{a-x}$$

$$\Rightarrow \quad \log\frac{a}{a-x} = \frac{2.0\times10^{-4}\times900}{2.303}$$

$$\Rightarrow \quad \log\frac{a}{a-x} = 0.0781$$

$$\Rightarrow \quad \frac{a}{a-x} = \text{antilog } (0.0781) = 1.197$$

$$\Rightarrow \quad a = 1.197\,a - 1.197\,x$$

$$\Rightarrow \quad 0.197\,a = 1.197\,x$$

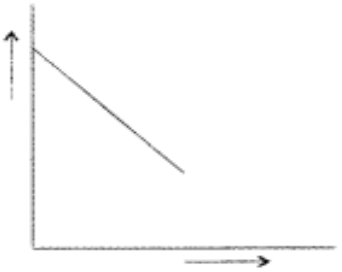
$$\therefore \quad \frac{x}{a} = \frac{0.197}{1.197} = 0.1645$$

$$\therefore \quad \%\text{ decomposed} = 0.1645 \times 100 = \mathbf{16.45\%}$$

Question 23.
Define the following terms :
(a) Pseudo first order reaction.
(b) Half life period of reaction ($t_{1/2}$). (Delhi 2014)
Answer:

(a) Those reactions which are not truly of the first order but under certain conditions become first order reactions are called pseudo first order reaction.
(b) The time taken for half of the reaction to complete is called half-life period.

Question 24.
For a chemical reaction R → P, the variation in the f concentration (R) vs. time (f) plot is given as
(i) Predict the order of the reaction.
(ii) What is the slope of the curve? (All India 2014)



Answer:
(i) It is zero order reaction.
(ii) Slope of the curve = -K

Question 25
Derive integrated rate equation for rate constant of a first order reaction. (Comptt. All India 2017)
Answer:
In a first order reaction, the rate of reaction, is directly proportional to the concentration of the reactant.
Let us consider the reaction,
A → Products
The instantaneous reaction rate can be expressed as:

$$\frac{-d[A]}{dt} = K[A] \qquad [K = \text{rate constant})$$

$$\frac{-d[A]}{[A]} = Kdt \qquad \ldots(i)$$

On integrating equation (*i*)

$$-\int \frac{d[A]}{[A]} = K\int dt$$

or $$-ln[A] = Kt + I \qquad \ldots(ii)$$

where, I = Integration constant

If t = 0 and [A] = $[A]_0$, where $[A]_0$ is the initial concentration of the reactant.
Then equation (ii) becomes
$-\ln[A]_0 = I$ ……. (iii)
Substitute the value of I in equation (ii)
$-\ln[A] = Kt - \ln[A]$
$\ln[A]_0 - \ln[A] = Kt$

$$ln\frac{[A]_0}{[A]} = Kt$$

or $$K = \frac{1}{t} ln \frac{[A]_0}{[A]}$$

$$K = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$$

This is called integrated rate equation for the first order reaction

Question 26.
(i) What is the order of the reaction whose rate constant has same units as the rate of reaction?

(ii) For a reaction A + H_2O → B; Rate ∝ [A],
What is the order of this reaction? (Comptt. All India 2017)
Answer:
(i) The reaction whose rate constant has same units as the rate of reaction, will have zero order of reaction.
(ii) The reaction A + H_2O → B Rate ∝ [A]
The order of this reaction will be pseudo first order reaction as the rate of reaction depends only on concentration of A only.

Question 27.
For a decomposition reaction the values of rate constant k at two different temperatures are given below :
$k_1 = 2.15 \times 10^{-8}$ L mol^{-1} s^{-1} at 650 K
$k_2 = 2.39 \times 10^{-7}$ L mol^{-1} s^{-1} at 700 K
Calculate the value of activation energy for this reaction.(R = 8.314 J K^{-1} mol^{-1}) (All India 2009)
Answer:
Given: $k_1 = 2.15 \times 10^{-8}$ L mol^{-1} s^{-1}, $T_1 = 650$ K
$k_2 = 2.39 \times 10^{-7}$ L mol^{-1} s^{-1}, $T_2 = 700$ K
R = 8.314 J K^{-1} mol^{-1} E_a =?

$$\text{According to formula : } \log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

$$\text{or} \quad \log \frac{2.39 \times 10^{-7}}{2.15 \times 10^{-8}} = \frac{E_a}{2.303 \times 8.314}\left[\frac{700 - 650}{700 \times 650}\right]$$

$$\text{or} \quad \log 1.111 \times 10 = \frac{E_a}{19.147}\left[\frac{50}{455000}\right]$$

$$\text{or} \quad \log 1.111 + \log 10 = \frac{E_a}{19.147} \times \frac{50}{455000}$$

$$\text{or} \quad 0.0457 + 1 = \frac{E_a}{19.147} \times \frac{1}{9100}$$

$$\text{or} \quad E_a = 1.0457 \times 19.147 \times 9100$$

$$\therefore \quad E_a = 1,82,200.36 \text{ J} = \mathbf{182.20\ KJ}$$

Question 28.
The rate constant for a first order reaction is 60 s^{-1}. How much time will it take to reduce the initial concentration of the reactant to its l/10th value? (Comptt. All India 2015)
Answer:
Given : k = 60 s^{-1}, t = ?
If initial concentration is $[A_0]$
Then $\frac{1}{10}^{th}$ of initial concentration is $\frac{[A_0]}{10}$
Using expression for first order reaction,

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

Substituting values,

$$t = \frac{2.303}{60\,s^{-1}}\log\frac{[A_0]}{[A_0]/10} \Rightarrow t = \frac{2.303}{60\,s^{-1}}\log 10$$

$$\Rightarrow t = \frac{2.303}{60\,s^{-1}} \times 1 \qquad \therefore t = 0.0383 \text{ s}$$

Question 29:

For the first order thermal decomposition reaction, the following data were obtained

$$SO_2Cl_2(g) \longrightarrow SO_2(g) + Cl_2(g)$$

Experiment	Time/ s^{-1}	Total pressure/atm
1	0	0.4
2	100	0.7

Calculate the rate constant. (Given: *log*2 = 0.301, , *log*4 = 0.6021) [ALL INDIA 2016]

$$\begin{array}{lcccc} & SO_2Cl_2 & \longrightarrow & SO_2 & + Cl_2 \\ At\ t=0 & 0.4 & & 0 & 0 \\ At\ t=100 & 0.4-x & & x & x \end{array}$$ [1]

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

$$0.7 = 0.4 + x$$

$$x = 0.3$$

$$K = \frac{2.303}{t}\log\frac{P_o}{2P_o - P_t}$$ [1]

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

$$= \frac{2.303}{1000}\log\frac{0.4}{0.1}$$

$$K = \frac{2.303\times 0.602}{100} = 1.38\times 10^{-2}s^{-1}$$ [1]

Question 30:

What is the effect of adding a catalyst on:(a) Activation energy (*E*a) and (b) Gibbs energy (Δ*G*) of a reaction?[ALL INDIA 2017]

(a) Catalyst provides a new reaction pathway in which a lower activation is offered. Hence, catalyst increases the rate of reaction by lowering the activation energy. **[1/2]**

(b) Gibbs free energy will remain same as for catalyzed & uncatalyzed reaction, as the equilibrium constant is not affected which is a function of Gibbs free energy. **[1/2]**

Question 31:

A reaction is of first order in reactant A and of second order in reactant B. How is the rate ofthis reaction affected when *(i)* the concentration of B alone is increased to three times *(ii)* the concentrations of A as well as B are doubled? [DELHI 2018]

(*i*) It is given that a reaction is first order in reactant A and second order in reactant B = *k*[*A*][*B*]2

Where r is the rate of reaction and k is the rate constant of the reaction

When concentration of B alone is increased three times, let the new rate be r1. **[1]**

$$\therefore\ r_1 = k[A]\ [3B]^2 = 9k\ [A]\ [B]^2 \text{ (Eq-2)}$$

Divide (Eq-2) by (Eq-1)

$$\therefore\ r_1 = 9r$$

Thus, when the concentration of B alone is increased to three times, rate of reaction increases by 9 times

(*ii*) When concentration of A and B are doubled, let the new rate be r2, **[1]**

$$\therefore\ r_2 = k[2A]\ [2B]^2 = 8k[A]\ [B]^2$$

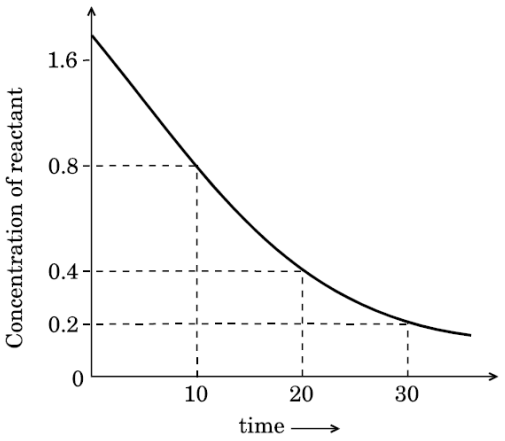
$$\therefore\ r_2 = 8r$$

Thus, when the concentration of A and B are doubled, the rate of reaction increases by 8 times.

Question 32:
The decomposition of NH3 on platinum surface is zero order reaction.If rate constant (k)is 4 x 10-3 Ms-1,how long will it take to reduce the initial concentration of NH3 from 0.1 M to 0.064 M?[CBSE 2019]
For a zero order reaction,
$K=1/t\ ([A]_0-[A])$
$t=1 \times (0.1-0.064)/4 \times 10^{-3}$
=9 s

Question 33:
For a reaction $2H_2O_2$----------→$2H_2O+O_2$ the proposed mechanism is as given below:
(i) $H_2O_2 + I^-$ --------→$H_2O + IO^-$(slow)
(ii) $H_2O_2+IO^-$ ---------→$H_2O + I^- + O_2$(fast)
(A)Write rate law for the reaction
(B)Write the overall order of reaction
(c) Out of steps(1) and (2),which one is the rate determining step? [CBSE 2019]
Ans:
(A)Rate=$k[H_2O][I^-]$
(B) Overall order of reaction is 2
(c)Step (1) being the slow step is the rate determining step of the reaction.

Question 34:
Analyse the given graph, drawn between concentration of reactant vs. time.



(a) Predict the order of reaction.
(b) Theoretically, can the concentration of the reactant reduce to zero after infinite time ? Explain. [CBSE 2020]

Ans: (a) 1 st order
(b) No, due to exponential relation / the curve never touches the x-axis.

Question 35:How will the rate of the reaction be affected when (a) Surface area of the reactant is reduced, (b) Catalyst is added in a reversible reaction, and (c) Temperature of the reaction is increased ?[CBSE 2020]
Answer: (a) Decreases. (b) Increases (c) Increases

Question 36:
Define rate of reaction. Write two factors that affect the rate of reaction.[CBSE 2022]
Ans: Rate of reaction :
Rate of chemical reaction is equal to change in concentration of reactant or product in unit time.
Two factors :
(1) Concentration of reactants
(2) Temperature of reactants

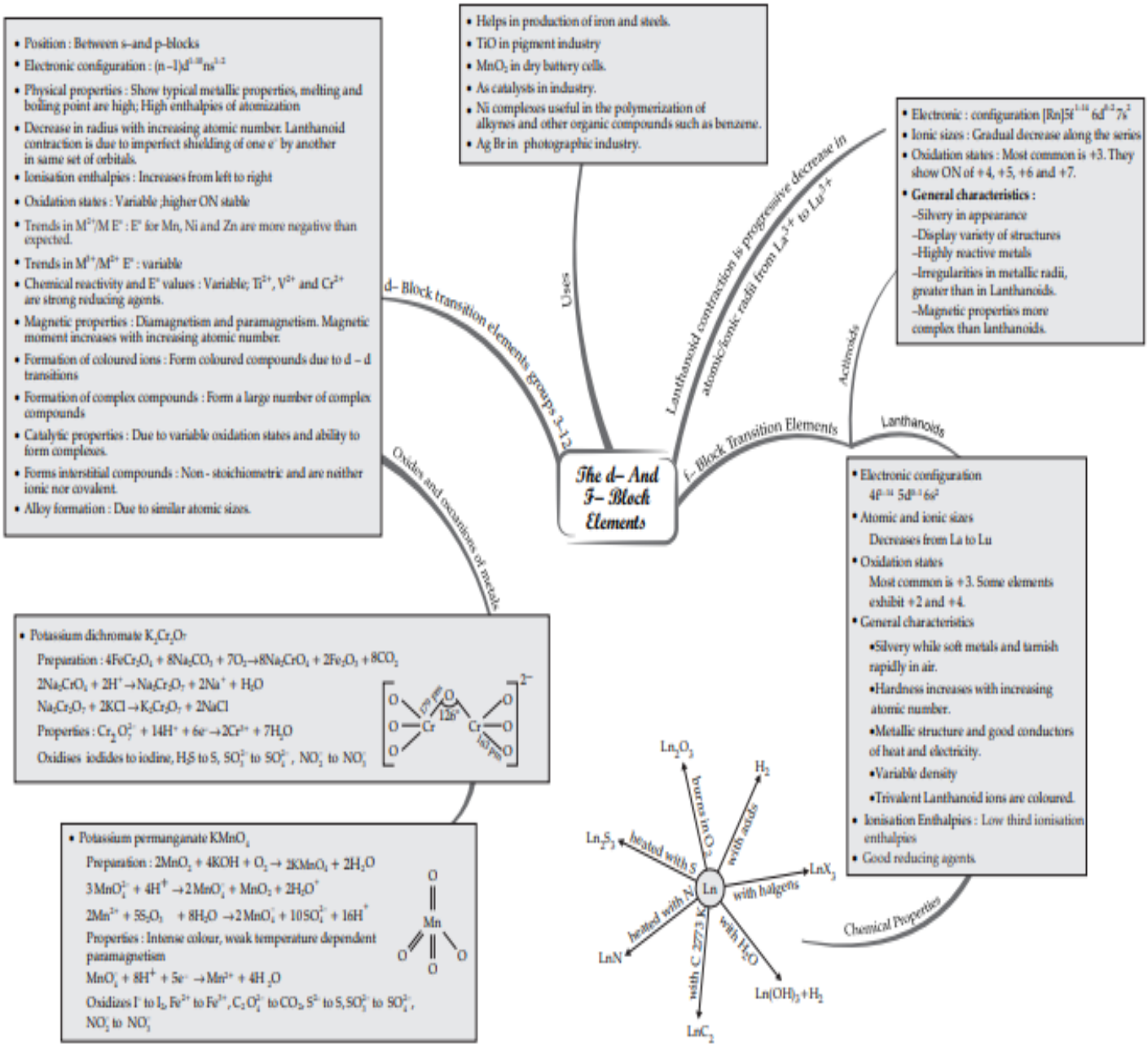
CHAPTER 8

THE d AND f BLOCK ELEMENTS

GIST OF THE LESSON

- Transition elements
- Configurations of d block elements
- General characteristics
- Metallic Character
- Melting point
- Atomic size and ionic size
- Density
- Ionisation Enthalpies
- Oxidation states
- Standard electrode potentials and trends in oxidation states
- Stability of higher oxidation states
- Chemical reactivity and electrode potentials
- Magnetic properties
- Formation of coloured compounds
- Formation of complex compounds
- Catalytic properties
- Formation of interstitial compounds
- Alloy formation
- Inner transition elements
- General properties of f-block elements
- Oxidation state of lanthanoids
- Uses of d & f block elements
- Preparation and properties of $K_2Cr_2O_7$ and $KMnO_4$
- Chemical reactivity of Lanthanoids and Actinoids- Electronic configuration, oxidation states and comparison with lanthanoids.

MIND MAP : LEARNING MADE SIMPLE CHAPTER - 8



MULTIPLE CHOICE QUESTIONS

1. Transition elements form alloys easily because they have

(a) Same atomic number
(b) Same electronic configuration
(c) Nearly same atomic size
(d) None of the above

Ans (c) Nearly same atomic size

2. **When manganese dioxide is fused with KOH in air. It gives**
   (a) potassium permanganate
   (b) potassium manganate
   (c) manganese hydroxide
   (d) Mn_3O_4.

   Ans (b) potassium manganate

3. **Which of the following are d-block elements but not regarded as transition elements?**
   (a) Cu, Ag, Au
   (b) Zn, Cd, Hg
   (c) Fe, Co, Ni
   (d) Ru, Rh, Pd

   Ans.(b) Zn, Cd, Hg

4. **The property which is not characteristic of transition metals is**
   (a) variable oxidation states.
   (b) tendency to form complexes.
   (c) formation of coloured compounds.
   (d) natural radioactivity.

   Ans.(d) natural radioactivity.

5. **Lanthanoid contraction is due to increase in**
   (a)atomic number
   (b)effective nuclear charge
   (c)atomic radius
   (d)valence electrons

   Ans. (b)effective nuclear charge

6. **Acidified potassium dichromate reacts with potassium iodide and oxidises it to I_2. What is the oxidation state of chromium in the products of the reaction?**
   (a) +4
   (b) +6
   (c) +3
   (d) +2

   Ans.c) +3

7. **In KMnO4 oxidation number of Mn is**
   (a) +2
   (b) + 4
   (c) + 6
   (d) + 7
   Ans. (d) + 7
8. **Which one of the following is diamagnetic ion?**

(a) Co2+
(b) Ni2+
(c) Cu2+
(d) Zn2+

Ans.(d) Zn2+

9. Zr and Hf have almost equal atomic and ionic radii because of
(a) diagonal relationship
(b) lanthanoid contraction
(c) actinoid contraction
(d) belonging to the same group

Ans.(b) lanthanoid contraction

10. Which of the following is likely to form white salts?
(a) Cu2+
(b) Sc3+
(c) Ti3+
(d) Fe3+

Ans (b) Sc3+

11. Which one of the following characteristics of the transition metals is associated with higher catalytic activity?
(a) High enthalpy of atomisation
(b) Paramagnetic behaviour
(c) Colour of hydrate ions
(d) Variable oxidation states

Ans.(d) Variable oxidation states

12. Colour of transition metal ions are due to absorption of some wavelength. This results in
(a) d-s transition
(b) s-s transition
(c) s-t/transition
(d) d-d transition

Ans.(d) d-d transition

13. Which of the following pairs of ions have the same electronic configuration?
(a) $Cu^{2+,}$ Cr^{2+}
(b) $Fe^{3+,}$ Mn^{2+}
(c) Co^{3+}, Ni^{3+}
(d) $Sc^{3+,}$ Cr^{3+}

Ans. (b) Fe^{3+}, Mn^{2+}

14. Anomalous electronic configuration in the 3d series are of

(a) Cr and Fe
(b) Cu and Zn
(c) Fe and Cu
(d) Cr and Cu

Ans d) Cr and Cu

15. Which metal has lowest melting point?

(a) Cs
(b) Na
(c) Hg
(d) Sn

Ans (c) Hg

ASSERTION REASON TYPE QUESTIONS

I

1. **Read the passage given below and answer the following questions:**
Transition elements are elements that have partially filled d-orbitals. The configuration of these elements corresponds to $(n - 1)d^{1-10} ns^{1-2}$. It is important to note that the elements mercury, cadmium and zinc (Ire not considered transition elements because of their electronic configurations, which corresponds to $(n - 1)d^{1-10} ns^{2}$.
Some general properties of transition elements are :
These elements can form coloured compounds and ions due to d-d transition;
These elements-.exhibit many oxidation states;
A large variety of ligands can bind themselves to these elements, due to this, a wide variety of stable complexes formed by these ions. The boiling and melting point of these elements are high. These elements have a large ratio of charge to the radius.
In these questions (i-iv), 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**: Tungsten has very high melting point. **Reason**: Tungsten is a covalent compound. Ans: (c): Tungsten is a transition element and is very hard due to high metallic bonding.
2	**Assertion:** Zn, Cd and Hg are normally not considered transition metals **Reason:** d-Orbitals in Zn, Cd and Hg elements are completely filled, hence these

		metals do not show the general characteristics properties of the transition elements Ans: a
	3	**Assertion:** Copper metal gets readily corroded in acidic aqueous solution such as HCl and dil. H_2SO_4 **Reason:** Free energy change for this process is positive. Ans: d Non-oxidising acids (HCI and dil. H_2SO_4) do not have any effect on copper. However, they dissolve the metal in presence of air. As it is a non-spontaneous process so, ΔG cannot be -ve.
	4	**Assertion**: Separation of Zr and Hf is difficult. **Reason**: Because Zr and Hf lie in the same group of the periodic table. Ans: b

II **Read the passage given below and answer the following questions:**

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

In these questions (i-iv), 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**: Cu^{2+} iodide is not known. **Reason** : Cu^{2+} oxidises I^- to iodine. Ans.(a)
2	**Assertion**: Actinoids form relatively less stable complexes as compared to lanthanoids. **Reason**: Actinoids can utilize their 5f orbitals along with 6d orbitals in bonding but lanthanoids do not use their 4f orbital for bonding

		Ans (d)
	3	**Assertion**: Cu cannot liberate hydrogen from acids. **Reason**: Because it has positive electrode potential. Ans(a)
	4	**Assertion**: The highest oxidation state of osmium is +8. **Reason**: Osmium is a 5d-block element Ans(b)

SHORT ANSWERS TYPE QUESTIONS

Question 1.
How would you account for the increasing oxidising power in the series:
$V0_2^+ < Cr_20_7^{2-} < Mn0_4^-$?
Answer:
This is due to the increasing stability of the lower species to which they are reduced.

Question 2.
Which metal in the first transition series exhibits a $^+1$ oxidation state most frequently and why?
Answer: Copper has electronic configuration 3d104s1. It can easily lose one (4s1) electron to give stable 3d10 configuration.

Metal ion	Magnetic moment (BM)
Sc_3^+	0.00
Cr_2^+	4.90
Ni_2^+	2.84
Ti_3^+	1.73

Question 3.
The magnetic moments of a few transition metal ions are given below:
(atomic no. Sc = 21, Ti = 22, Cr = 24, Ni = 28)
Which of the given metal ions:
(i) has the maximum number of unpaired electrons?
Answer:
Cr^{2+}

(ii) forms colourless aqueous solution?
Answer:
Sc^{3+}

(iii) exhibits the most stable +3 oxidation state?
Answer:
Sc^{3+}

Question 4.
Based on the data, arrange Fe^{2+}, Mn^{2+} and Cr^{2+} in the increasing order of stability of +2 oxidation state: $E°_{Cr^{3+}/Cr^{2+}} = -0.4$ V, $E°_{Mn^{3+}/Mn^{2+}} = 1.5$ V, $E°_{Fe^{3+}/Fe^{2+}} = 0.8$ V
Answer:
As the value of reduction potential increases, the stability of +2 oxidation state increases. Therefore, correct order of stability is $Cr^{3+} \mid Cr^{2+} < Fe^{3+} \mid Fe^{2+} < Mn^{3+} \mid Mn^{2+}$.

Question 5.
(i) Name the element showing the maximum number of oxidation states among the first series of transition metals from Sc (Z = 21) to Zn (Z = 30).
Answer:
Manganese

(ii) **Name the element which shows only +3 oxidation state**.
Answer:
Scandium

Question 6.
Identify the oxo anion of chromium which is stable in an acidic medium.
Answer:
$Cr_2O_7^{2-}$

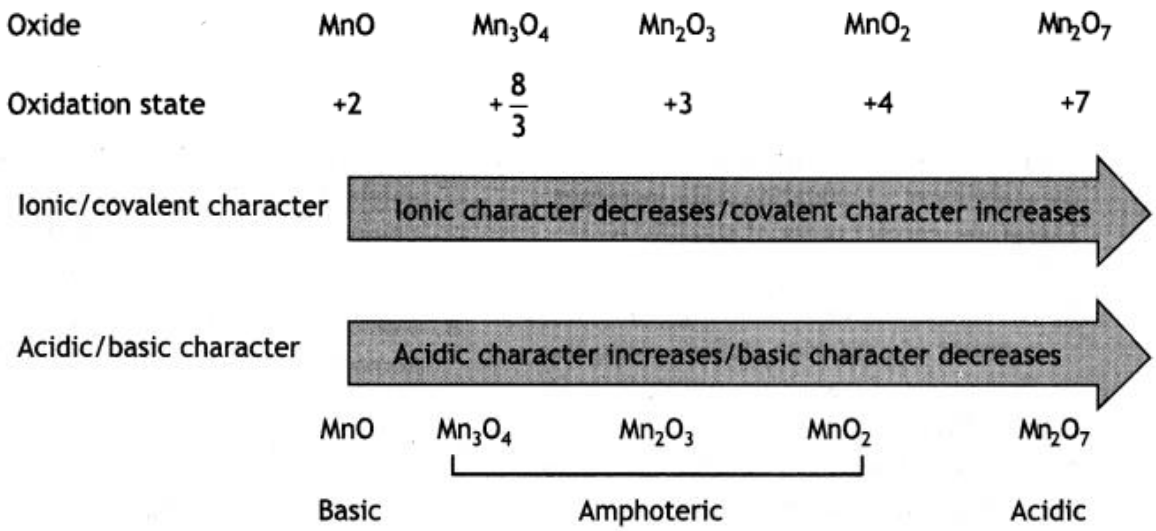
Question 7.
Actinoid contraction is greater from element to element than lanthanoid contraction. Why?
Answer:
This is because of relatively poor shielding by 5f electrons in actinoids in comparison with shielding of 4f electrons in lanthanoids.

Question 8.
Assign reasons for the following:
(i) Cu(I) is not known in an aqueous solution.
Answer:
Because of the Lesser hydration enthalpy of Cu(I), It Is unstable in an aqueous solution and therefore, It undergoes disproportionation.

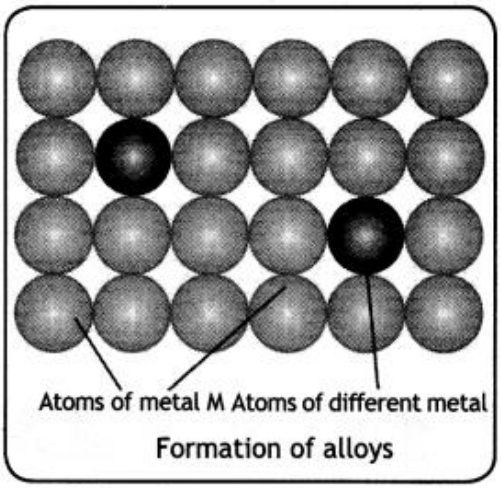
(ii) **Actinoids exhibit a greater range of oxidation states than lanthanoids**.
Answer:

Lanthanoids show Limited number of oxidation states, such as + 2, + 3 and + 4 + 3 is the principal oxidation state). This is because of the large energy gap between 5d and 4f subshells. On the other hand, actinoids also show a principal oxidation state of + 3 but show a number of other oxidation states also. For example, uranium (Z = 92) exhibits oxidation states of + 3, + 4, + 5, + 6 and + 7 and neptunium (Z = 94) shows oxidation states of + 3, +4, + 5, + 6 and + 7. This is because of the small energy difference between 5f and 6d orbitals.

Question9.
Give reasons:
(a) MnO is basic whereas Mn_2O_7 is acidic in nature.
Answer:
When a metal is in a high oxidation state, its oxide Is acidic and when a metaL is in a low oxidation state its oxide is basic.
The oxides of manganese have the following behavior:



(b) **Transition metals form alloys**.
Answer:
The transition metals are quite similar in size and, therefore, the atoms of one metal can substitute the atoms of other metal in its crystal lattice. Thus, on cooling a mixture solution of two or more transition metals, solid alloys are formed which is shown in Fig.



Formation of alloys

Question10.
Explain why the E^{θ} value for the Mn^{3+}/Mn^{2+} couple is much more positive than that for Cr^{3+}/Cr^{2+} or Fe^{3+}/Fe^{2+}.
Answer:
Mn^{2+} has 3d5 electronic configuration. It is stable because of the half-filled configuration of the d-subshell. Therefore, Mn has a very high third ionization enthalpy for the change from d5 to d4 and it is responsible for a much more positive E^{θ} value for Mn^{3+}/Mn^{2+} couple in comparison to Cr^{3+}/Cr^{2+} and Fe^{3+}/ Fe^{2+} couples.

Question 11.
Complete the following chemical equations:
(i) $Cr_2O_7^{2+} + H^+ + I^- \rightarrow$
Answer:
$Cr_2O_7^{2+} + 6I^- + 14H^+ \rightarrow 2Cr^{3+} + 3I_2 + 7H_2O$

(ii) **$MnO_4^- + NO_2^- + H^+ \rightarrow$**
Answer:
$2MnO_4^- + 5N0_2^- + 6H+ \rightarrow 2Mn2+ + 5NO_3^- + 3H_2O$

Question 12
Out of Fe and Cu, which has a higher melting point and why?
Answer: Fe has a higher melting point. The metallic bond is formed due to the interaction of electrons in the outermost orbitals. The strength of bonding is related to the number of unpaired electrons. Fe has more unpaired electrons leading to stronger metallic bonding. So, it has a higher melting point.

Question13.
How would you account for the following:
(i) Cr^{2+} is reducing in nature while with the same d-orbital configuration (d^4), Mn^{3+} is an oxidizing agent.
Answer:
Cr^{2+} is reducing as its configuration changes from d^4 to d^3, the latter having a half-filled t_{2g} level. On the other hand, the change from Mn^{3+} to Mn^{2+} results in the half-filled (d^5) configuration which has extra stability.

(ii) In a transition series of metals, the metal which exhibits the greatest number of oxidation states occurs in the middle of the series.
Answer:
This is because, in the middle of the transition series, the maximum number of electrons are available for sharing with others. The small number of oxidation states at the extreme left side is due to the lesser number of electrons to lose or share. On the other hand, at the extreme right-hand side, due to a large number of electrons, only a few orbitals are available in which the electrons can share with others for higher valence.

Question14.
When MnO_2 is fused with KOH in the presence of KNO_3 as an oxidizing agent, it gives a dark green compound (A). Compound (A) disproportionates in an acidic solution to give a purple

compound (B). An alkaline solution of compound (B) oxidizes Kl to compound (C), whereas an acidified solution of compound (B) oxidizes Kl to (D). Identify (A), (B), (C), and (D).

Answer:

When MnO_2 is fused with KOH in the presence of KNO_3, as an oxidizing agent, it gives a dark green compound (A).

$$MnO_2 + 2KOH + KNO_3 \longrightarrow \underset{\substack{\text{(A)}\\\text{Green mass}\\\text{Potassium manganate}}}{K_2MnO_4} + KNO_2 + H_2O$$

$$3K_2MnO_4 + 4H^+ \longrightarrow 2KMnO_4 + MnO_2 + 2H_2O + 4K^+$$

(B) Purple Potassium permanganate

$$\underset{\text{(B)}}{2KMnO_4} + KI + H_2O \longrightarrow 2MnO_2 + 2KOH + \underset{\text{(C)}}{KIO_3}$$

$$\underset{\text{(B)}}{2KMnO_4} + 10KI + 8H_2SO_4 \longrightarrow 6K_2SO_4 + 2MnSO_4 + 8H_2O + \underset{\text{(D)}}{5I_2}$$

A: K_2MnO_4 , B: $KMnO_4$

C: KIO_3 , D: I_2

Question 15

Manganese exhibits the highest oxidation state of +7 among the 3d-series of transition elements.

Answer:

Manganese has the electronic configuration [Ar] $3d^5\ 4s^2$. It can lose seven electrons due to the participation of 3d and 4s electrons and therefore, exhibits the highest oxidation state of +7 in its compounds.

LONG ANSWER TYPE QUESTIONS [5 Marks]

Question 1

[i]What happens, when [a] manganate ion reacts with thiosulphate? [b] dichromate ion reacts with iron in presence of acid?

[ii] Explain the following trends in the properties of the members of the transition elements.

[a] Mn^{2+} is more stable than Fe^{2+} towards oxidation to +3 state.

[b] The enthalpy of atomization is lowest for Zn in 3d-seriesof the transition elements.

[c] The E^0 value for the Mn^{3+}/Mn^{2+} couples much more positive than that forCr^{3+}/Cr^{2+} couple.

Ans [i][a] Manganate ion reacts with thiosulphate

$8MnO_4^-[aq]+3S_2O_3^{2-}[aq]+H_2O \longrightarrow 8MnO_2+ +6SO_4^{2-} +2OH^-$

[b] Dichromate ion reacts with iron in the presents of acid

$Cr_2O_7^{2-}[aq]+6Fe^{2+}[aq]+14\ H^+[aq] \longrightarrow 2Cr^{3+} +6Fe^{3+} +7H_2O$

[ii] [a] Electronic configuration of Mn^{2+} =[Ar] $3d^5$ Electronic configuration of Fe^{2+} =[Ar]$3d^6$ Mn^{2+} having half filled d orbitals will be more stable than Fe^{2+} as it has partially filled d orbitals

[b]Zinc has completely filled d orbitals, which limits its tendency to form metallic bonds. Thus it

requires least enthalpy to get atomized.
[c] $Mn^{3+}[3d^4]$ is less stable than $Mn^{2+}[3d^5]$ because Mn^{2+} has stable half filled configuration, Cr^{3+} has stable $3d^3[t_2g^3]$ configuration, therefore Cr^{3+} cannot be reduced toCr^{2+}.

Question 2

Assign reasons for the following:

a) The enthalpies of atomization of transition elements are high.
b) The transition metals and many of their compounds act as good catalysts.
c) There is a gradual decrease in the atomic sizes of transition elements in a series with increasing atomic numbers.
d) The transition elements have a great tendency for complex formation.
e) Transition metals generally form coloured compounds.

a) This is because transition elements have strong metallic bonds as they have a large number of unpaired electrons, therefore they have greater interatomic overlap.
b) The catalytic activity of transition metals is attributed to the following reasons-
i) Because of their variable oxidation state, transition metals form unstable intermediate compounds and provide a new path with the lower activation energy for the reaction.
ii) In some cases, the transition metal provides a suitable large surface area with free valencies on which reactants are adsorbed.
c) There is a gradual decrease in the atomic sizes of transition elements in a series with increasing atomic numbers due to poor shielding effects of the d-electrons, the net electrostatic attraction between the nucleus and the outermost electrons increases
d) orbitals of suitable energy, the small size of cations, and higher nuclear charge.
e) Due to the presence of unpaired electrons in d-orbitals which undergoes a d-d transition.

Question 3

a) **Complete the following chemical reaction equations** :

(*i*) $MnO_4^-(aq) + C_2O_4^{2-}(aq) + H^+(aq) \longrightarrow$

(*ii*) $Cr_2O_7^{2-}(aq) + Fe^{2+}(aq) + H^+(aq) \longrightarrow$

(b) Explain the following observations about the transition/inner transition elements :
(i) There is in general an increase in density of element from titanium (Z=22) to copper (Z=29).
(ii) There occurs much more frequent metal-metal bonding in compounds of heavy transition elements (3rd series).
(iii) The members in the actinoid series exhibit a larger number of oxidation states than the corresponding members in the lanthanoid series.

Answer:
(a)

(*i*) $2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 8H_2O + 10CO_2$

(*ii*) $Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$

(b) (i) As we move along a transition series from left to right, the atomic radii decrease due to

increase in nuclear charge. Hence, the atomic volume decreases. At the same time, atomic mass increases from Ti to Cu, therefore density increases.
(ii) It is due to their low ionization energies and variable oxidation state.
(iii) Because of very small energy gap between 5f, 6d and 7s subshells all their electrons can take part in
bonding and shows variable oxidation states

Question 4

4 (a) **Complete the following chemical equations for reactions** :

(i) $MnO_4^-(aq) + S_2O_3^{2-}(aq) + H_2O(l) \longrightarrow$

(ii) $Cr_2O_7^{2-}(aq) + H_2S(g) + H^+(aq) \longrightarrow$

(b) Give an explanation for each of the following observations :
(i) The gradual decrease 'n' size (actinoid contraction) from element to element is greater among the actinoids than that among the lanthanoids (lanthanoid contraction).
(ii) The greatest number of oxidation states are exhibited by the members in the middle of a transition series.
(iii) With the same d-orbital configuration d^4, Cr^{2+} ion is a reducing agent but Mn^{3+} ion is an oxidising agent.

Ans(a)

(i) $8MnO_4^- + 3S_2O_3^{2-} + H_2O \longrightarrow$ ($S_2O_3^{2-}$: Thiosulphate ion)
$8MnO_2 + 6SO_4^{2-} + 2OH^-$

(ii) $Cr_2O_7^{2-} + 3H_2S + 8H^+ \longrightarrow 2Cr^{3+} + 7H_2O + 3S$

(b) (i) The actinoid contraction is greater than lanthanoid contraction due to poorer shielding of 5f electrons as they are extended in space beyond 6s and 6p orbitals whereas 4f orbitals are buried deep inside the atom.
(ii) Due to presence of more unpaired electrons and use of all 4s and 3d electrons in the middle of series.
(iii) Cr^{2+} has the configuration $3d^4$ which easily changes to d^3 due to stable half filled t_2g orbitals. Therefore Cr^{2+} is reducing agent. While Mn^{2+} has stable half filled d^5 configuration. Hence Mn^{3+} easily changes to Mn^{2+} and acts as oxidising agent.

Question 5

[a] When chromite ore $FeCr_2O_4$ is fused, with NaOH in presence of air, a yellow-colored compound (A) is obtained, which on acidification with dilute sulphuric acid gives a compound (B). Compound (B) on reaction with KCI forms an orange colored crystalline compound (C).
(i) Write the formulae of the compounds (A), (B), and (C).
(ii) Write one use of the compound (C).

[b] Complete the following chemical equations:
(i) $8MnO_4^- + 3S_2O_3^{2-} + H_2O \rightarrow$
(ii) $Cr_2O_7^{2-} + 3Sn^{2+} + 14H^+ \rightarrow$
Answer:

$$4FeCr_2O_4 + 16NaOH + 7O_2 \longrightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8H_2O$$

(A)

Yellow coloured

$$2Na_2CrO_4 + H_2SO_4 \rightarrow Na_2Cr_2O_7 + H_2O + Na_2SO_4$$

(B)

$$Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$$

(C)

(ii) Potassium dichromate (C) is used as a powerful oxidizing agent in redox titrations in the laboratories.

[b] (i) $8MnO_4^- + 3S_2O_3^{2-} + H_2O \rightarrow 8MnO_2 + 6SO_4^{2-} + 2OH^-$

(ii) $Cr_2O_7^{2+} + 3Sn^{2+} + 14H^+ \rightarrow 2Cr3+ + 3Sn^{4+} + 7H_2O$

CASE BASED QUESTIONS

I. Read the following paragraph and answer to the questions given below.

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

1	**Name a member of the lanthanide series which is well known to exhibit +4 oxidation state.** (a) Cerium (X=58) (b) Europium (Z=63) (c) Lanthanum (Z=57) (d) Gadolinium (Z=64) Ans(iii) a
2	**Identify the incorrect statement among the following.** (a) Lanthanide contraction is the accumulation of successive shrinkages. (b) the different radii of Zr and Hf due to consequences of the lanthanide contraction. (c) Shielding power of 4f electrons is quite weak. (d) There is a decrease in the radii of the atoms or ions proceeds from La to Lu Ans(iv) b
3	Out of the following elements, identify the one which does not show variable oxidation state. (a) Cr (b) Co (c) Zn Ans (c)Zn
4	What is the shape of chromate ions? a) octahedral b) tetrahedral (c) square planar (d) pyramidal Ans: tetrahedral
5	What is the shape of permanganate ions? a) octahedral b) tetrahedral (c) square planar (d) pyramidal Ans: tetrahedral

II **Read the passage given below and answer the following questions:**

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

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

1	Which of the following characteristics of transition metals is associated with higher catalytic activity? **(a) High enthalpy of atomisation** **(b) Variable oxidation states** **(c) Paramagnetic behaviour** **(d) Colour of hydrated ions** **Ans:(b) Variable oxidation states**
2	Transition elements form alloys easily because they have **(a) same atomic number** **(b) same electronic configuration** **(c) nearly same atomic size** **(d) same oxidation states.** **Ans:(c) nearly same atomic size**
3	Which one of the following outer orbital configurations may exhibit the largest number of oxidation states? **(a) $3d^5 4s^1$** **(b) $3d^5 4s^2$** **(c) $3d^2 4s^2$** **(d) $3d^3 4s^2$** Ans: **(b) $3d^5 4s^2$**
4	The oxidation state of vanadium in V_2O_5 is **(a) +5/2** (b) **+7** (c) **+5** (d) +6 Ans: +5
5	Predict magnetic behaviour of manganate ion? **(a) ferromagnetic** **(b) diamagnetic** **(c) paramagnetic**

			Ans: **paramagnetic**	

CBSE BOARD QUESTIONS

1. What is meant by 'lanthanoid contraction' ? (1)

2. How would you account for the following :
   (a) Cr^{2+} is reducing in nature while with the configuration (d^4) Mn^{3+} is an oxidising agent.
   (b) In a transition series of metals, the metal which exhibits the greatest number of oxidation states occurs in the middle of the series.

3. Complete the following chemical equation :

   i. $Cr_2O_7^{-2}$ (aq) + Fe^{2+} (aq) + H^+ (aq) →

   OR

   State reasons for the following :

   i. Cu (I) ion is not stable in an aqueous solution.

   ii. Unlike Cr^{3+}, Mn^{2+}, Fe^{3+} and the subsequent other M^{2+} ions of the 3d series of elements, the 4d and the 5d series metals generally do not form stable. cationic species.

4. What are the transition elements? Write two characteristics of the transition elements.

5. Identify the following :
   (i) Transition metal of 3d series that exhibits the maximum number of oxidation states.
   (ii) An alloy consisting of approximately 95% lanthanoid metal used to produce bullet, shell and lighter flint.

6. When MnO_2 is fused with KOH in the presence of KNO_3 as an oxidizing agent, it gives a dark green compound (A). Compound (A) disproportionates in acidic solution to give purple 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).

7. Complete and balance the following chemical equations :

   (a) $MnO_4^- + H_2O + I^- \longrightarrow$

   (b) $MnO_4^- + H^+ + I^- \longrightarrow$

8. (a) How would you account for the following:

(i) Actinoid contraction is greater than lanthanoid contraction.

(ii) Transition metals form coloured compounds.

(b) Complete the following equation :

$$2\ MnO_4^- + 6H^+ + 5NO_2^- \longrightarrow$$

9. When chromite ore $FeCr_2O_4$ is fused with NaOH in presence of air, a yellow coloured compound (A) is obtained which on acidification with dilute sulphuric acid gives a compound (B). Compound (B) on reaction with KC*l* forms a orange coloured crystalline compound (C).

(i) Write the formulae of the compounds (A), (B) and (C).

(ii) Write one use of compound (C).

OR

Complete the following chemical equations :

(i) $8MnO_4^- + 3S_2O_3^{2-} + H_2O \rightarrow$

(ii) $Cr_2O_7^{2-} + 3Sn^{2+} + 14H^+ \rightarrow$

10. Give reasons :

(i) Mn shows the highest oxidation state of +7 with oxygen but with fluorine it shows the highest oxidation state of +4.

(ii) Transition metals show variable oxidation states.

(iii) Actinoids show irregularities in their electronic configurations.

11. Give reasons for the following :

(i) Transition elements and their compounds act as catalysts.

(ii) E° value for $(Mn^{2+}|Mn)$ is negative whereas for $(Cu^{2+}|Cu)$ is positive.

(iii) Actinoids show irregularities in their electronic configuration.

12. (a) **Account for the following :**

(i) **Transition metals show variable oxidation states.**

(ii) **Zn, Cd and Hg are soft metals.**

(iii) **E° value for the Mn^{3+}/Mn^{2+} couple is highly positive (+ 1·57 V) as compared to Cr^{3+}/Cr^{2+}.**

(b) Write one similarity and one difference between the chemistry of lanthanoid and actinoid elements.

OR

(a) Following are the transition metal ions of 3d series :

Ti^{4+}, V^{2+}, Mn^{3+}, Cr^{3+}

(Atomic numbers : Ti = 22, V = 23, Mn = 25, Cr = 24)

Answer the following :

(i) Which ion is most stable in an aqueous solution and why ?

(ii) Which ion is a strong oxidising agent and why ?

(iii) Which ion is colourless and why ?

(b) Complete the following equations :

(i) $2\ MnO_4^- + 16\ H^+ + 5\ S^{2-} \longrightarrow$

(ii) $KMnO_4 \xrightarrow{heat}$

13. (a) Complete the following equations :

(i) $Cr_2O_7^{2-} + 2OH^- \rightarrow$

(ii) $MnO_4^- + 4H^+ + 3e^- \rightarrow$

(b) Account for the following :

(i) Zn is not considered as a transition element.

(ii) Transition metals form a large number of complexes.

(iii) The E^0 value for the Mn^{3+}/Mn^{2+} couple is much more positive than that for Cr^{3+}/Cr^{2+} couple.

OR

(i) With reference to structural variability and chemical reactivity, write the differences between lanthanoids and actinoids.

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

(iii) Complete the following equation :

$MnO_4^- + 8H^+ + 5e^- \rightarrow$

(iv) Out of Mn^{3+} and Cr^{3+}, which is more paramagnetic and why ?

(Atomic nos. : Mn = 25, Cr = 24)

14. (a) Complete the following equations :

(i) $Cr_2O_7^{2-} + 2OH^- \rightarrow$

(ii) $MnO_4^- + 4H^+ + 3e^- \rightarrow$

(b) Account for the following :

(i) Zn is not considered as a transition element.

(ii) Transition metals form a large number of complexes.

(iii) The E° value for the Mn^{3+}/Mn^{2+} couple is much more positive than that for Cr^{3+}/Cr^{2+} couple.

OR

(i) With reference to structural variability and chemical reactivity, write the differences between lanthanoids and actinoids.

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

(iii) Complete the following equation :

$MnO_4^- + 8H^+ + 5e^- \rightarrow$

(iv) Out of Mn^{3+} and Cr^{3+}, which is more paramagnetic and why ?
(Atomic nos. : Mn = 25, Cr = 24)

15. (i) Complete the following equations :

(a) $2MnO_4^- + 5SO_3^{2-} + 6H^+ \rightarrow$

(b) $Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow$

(ii) Based on the data, arrange Fe^{2+}, Mn^{2+} and Cr^{2+} in the increasing order of stability of +2 oxidation state.

$E^\circ_{Cr^{3+}/Cr^{2+}} = -0.4$ V

$E^\circ_{Mn^{3+}/Mn^{2+}} = +1.5$ V

$E^\circ_{Fe^{3+}/Fe^{2+}} = +0.8$ V

OR

Write the preparation of following :

(i) $KMnO_4$ from K_2MnO_4

(ii) Na_2CrO_4 from $FeCr_2O_4$

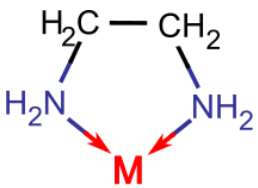
(iii) $Cr_2O_7^{2-}$ from CrO_4^{2-}

CHAPTER 9

COORDINATION COMPOUNDS

GIST OF THE LESSON

- **Co-ordination compounds or Complexes**
  Co-ordination compounds are the compounds in which the central metal atom is linked to a number of ions or neutral molecules by co-ordinate bonds, by donation of lone pairs of electrons by ions or neutral molecules to the central metal atom
  Example: $[Co(NH_3)_6]Cl_3$
  They do not dissociate into simple ions when dissolved in water.
- **Difference between coordination compound and double salt**:
  Double salt (like Mohr's salt, Potash alum) dissociates completely into simple ions when dissolved in water whereas the complex ion does not dissociate. Hence the double salt loses its identity in solution, but the complex retains its identity in solution.
- **Ligands:**
  Ions or molecules capable of donating a pair of electrons to the central atom and form a co-ordinate bond with it.
  *Unidentate ligands: Ligands bound to the metal ion through a single donor atom
  E.g. NH_3, Cl^-, H_2Oetc.
  *Didentate ligands: Ligands bound to the metal ion through two donor atoms,
  E.g. ethane-1,2-diamine, $C_2O_4^{2-}$(oxalate ion) etc.
  *Polydentate ligands: Ligands which have several donor atoms.
  E.g. EDTA (hexadentate ligand)
- **Denticity** : The number of ligating groups present in a ligand
- **Ambidentate ligand:**
  Ligands which can ligate (link) through two different atoms present in it are called ambidentate ligand.
  Example: NO_2^- can co ordinate either through nitrogen or through oxygen to a central atom
  SCN^- can co ordinate through sulphur or nitrogen atom
- **Coordination number:**
  The coordination number (CN) of a metal ion in a complex can be defined as the number of ligand donor atoms to which the metal is directly bonded.
  Example: In the complex $K_4[Fe(CN)_6]$, the coordination number of Fe is 6.
- **Chelate Ligands:**
  Di or polydentate ligand using two or more donor atoms to bind a single metal ion. eg: ethane-1,2-diamine
  Example: Ethane-1,2-diamine ($NH_2CH_2CH_2NH_2$)
  These ligands produce a ring like structure called chelate.Chelation increases the stability of complex.



- **Homoleptic complexes**
  Complexes in which metal is bound to only one kind of donor groups.Eg: $[Co(NH_3)_6]^{3+}$
- **Heteroleptic complexes**:
  Complexes in which metal is bound to more than one kind of donorgroups. For example:

$[Co(NH_3)_4Cl_2]^+$

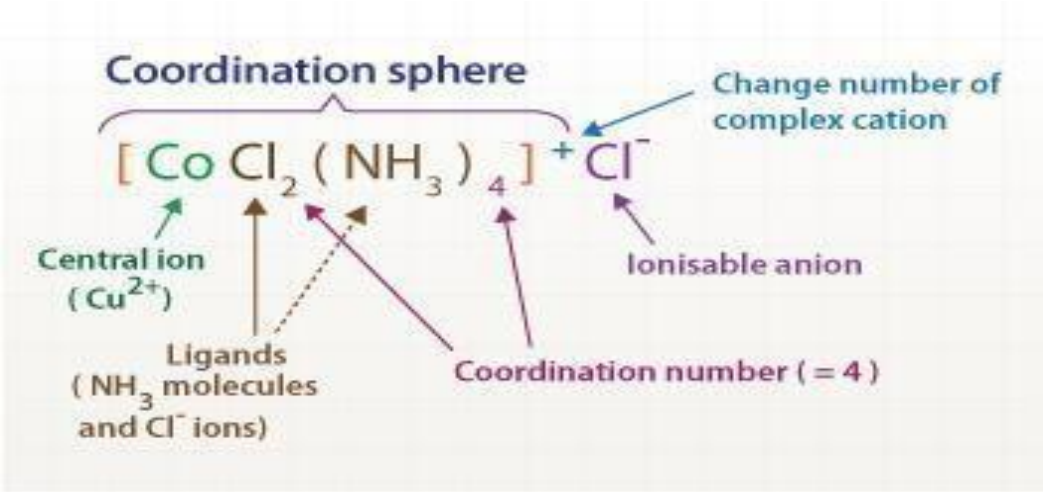
- **Werner's Theory:**

*Metals possess two types of valencies i.e. primary (ionizable) valency and secondary (non-ionizable) valency.

*Secondary valency of a metal is equal to the number of ligands attached to it i.e. coordinationnumber.

*Primary valencies are satisfied by negative ions, while secondary valencies may be satisfied by neutral or negative ions.

*Secondary valencies have a fixed orientation around the metal in space.



$[Co(NH_3)_6]Cl_3$

Primary Valencies = 3 Cl^-
Secondary Valencies = 6 NH_3 Coordination Sphere = $[Co(NH_3)_6]^{3-}$

NOMENCLATURE OF COMPLEXES

(i)Negative ligands are named by adding suffix – o. Neutral ligands are named as aqua (H_2O), ammine (NH_3), carbonyl (CO), nitrosyl (NO)

(ii) Ligands are named in alphabetical order before the name of the central atom/ion.

(iii)Name of the ligands is written first followed by name of metal with its oxidation number mentioned in roman numerals in simple parenthesis.

(iv)Prefixes like mono,bi,tri, etc are used to indicate the number of individual ligands; when the names of ligands include a numerical prefix then bis, tris etc are used

(v)When the complex ion is a cation, the metal is named as the element, If the complex ion is an anion, the name of the metal ends with the suffix-ate. eg: cobalt in a complex cation is named as cobalt and in a complex anion, it is named as cobaltate

Negative				Neutral	
CH_3COO^-	Acetato	NO_2^-	Nitrito-N	H_2O	Aqua
CN^-	Cyano	ONO^-	Nitrito-O	NH_3	Ammine

NC^-	Isocyanido	SCN^-	Thiocyanato	CO	Carbonyl
Br^-	Bromo	NCS^-	Isothiocyanato	CH_3NH_2	Methylamine
Cl^-	Chlorido	OH-	Hydroxo	NO	Nitrosyl
F^-	Fluorido	$O2^-$	Superoxo	C_5H_5N	Pyridine
$S_2O_3^{2-}$	Thiosuphato	SO_4^{2-}	Sulphato	NH_2CH_2 CH_2NH_2	Ethane-1,2-diamine
$C_2O_4^{2-}$	Oxalato	O^{2-}	Oxo		

ISOMERISM

Two types: **Structural isomerism and Stereo isomerism**

Structural isomerism: Isomerism arises due to difference in structures of co ordination compounds.

Stereo isomerism: Isomerism on account of the different positions and arrangements of ligands in space around the metal ion

Structural Isomerism: Four types

(i) Ionisation isomerism: This type of isomerism arises when the counter ion of the complex is itself a potential ligand. It can displace a ligand and then become a counter ion eg: $[Co(NH_3)_5Br]SO_4$ is red violet and gives a precipitate with $BaCl_2$ and $[Co(NH_3)_5SO_4]Br$ is red and doesnot give test for sulphate ion instead gives a precipitate of AgBr with $AgNO_3$

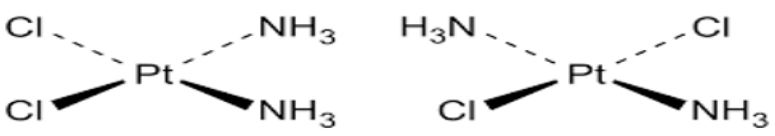
(ii) Solvate or hydrate isomerism: Due to difference in number of solvent molecules present as ligands and as free solvent molecules in the crystal lattice. Eg: $[Cr(H_2O)_6]Cl_3$(violet), $[Cr(H_2O)_5Cl]Cl_2.H_2O$(blue green)

(iii) Linkage isomerism: Arises in a co ordination compound containing ambidentate ligand.eg: complexes containing SCN-, either S or N can act as donor

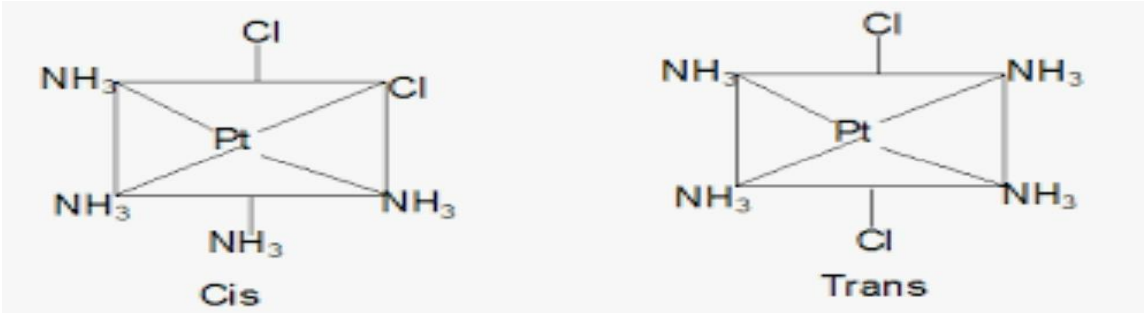
(iv) Co ordination Isomerism: This type of isomerism arises when both positive and negative ions are complex ions and there is interchange of ligands between cationic and anionic entities. Eg: $[Cr(NH_3)_6][Co(CN)_6]$ and $[Co(NH_3)_6][Cr(CN)_6]$

Stereo isomerism: Two types

(i) Geometrical isomerism: This type of isomerism arises in heteroleptic complexes due to different possible geometric arrangements of the ligands. In square planar complexes of formula MA_2B_2, isomers are cis and trans. Other square planar complexes of the type MABCD show two cis and one trans isomers.

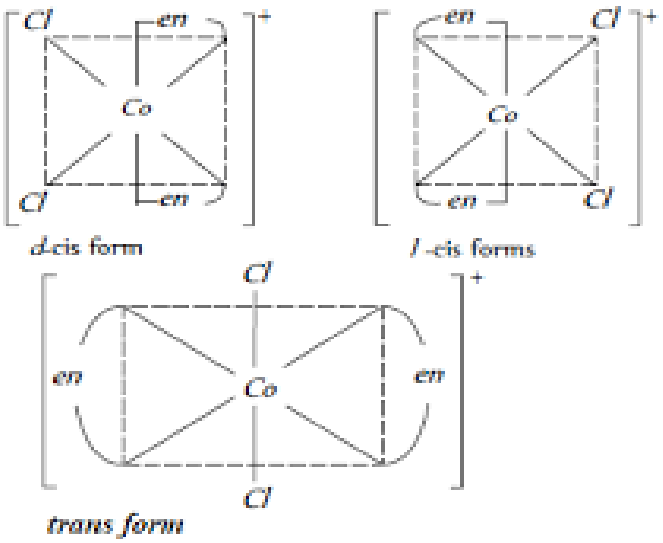


Cis platin



(ii) Optical isomerism: Arises due to the presence of non superimposable mirror image of each other. Optical isomers are also called enantiomers and are denoted as d (dextro) and l (leavo) forms

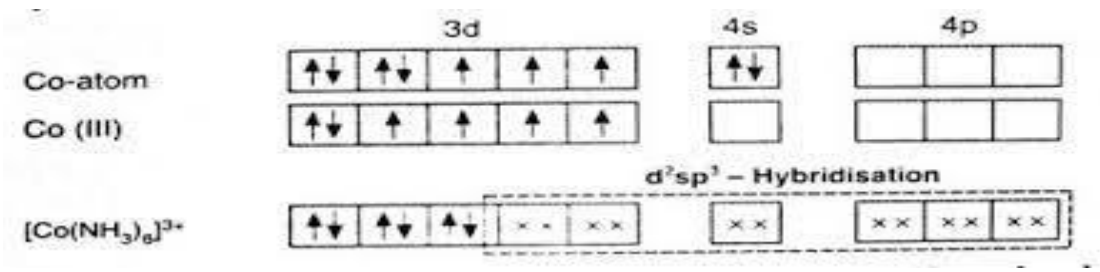
Eg: $[Co(en)_2Cl_2]^+$



VALENCE BOND THEORY

1. According to this theory, the metal atom or ion under the influence of ligands can use its (n- 1)d, ns, np or ns, np, nd orbitals for hybridisation to yield a set of equivalent orbitals of definite geometry such as octahedral, tetrahedral, and square planar.
2. These hybridised orbitals are allowed to overlap with ligand orbitals that can donate electronpairs for bonding.

   Eg:$[Co(NH_3)_6]^{3+}$



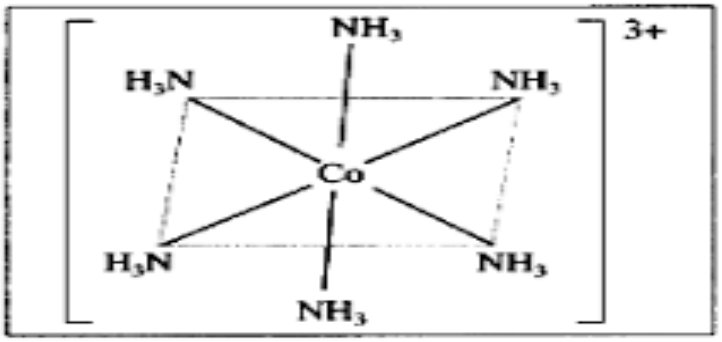


Fig. : Structure of $[Co(NH_3)_6]^{3+}$

When the 3d orbital istaking part in hybridization, it is called an inner orbital complex. **Eg:** d^2sp^3 hybridization of $[Co(NH_3)_6]^{3+}$ involves 3d, 4s and 4p orbital, hence it is an inner orbital complex.

When the 4d orbital is taking part in hybridization, it is called an outer orbital complex.

Eg: sp^3d^2 hybridization of $[CoF_6]^{3-}$ involves 4*d*, 4*s* and 4*p* orbital, hence it is an outer orbital complex.

Geometry:

Coordination Number	Type of hybridisation	Shape of hybrid
4	sp^3	Tetrahedral
4	dsp^2	Square planar
5	sp^3d	Trigonal bipyramidal
6	sp^3d^2 (nd orbitals are involved – outer orbital complexor high spin or spin free complex)	Octahedral
6	d^2sp^3 ($n-1$ d orbitals are involved –inner orbital orlow spin or spin paired complex)	Octahedral

***Magnetic Properties:**

A coordination compound is paramagnetic, if it has unpaired electrons and diamagnetic if all the electrons in the coordination compound are paired.

Magnetic $\mu = \sqrt{n(n+2)}$ where n is number of unpaired electrons.

Limitations of VBT:

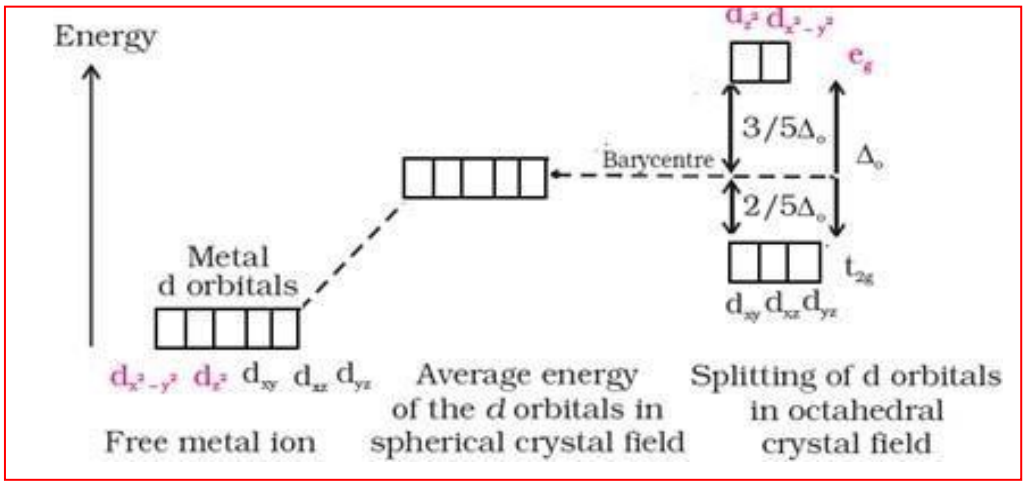
This theory could not give quantitative interpretation of magnetic data, existence of inner orbital and outer orbital complexes by distinguishing between strong and weak ligands. Theory does not explain thermodynamic or kinetic stabilities and colourof complexes.

CRYSTAL FIELD THEORY:

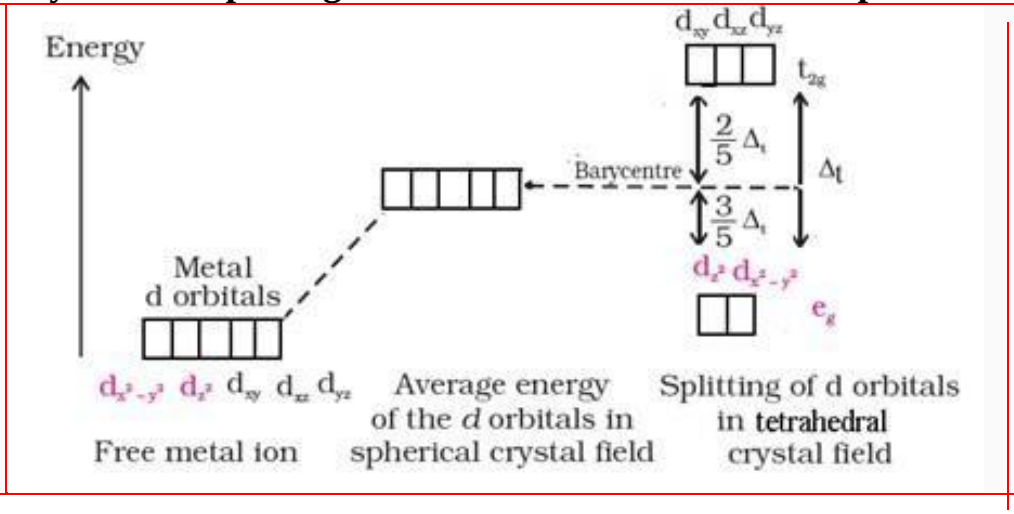
1. It assumes the ligands to be point charges and there is electrostatic force of attractionbetween ligands and metal atom or ion.
2. It is theoretical assumption.

Crystal field splitting in octahedral coordination complexes:

Strong field ligand causes greater repulsion and thus results in the formation of low spin complexesby pairing of electrons.



Crystal field splitting in tetrahedral coordination complexes:



For the same metal, the same ligands and metal-ligand distances, the difference in energy between

eg and t_2g level is $\Delta_t = -\frac{4}{9}\Delta_0$

*Weak field ligands result in the formation of high spin complexes

*Order of strength of ligands: $CO > CN^- > NO_2^- > en > py = NH_3 > H_2O > OH^- > F^- > Cl^- > SCN^- > Br^- > I^-$. Series is called spectrochemical series

*Octahedral Complexes: e_g orbital are of higher energy than t_{2g} orbital.

*Tetrahedral Complexes: eg orbitals are of lower energy than t_{2g} orbitals.
$\Delta t = (4/9)\ \Delta o$

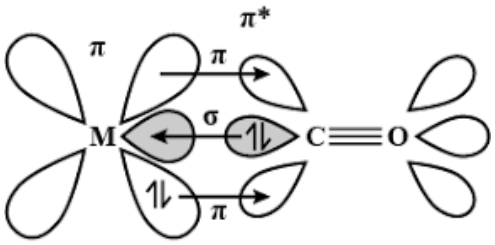
*Colour in co ordination compounds can be readily explained in terms of CFT, it attributes colour to d-d transition of electron

Drawbacks of CFT:

(a) From the assumption that ligands are point charges, it follows that anionic ligands should exertgreatest splitting effect. But anionic ligands actually are found at the low end of the spectro chemical series.

(b) It does not take into account for the covalent character of bonding between the ligand and thecentral atom.

BONDING IN METAL CARBONYLS: The metal carbon bond in metal carbonyls possess both sigma and pi character. The M-C bond is formed by donation of lone pair of electrons from CO into the vacant orbital of the metal. The M-C pi bond is formed by the donation of a pair of electrons from a filled d orbital of a metal to vacant orbital of CO, causing a synergic effect and thus strengthening the bond.



Synergic bonding in metal carbonyls

Stepwise and overall stability constants:

Overall stability constant= Product of stepwise stability constants
Instability or dissociation constant is the reciprocal of stability constant

Importance and applications of coordination compounds:

(a) In many quantitative and qualitative chemical analysis.
(b) In extraction processes of metals, like silver and gold.
(c) Purification of metals like Ni can be achieved through formation and subsequent decomposition of their coordination compounds.
(d) In biological systems the pigment responsible for photosynthesis is chlorophyll, is a co-ordination compound of magnesium. Haemoglobin, coordination compound, of Fe, acts as anoxygen carrier.
(e) Case of chelate therapy in medicinal chemistry.

MULTIPLE CHOICE QUESTIONS

1. **The oxidation number of Cobalt in $K[Co(CO)_4]$ is**

(a) +1

(b) +3

(c) -1

(d) -3

2. **Fac-mer isomerism is associated with which one of the following complexes?**

(a) $[M(AA)_2]$

(b) $[MA_3B_3]$

(c) $[M(AA)_3]$

(d) $[MA_4B_2]$

3. **Which type of isomerism is shown by the complex compounds $[Co\ (NH_3)_5Br]SO_4$ and $[Co\ (NH_3)_5SO_4]Br$**

(a) Ionisation

(b) Optical

(c) Linkage

(d) Coordination

4. **Amongst the following ions, which one is highly paramagnetic?**

(a) $[Cr\ (H_2O)_6]^{3+}$

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

(c) $[Cu\ (H_2O)_6]^{2+}$

(d) $[Zn\ (H_2O)_6]^{2+}$

5. **The geometry of $[Ni(CN)_4]^{2-}$ and $[NiCl_4]^{2-}$ are**

(a) Both square planar

(b) Both tetrahedral

(c) Tetrahedral and square planar respectively

(d) Square planar and tetrahedral respectively

6. **$[Fe(NO_2)_3Cl_3]$ and $[Fe\ (ONO)_3Cl_3]$ show**

(a) Linkage isomerism

(b) Optical isomerism

(c) Geometrical isomerism

(d) None of these

7. **The diamagnetic species is**

(a) $[Ni(CN)_4]^{2-}$

(b) $[NiCl_4]^{2-}$

(c) $[CuCl_4]^{2-}$

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

8. **The oxidation state of Cr in $[Cr(NH_3)_4Cl_2]^+$ is**

(a) +3

(b) +1

(c) +2

(d) 0

9. **The spin only magnetic moment of $[Ni(Cl_4)]^{2-}$ is**

(a) 1.82 BM

(b) 5.46 BM

(c) 2.82BM

(d) 1.41 BM

10. **The type of isomerism shown by the complex $[CoCl_2(en)_2]$ is**

(a) Ionization isomerism

(b) Coordination isomerism

(c) Geometrical isomerism

(d) Linkage isomerism

11. **The geometry and magnetic behaviour of the complex $[Ni(CO)_4]$ are**

(a) Square planar and paramagnetic

(b) Tetrahedral and diamagnetic

(c) Square planar and diamagnetic

(d) Tetrahedral and paramagnetic

12. **Correct increasing order for the wavelengths of absorption in the visible region in the complexes of Co^{3+} is**

(a) $[Co(H_2O)_6]^{3+}$, $[Co\ (en)_3]^{3+}$, $[Co(NH_3)_6]^{3+}$

(b) $[Co(H_2O)_6]^{3+}$, $[Co(NH_3)_6]^{3+}$, $[Co\ (en)_3]^{3+}$

(c) $[Co(NH_3)_6]^{3+}$, $[Co\ (en)_3]^{3+}$, $[Co(H_2O)_6]^{3+}$

(d) $[Co\ (en)_3]^{3+}$,$[Co(NH_3)_6]^{3+}$, $[Co(H_2O)_6]^{3+}$

13. **Which of the following complexes is used to be as an anticancer agent**

(a) Na_2CoCl_4

(b) cis-$[PtCl_2(NH_3)_2]$

(c) mer-$[Co\ (NH_3)_3Cl_3]$

(d) cis-$K_2\ [PtCl_2Br_2]$

14. **The IUPAC name of complex ion ,$[Fe(CN)_6]^{3-}$ is**

(a) Hexacyanidoiron(III)ion

(b) Hexacyanatoferrate (III)ion

(c) Hexacyanidoferrate (III)ion

(d) Tricyanoiron(III)ion

15. **Cobalt(III)chloride forms several octahedral complexes with ammonia .Which of the following will not give test for chloride ions with silver nitrate at 250^0C ?**

(a) $CoCl_3.4NH_3$

(b) $CoCl_3.5NH_3$

(c) $CoCl_3.6NH_3$

(d) $CoCl_3.3NH_3$

16. **Which one of the following is an outer orbital complex and exhibits paramagnetic behaviour :**

(a) $[Cr\ (NH_3)_6]^{3+}$

(b) $[Co\ (NH_3)_6]^{3+}$

(c) $[Ni\ (NH_3)_6]^{2+}$

(d) $[Zn(NH_3)_6]^{2+}$

17. **Which of the following complex has minimum magnitude of Δo ?**

(a) $[Cr\ (CN)_6]^{3-}$

(b) $[Co\ (NH_3)_6]^{3+}$

(c) $[Co\ (Cl)_6]^{3-}$

(d) $[Cr\ (H_2O)_6]^{3+}$

18.**The hybridisation involved in the complex $[Ni(CN)_4]^{2-}$ is**

(a) d^2sp^2

(b) d^2sp^3

(c) dsp^2

(d) sp^3

ANSWERS

1.c	**2.b**	**3.a**	**4.b**	**5.d**	**6.a**	**7.b**	**8.a**	**9.c**	**10.c**
11.b	**12.d**	**13.b**	**14.c**	**15.d**	**16.c**	**17.c**	**18.c**		

ASSERTION – REASON TYPE QUESTIONS

In the following questions, a statement of Assertion followed by a statement of Reason is given.

Choose the correct option out of the following choices.

(a) Assertion and Reason both are true, Reason is the correct explanation of Assertion .
(b) Assertion and Reason both are true but Reason is not the correct explanation of Assertion .(c) Assertion is true, Reason is false.
(d) Assertion is false, Reason is true.

1. **Assertion** : F^- ion is a weak ligand and forms outer orbital complex.
Reason : F^- ion cannot force the electrons of dz^2 and $d_{x^2-y^2}$ orbitals of the inner shells to occupy dxy ,dyz and dxz orbitals of the same subshell

2. **Assertion** : The crystal field theory is successful in explaining the formation, structure, colour and magnetic properties of coordination compounds.
Reason : crystal field theory considers the metal-ligand bond to be ionic.

3. Assertion : $[Ni(CN)_4]^{2-}$ is a diamagnetic complex
Reason :It involves dsp^2 hybridisation and there is no unpaired electron

4. Assertion : Out of $[Fe(H_2O)_6]^{3+}$ and $[Fe(C_2O_4)_3]^{3-}$ the most stable complex is $[Fe(C_2O_4)_3]^{3-}$
Reason : Oxalate ion is an ambidentate ligand.

5. Assertion : Linkage isomerism arises in coordination compounds containing ambidentate ligands
Reason : Ambidentate ligand has two different donor atoms

6. Assertion : $[Ti(H_2O)_6]^{3+}$ is coloured while $[Sc(H_2O)_6]^{3+}$ is colourless.
Reason : d-d transition is not possible in $[Sc(H_2O)_6]^{3+}$.

7. Assertion : Square planar complexes with coordination number 4 exhibit geometrical isomerism but tetrahedral complexes do not show geometrical isomerism.
Reason : The relative positions of the ligands in the tetrahedral complexes are the same with respect to each other .

8. **Assertion** : Tetrahedral complexes have high spin configuration
Reason : crystal field splitting energy so small to force pairing up of the electrons

9. Assertion :CO is stronger ligand than NH_3 for many metals
Reason : NH_3 can form pi bonds by back bonding

10. **Assertion** :Nickel form low spin complexes
Reason: d^2sp^3 hybridisation is not possible in Nickel to form octahedral complexes.

ANSWER KEY

1.a	**2.b**	**3.a**	**4.c**	**5.a**	**6.a**	**7.a**	**8.a**	**9.c**	**10.d**

SHORT ANSWER TYPE QUESTIONS

1.Write the IUPAC names of the following coordination compounds.

(i) $K_3[Fe(C_2O_4)_3]$ Potasium trioxalatoferrate(III)

(ii)$K_2[PdCl_4]$ Potasium tetrachloridopalladate(II)

(iii) $K_3[FeF_6]$ Potassium hexafluoroferrate (III)

(iv) $[Zn(OH)_4]^{-2}$ Tetrahydroxozincate (II) ion

(v)$[Pt(NH_3)_4Cl_2]$ $[PtCl_6]$ Tetraamminedichloroplatinum (IV) hexachloroplatinate (IV)

2.**Write the formula for each of the following complex compounds or ions**.

(i)Hexaamminecobalt (III) chloride $[Co(NH_3)_6]Cl_3$

(ii)Diamminetetrabromoplatinum (VI) bromide $[Pt(NH_3)_2Br_4]Br_2$

(iii)Tetraaquacadmium (II) nitrate $[Cd(H_2O)_4](NO_3)_2$

(iv)Sodium tetracyanocuprate (I) $Na_3[Cu(CN)_4]$

(v)Silver hexacyanoferrate (II) $Ag_4[Fe(CN)_6]$

3.**Give reasons**

(i)$CuSO_4$ $5H_2O$ is blue in colour while $CuSO_4$ is colourless.

Ans. In $CuSO_4$ $5H_2O$, water acts as ligand and causes crystal field splitting. Hence d-d transitionis possible and shows colour.

In anhydrous $CuSO_4$ crystal field splitting is not possible due to absence of ligand and is colourlesss.

(ii)Low spin tetrahedral complexes not formed

Ans:In a tetrahedral complex, the d-orbital is split too small as compared to octahedral complex. For the same metal and same ligand $\Delta_t = 4/9\Delta_o$.Hence, the orbital energies are not enough to force pairing. As a result, low spin configurations are rarely observed in tetrahedral complexes.

4. **Arrange the following complexes in the increasing order of conductivity of their solution:**

$[Co(NH_3)_3Cl_3]$, $[Co(NH_3)_4Cl_2]CI$, $[Co(NH_3)_6]Cl_3$, $[Cr(NH_3)_5Cl]Cl_2$

Ans: $Co(NH_3)_3Cl_3] < [Co(NH_3)_4Cl_2]Cl < [Cr(NH_3)_5Cl]Cl_2 < [Co(NH_3)_6]Cl_3$

Here, the number of ions increases and conductivity increases.

5. A coordination compound $CrCl_3.4H_2O$ precipitates silver chloride when treated with silver nitrate. The molar conductance of its solution corresponds to a total of two ions. Write the structural formula of the compound and name it.

Ans: Silver chloride precipitates when treated with silver nitrate because there is chloride ion outside the complex. There is only one chloride ion outside the complex since only two ions are generated. As a result, the compound's structural formula and nomenclature are:

$[Co(H_2O)_4Cl_2]Cl$ – Tetraaquadichloridocobalt(III) chloride.

6. Explain why $[Fe(H_2O)_6]^{3+}$ has a magnetic moment value of 5.92 BM whereas $[Fe(CN)_6]^{3-}$ has a value of only 1.74 BM.

Ans: $[Fe(CN)_6]^{3-}$ involves d^2sp^3 hybridisation with one unpaired electron and $[Fe(H_2O)_6]^{3+}$ involves sp^3d^2 hybridisation with five unpaired electrons. This difference is due to the presence of strong ligand CN^- and weak ligand H_2O in these complexes.

7. **Arrange the following complex ions in increasing order of crystal field splitting energy (Δ_o) : $[Cr(Cl)_6]^{3-}$, $[Cr(CN)_6]^{3-}$, $[Cr(NH_3)_6]^{3+}$.**

Ans: The order of increasing Δ_o value for the complex ions is:

$[Cr(Cl)_6]^{3-} < [Cr(CN)_6]^{3-} < [Cr(NH_3)_6]^{3+}$

This is because of the increasing order of the Δ_o values of the ligands in the spectrochemical series.

8. **Give the electronic configuration of the following complexes on the basis of Crystal Field Splitting theory.**

$[CoF_6]^{3-}$, $[Fe(CN)_6]^{4-}$ and $[Cu(NH_3)_6]^{2+}$.

Ans: $[CoF_6]^{3-} = Co^{3+} = (d)^6 = t_{2g}^4 e_g^2$

$[Fe(CN)_6]^{4-} = Fe^{2+} = (d)^6 = t_{2g}^6 e_g^0$

$[Cu(NH_3)_6]^{2+} = Cu^{2+} = (d)^9 = t_{2g}^6 e_g^3$

9. **$[Ni(CN)_4]^{2-}$ is colourless where as $[Ni(H_2O)_6]^{2+}$ is green. Why?**

Ans: In $[Ni(CN)_4]^{2-}$, Ni is in +2 oxidation state with electronic configuration $3d^8$. In the presence of strong CN^- ligand the two unpaired electron in 3d orbital pair up. As there is no unpaired electron, it is colourless.

In $[Ni(H_2O)_6]^{2+}$ Ni is +2 oxidation state and electronic configuration $3d^8$. The two unpaired electrons do not pair up in the presence of weak ligand H_2O. The d-d transition absorbs red lightand complementary green light is emitted.

10. **Give the formula of each of the following coordination entities:**

(i) Co^{3+} ion bound to one Cl^-, one NH_3 molecule and two ethylene diamine molecules.

(ii) Ni^{2+} ion is bound to two water molecules and two oxalate ions.

Ans. (i) $[Co(NH_3)Cl(en)_2]^{2+}$ (ii) $Ni(H_2O)_2(ox)_2]^{2-}$

11. **A metal complex having composition $Cr(NH_3)_4Cl_2Br$ has been isolated in two forms A & B. The form A reacts with $AgNO_3$ solution to give a white precipitate soluble in aq. Ammonia whereas B gives a pale yellow precipitate soluble in concentrated ammonia. Write the formulae of A&B.**

Ans. A is $[Cr(NH_3)_4ClBr]Cl$ B is $[Cr(NH_3)_4Cl_2]Br$

12. **Give an example in each case the role of coordination compound in (i) Biological systems (ii) Medicinal chemistry (iii) Heterogeneous catalysis (iv) extraction of metals**

Ans: (i) In biological system Chlorophyll & Hemoglobin is a complex of Mg^{2+} & Fe^{3+} respectively.

(ii) cis-platin or cis- $[Pt(NH_3)_2Cl_2]$ is used in the treatment of cancer.

(iii)Wilkinson catalyst $[(Ph_3)_3RhCl]$ is used for hydrogenation of alkenes.

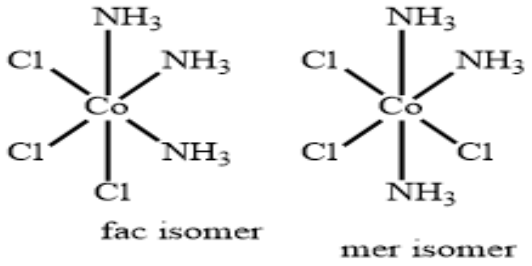
(iv) In extraction of metals like gold silver complex Na $[Ag(CN)_2]$is formed.

13**. Tetrahedral complexes do not show geometrical isomerism. Why?**

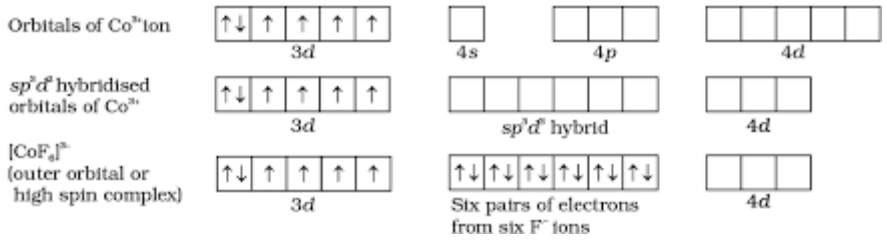
Ans (i)All four ligands in tetrahedral complex are adjacent or equidistant to one another

(ii) The relative positions of donor atoms of ligands attached to the central atom are the same with respect to each other

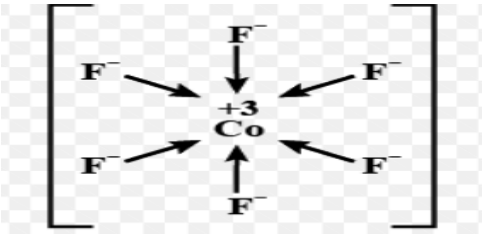
14. **Draw isomers for $[Co(NH_3)_3Cl_3]$**



15. **Using valence bond theory explain hybridisation, magnetic behaviour and geometry of the complex $[CoF6]^{3-}$**



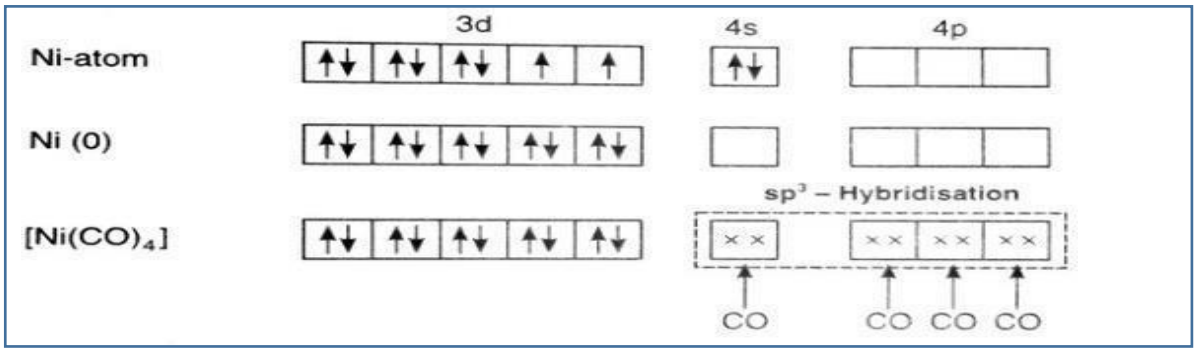
Paramagnetic behaviour



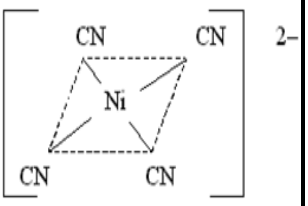
LONG ANSWER TYPE QUESTIONS

1.**$[Ni(CO)_4]$ possesses tetrahedral geometry while $[Ni(CN)_4]^{2-}$ is square planar. Why?**

Ans. In $[Ni(CO)_4]$ Ni is in 0 oxidation state and its electronic configuration is $3d^8\ 4s^2$. CO is strongligand. Hybridization is sp3 and it is tetrahedral.



In $[Ni(CN)_4]^{2-}$] Ni is in +2 oxidation state and its electronic configuration is $3d^8$. CN^- is strongligand. Hybridization is dsp2 and it is square planar.



2**. $FeSO_4$ solution mixed with $(NH_4)_2SO_4$ solution in 1:1 molar ratio gives the test of Fe^{2+} ion but $CuSO_4$ solution mixed with aqueous ammonia in 1:4 molar ratio does not give the test of Cu^{2+} ion. Explain why?**

Ans. $(NH_4)_2SO_4 + FeSO_4 + 6H_2O \rightarrow FeSO_4\ (NH_4)_2SO_4.6H_2O$(Mohr's salt)

$CuSO_4 + 4NH_3 + 5H_2O \rightarrow [Cu(NH_3)_4]SO_4.5H_2O$ (Teraaminecopper(II) sulphate)

Both the compounds fall under the category of addition compounds with only one major difference i.e., the former is an example of a double salt, while the latter is a coordination compound. A double salt is an addition compound that is stable in the solid state but that which breaks up into its constituent ions in the dissolved state. These compounds exhibit individual properties of their constituents. For e.g. $FeSO_4.(NH_4)_2SO_4.6H_2O$ breaks into Fe^{2+}, NH_4^+, and SO_4^{2-} ions. Hence, it gives a positive test for Fe^{2+} ions.

A coordination compound is an addition compound which retains its identity in the solid as well as in the dissolved state. However, the individual properties of the constituents are lost. $[Cu(NH_3)_4]SO_4.5H_2O$ does not show the test for Cu^{2+}.The ions present in the solution of $[Cu(NH_3)_4]SO_4.5H_2O$ are $[Cu(NH_3)_4]^{2+}$ and SO_4^{2-}

3.**What is meant by crystal field splitting? How t_{2g} and e_g orbitals are formed in anoctahedral complex?**

Ans. In case of free metal ion all the five d orbitals have the same energy and are called degenerate orbitals. The five degenerate orbitals of metal ion split into different sets of orbitals having different energies in the presence of electrical field of ligands. This is called crystal field splitting.

In an octahedral complex, the ligands are present at the corners of an octahedron. As lobes of dx^2- y^2 and d_z^2 lie along the axes, ie along the ligands the repulsions are more along the axis. The degeneracy of d orbitals is lifted and these split into two set of orbitals t_{2g} and e_g, slightly different in energy.

4.**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)Write the coordination number of the metal ion.

(ii)What type of hybridisation will M^{n+} have?

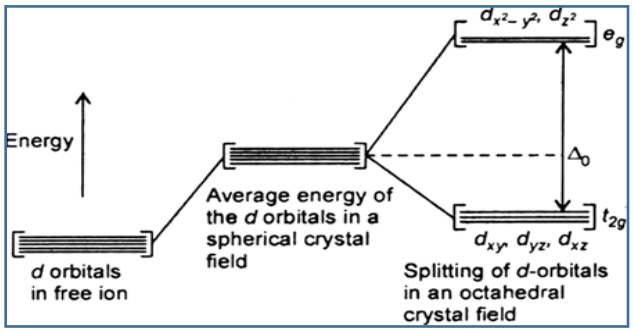
(iii)Draw the diagram showing d-orbital splitting during this complex formation.

(iv)Write the electronic configuration of the metal.

Ans. (i) 6

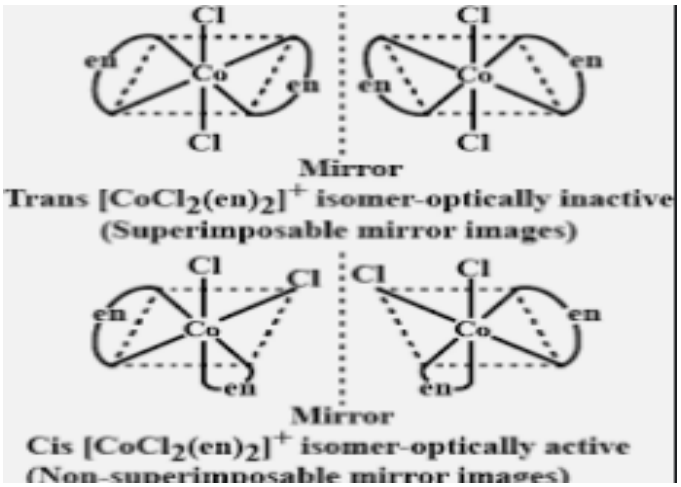
(ii) d2sp3

(iii)



(iv)$t2g^4$ eg^0

5. **Depict isomers for the complex$[CoCl_2(en)_2]^{2+}$**



CASE BASED QUESTIONS

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

Complex compounds play an important role in our daily life. Werner's theory of complex compounds says every metal atom or ion has primary valency (oxidation state) which is satisfied by –vely charged ions, ionisable where secondary valency (coordination number) is non-ionisable, satisfied by ligands (+ve, –ve, neutral) but having lone pair. Primary valency is non-directional, secondary valency is directional. Complex compounds are name according to IUPAC system. Valence bond theory helps in determining shapes of complexes based on hybridisation, magnetic properties, outer or inner orbital complex. Complex show ionisation, linkage, solvate and coordination isomerism also called structural isomerism. Some of them also show stereoisomerism i.e. geometrical and optical isomerism. Ambidentate ligand are essential to show linkage isomerism. Polydentate ligands form more stable complexes then unidentate ligands. There are called chelating agents. EDTA is used to treat lead poisoning, cis-platin as anticancer agents. Vitamin B_{12} is complex of cobalt. Haemoglobin, oxygen carrier is complex of Fe^{2+} and chlorophyll essential for photosynthesis is complex of $Mg^{2+.}$

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

Ans. Zero

(b) **One mole of $CrCl_3 . 6H_2O$ reacts with excess of $AgNO_3$ to yield 2 mole of AgCl. Write formula of complex. Write IUPAC name also**.

Ans. $[Cr(H_2O)_5Cl]Cl_2 . H_2O$, pentaaquachloridochromium (III) chloride.

(c) **Out Cis – $[Pt(en)_2 Cl_2]^{2+}$ and trans $[Pt(en)_2Cl_2]^{2+}$ which one shows optical isomerism**?

Ans. Cis – $[Pt(en)_2 Cl_2]^{2+}$ shows optical isomerism.

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

Ans. $EDTA^{4-}$ (ethylenediamine tetraacetate)

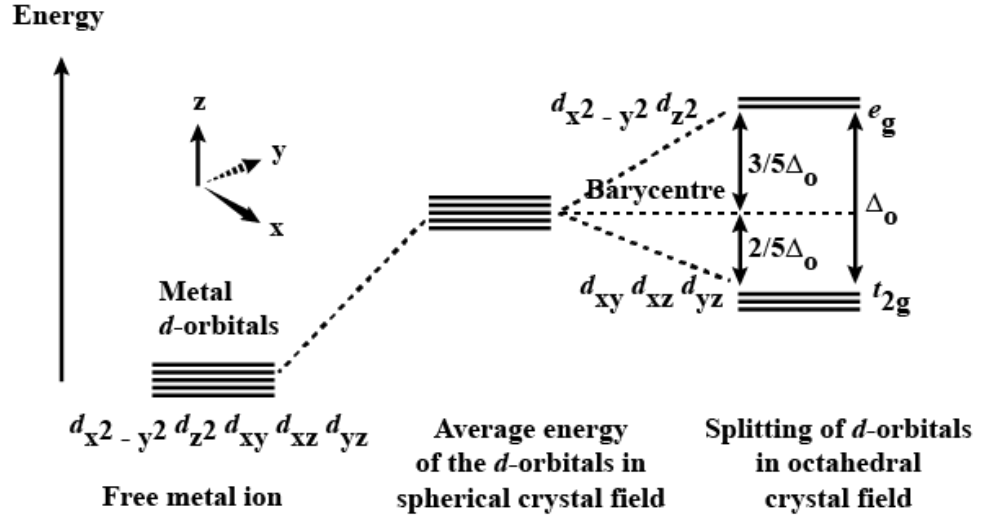
(e) **What is hybridisation of $[CoF_6]^{3-}$? [Co = 27] Give its shape and magnetic properties**.

Ans. Sp^3d^2 , octahedral, paramagnetic.

(f) **What type of isomerism is shown by $[Cr(H_2O)_6] Cl_3$ and $[Cr(H_2O)_5 Cl] Cl_2 .H_2O$**?

Ans. Solvate isomerism.

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



(a) **What is crystal field splitting anergy?**

Ans. The energy difference between the two sets of d-orbitals is called crystal field splitting energy denoted by Δ_0.

(b) **Arrange the following complex ions in the increasing order of Crystal field splitting energy $[CrCl_6]^{3-}$, $[CrCN_6]^{3-}$,$[Cr(NH_3)_6]^{3+}$**

Ans. $[CrCl_6]^{3-}$,$[Cr(NH_3)_6]^{3+}$,$[CrCN_6]^{3-}$

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

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

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

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

(e) **What is spectrochemical series**?

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

3. Read the following paragraph and answer the questions.

Isomerism is a phenomenon in which compounds have the same molecular formula but different physical and chemical properties on account of different structures. The two major types of isomerism are structural and stereo isomerism. The structural isomerism is further divided into four types. Linkage, coordination, ionisation and solvate isomerism while the stereo isomerism is divided into two types: Geometrical and optical isomerism.

(a)**Name the type of isomerism exhibited by $[Co(NH_3)_3NO_2]_3$**

Ans. Linkage isomerism

(b)**The complexes $[Co(NH_3)_6]$ $[Cr(CN)_6]$ and $[Cr(NH_3)_6]$ $[Co(CN)_6]$are the examples of which type of isomerism**

Ans. Coordination isomerism

(c) **Square planar complexes of MX_2L_2 type with coordination number 4 exhibit geometrical isomerism whereas tetrahedral complexes with similar composition do not .Why?**

Ans. Because the relative positions of the ligands attached to the central metal atom are same with respect to each other in tetrahedral complexes.

(d)Name the type of structural isomerism exhibited by the compound $[Co(NH_3)_5SO_4Br]$

Ans. Ionization isomerism

(e)**Write the name of the linkage isomer of $[Co(NH_3)_5NO_2Cl_2]$**

Ans. Pentaamminenitrito-O-cobalt(III)chloride

4.**Read the following paragraph and answer the questions**.

In 1823, Werner put forth this theory to describe the structure and formation of complex compounds or coordination compounds. It is because of this theory that he got the Nobel prize and is known as the father of coordination chemistry. According to his theory The central metals of coordination compounds exhibit two types of valencies, primary valency and secondary valency. The primary valencies are ionizable. These are written outside the coordination sphere. These are non-directional and do not give any geometry to complex compound. The secondary valency of metals is either by negative ions or neutral molecules or both. In modern terminology it represents the coordination number of the metal. Secondary valencies are written inside the coordination sphere. These are directional in nature and give definite geometry to the complex. These are non-ionisable.

(a)**A coordination compound $CrCl_3.4H_2O$ precipitates silver chloride when treated with silver nitrate. The molar conductance of its solution corresponds to a total of 2 ions. Write the structural formula of the complex.**
Ans. $[Co(H_2O)_4Cl_2]Cl$
(b)**The increasing order of conductivity of the following complexes in their solutions**
$[Co(NH_3)_3Cl_3]$, $[Co(NH_3)_6Cl_3$,$[Co\ (NH_3)_4Cl_2]Cl$
Ans. $[Co(NH_3)_3Cl_3]$, ,$[Co\ (NH_3)_4Cl_2]Cl$, $[Co(NH_3)_6Cl_3$
(c)**Write the correct formula for the following coordination compound $CrCl_3.6H_2O$ with 3 chloride ions precipitated as AgCl**.
Ans.$[Cr(H_2O)_6]Cl_3$
(d) **How many ions are produced from the complex $[Co(NH_3)_5Cl]Cl_2$ in solution** ?
Ans.3
(e)**When a coordination compound $PdCl_2.4NH_3$ is mixed with $AgNO_3$, 2 moles of AgCl are precipitated per mole of the compound. Assign secondary valency to the metal**.
Ans.4

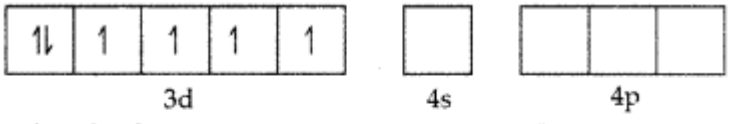
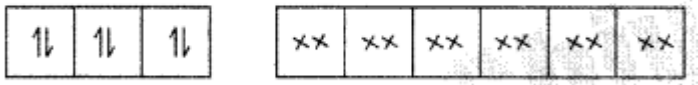
5.**Read the following paragraph and answer the questions.**

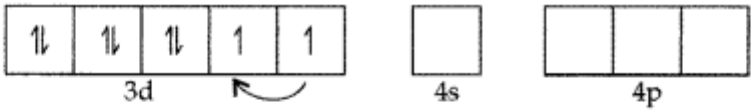
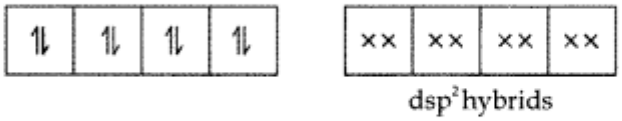
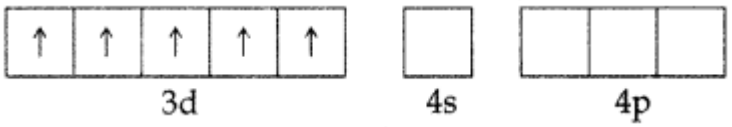
Valence bond theory considers the bonding between metal and the ligands as purely covalent. On the other hand the crystal field theory considers the bond to be ionic purely arising from electrostatic interactions between the metal ion and the ligands. In coordination compounds the interaction between the metal ion and the ligands causes the 5 d orbitals to split up. This is called crystal field splitting and the energy difference between the two sets of orbitals is called crystal field splitting energy. CFSE depends upon the nature of the ligand.

(a)**Write the electronic configuration of $[CoF_6]^{3-}$ on the basis of crystal field theory**
Ans. Co^{3+} has (d^6) ; $t_{2g}^4e_g^{\ 2}$ configuration
(b)**Arrange the following complex ions in the increasing order of crystal field splitting energy $[CrCl_6]^{3-}$, $[Cr(CN)_6]^{3-}$,$[Cr(NH_3)_6]^{3+}$**
Ans. $[CrCl_6]^{3-}$, $[Cr(NH_3)_6]^{3+}$,$[Cr(CN)_6]^{3-}$
(c)**A metal M^{n+} having d^4 valence electronic configuration combines with three bi dentate ligands to form a complex compound. On the basis of CFT write the electronic configuration assuming $\Delta o < P$**
Ans. $t_{2g}^3e_g^{\ 1}$
(d)**Among the ligands ,NH_3 ,en and CO which ligand is having the highest field strength ?**
Ans.CO
(e)**What will be the increasing order for the wave lengths of absorption in the visible region of the following : $[Ni\ (NO_2)_6]^{4-}$, $[Ni\ (NH_3)_6]^{2+}$,$[Ni\ (H_2O)_6]^{2+}$**
Ans. $[Ni\ (H_2O)_6]^{2+}$, $[Ni\ (NH_3)_6]^{2+}$, $[Ni\ (NO_2)_6]^{4-}$

CBSE BOARD QUESTIONS

1	**Indicate the types of isomerisms exhibited by the complex $[Co(NH_3)_5\ (NO_2)]\ (NO_3)_2$. (At. no. Co = 27)** Answer: It shows ionisation isomerism and linkage isomerism.	
2	**Give IUPAC name of the ionization isomer of $[Ni(NH_3)_3NO_3]Cl$.** Answer: IUPAC name : Triammine chlorido nickel (II) nitrate $[Ni(NH_3)_3NO_3]Cl$	

3	**What is meant by chelate effect?** Answer: Chelate effect : When a bidentate or a polydentate ligand contains donor atoms positioned in such a way that when they coordinate with the central metal ion, a five or a six membered ring is formed. This effect is called Chelate effect. As a result, the stability of the complex increases.	
4	**Why are low spin tetrahedral complexes not formed?** Answer: Law spin tetrahedral complexes are rarely observed because orbital splitting energies for tetrahedral complexes are sufficiently large for forcing pairing.	
5	**Give two examples of ligands which form coordination compounds useful in analytical chemistry.** Answer: Examples : (i) EDTA (Ethylene diamine tetra-acetic acid) (ii) Dimethyl glyoxime (DMG)	
6	**Name the following coordination compounds according to IUPAC system of nomenclature :** **(i) $[Co(NH_3)_4 (H_2O)Cl]Cl_2$** **(ii) $[CrCl_2(en)_2]Cl$,** **(en = ethane – 1, 2 – diamine) (Delhi 2010)** Answer: (i) $[CO(NH_3)_4 (H_2O)Cl]Cl_2$ Tetraammine aquachlorido cobalt (III) chloride (ii) $[CrCl_2(en)_2]Cl$ Dichlorobis (ethane-1, 2-diamine) chromium (III) chloride Question 21. Describe the shape and magnetic behaviour of following complexes : (i) $[Co(NH_3)_6]^{3+}$ (ii) $[Ni(CN)_4]^{2-}$ (At. No. Co = 27, Ni = 28) (Delhi 2010) Answer: (i) $[Co(NH_3)_6]^{3+}$: Orbitals of Co^{3+} ion :  d^2sp^3 hybridised orbitals of CO^{3+} :  d^2sp^3 hybrid Six pair of electrons from six NH_3 molecules Hybridization : d^2sp^3 Shape : Octahedral Magnetic behaviour : Diamagnetic (absence of unpaired electrons)	

	(ii) $[Ni(CN)_4]^{2-}$ Ni^{2+} orbitals =  dsp^2 hybridised orbitals of Ni^{2+} =  Containing 4 pairs of electrons from 4 CN ***Shape :*** Square planar ***Hybridisation :*** dsp^2 ***Magnetic behaviour :*** Diamagnetic (no unpaired electrons)	
7	**$[Fe(H_2O)_6]^{3+}$ is strongly paramagnetic whereas $[Fe(CN)_6]^{3-}$ is weakly paramagnetic. Explain. (At. no. Fe = 26)** Answer: In both the cases, Fe is in oxidation state +3. Outer electronic configuration of Fe^{+3} is :  In the presence of CN^-, the 3d electrons pair up leaving only one unpaired electron. The hybridisation involved is d^2sp^3 forming inner orbital complex which is weakly paramagnetic. In the presence of H_2O (a weak ligand), 3d electrons do not pair up. The hybridisation involved is sp^3d^2 forming an outer orbital complex. As it contains five unpaired electrons so it is strongly paramagnetic. .	
8	**Explain why $[Co(NH_3)_6]^{3+}$ is an inner orbital complex whereas $[Ni(NH_3)_6]^{2+}$ is an outer orbital complex. (At. no. Co = 27, Ni = 28)** Answer: In $[Co(NH_3)_6]^{3+}$, the d-electrons of Co^{3+} ($[Ar]3d^6$ 45°) get paired leaving behind two empty d-orbital and undergo d^2sp^3 hybridization and hence inner orbital complex, while in $[Ni(NH_3)_6]^{2+}$ the d-electrons of Ni^{2+} ($[Ar]3d^8$ 45°) do not pair up and use outer 4d subshell hence outer orbital complex.	
9	When a co-ordination compound $CrCl_3.6H_2O$ is mixed with $AgNO_3$, 2 moles of AgCl are precipitated per mole of the compound. Write (i) Structural formula of the complex. (ii) IUPAC name of the complex. (Delhi 2016) Answer: (i) The complex formed on mixing a coordination compound $CrCl_3.6H_2O$ with $AgNO_3$ is as follows $CrCl_3.6H_2O + AgNO_3 \rightarrow [Cr(H_2O_5)Cl]Cl_2.H_2O$ (ii) Pentaaquachloridochromium (III) chloride monohydrate	
10	**Using IUPAC norms write the formulae for the following:** **(a) Potassium trioxalatoaluminate (III)** **(b) Dichloridobis(ethane-l, 2-diamine) cobalt (III)** Answer: (a) $K_3[Al(C_2O_4)_3]$ (b) $[Co(Cl)_2(en)_2]^+$	

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For the complex $[Fe(en)_2Cl_2]$, Cl, (en = ethylene diamine), identify
(i) the oxidation number of iron,
(ii) the hybrid orbitals and the shape of the complex,
(iii) the magnetic behaviour of the complex,
(iv) the number of geometrical isomers,
(v) whether there is an optical isomer also, and
(vi) name of the complex. (At. no. of Fe = 26)

Answer:

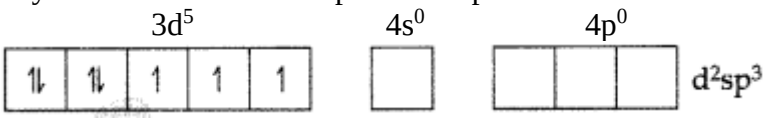
(i) $[Fe(en)_2Cl_2]$ Cl or $x + 0 + 2(-1) + (-1) = 0$

$x + (-3) = 0$ or $x = +3$

∴ Oxidation number of iron, $x = +3$

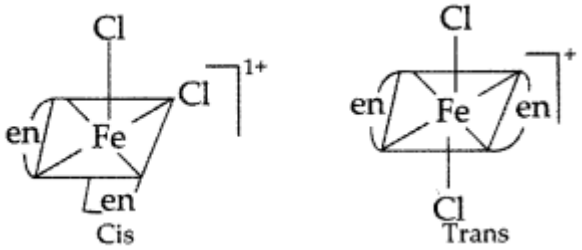
(ii) The complex has two bidentate ligands and two monodentate ligands. Therefore, the coordination number is 6 and hybridization will be d2sp3 and shape will be octahedral.

(iii) In the complex $_{26}Fe^{3+}$ =



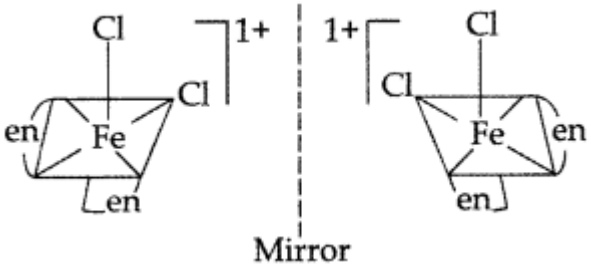
Due to presence of one unpaired electrons in d orbitals the complex is paramagnetic.

(iv)



The number of geometrical isomers are two.

(v) In coordination complex of [Fe(en)2Cl2] Cl, only cis-isomer shows optical isomerism.



(vi) Name of complex: Dichloridobis (ethane-1, 2- diamine) Iron (III) chloride.

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Compare the following complexes with respect to their shape, magnetic behaviour and the hybrid orbitals involved :
(i) $[CoF_4]^{2-}$
(ii) $[Cr(H_2O)_2(C_2O_4)_2]-$
(iii) $[Ni(CO)_4]$ (Atomic number : Co = 27, Cr = 24, Ni = 28)

Answer:

(i) $[COF_4]^{2-}$: Tetrafluorido cobalt (III) ion

Coordination number = 4 Shape = Tetrahedral Hybridisation = sp^3

∴ ***Magnetic moment*** $(\mu) = \sqrt{n(n+2)}$ BM $= \sqrt{3(3+2)} = \sqrt{15} =$ **3.87 BM**

(*ii*) $[Cr(H_2O)_2(C_2O_4)_2]^-$: Diaquadioxalato chromium (III) ion

Coordination number = 6 *Shape* = Octahedral *Hybridisation* = d^2sp^3

∴ ***Magnetic moment*** $(\mu) = \sqrt{n(n+2)}$ BM $= \sqrt{15} =$ **3.87 BM**

(*iii*) $[Ni(CO)_4]$: Tetracarbonyl nickel (O)

Coordination no. = 4 *Shape* = Tetrahedral *Hybridisation* = sp^3

∴ ***Magnetic moment*** $(\mu) = \sqrt{n(n+2)}$ BM $= \sqrt{0(0+2)} = 0$

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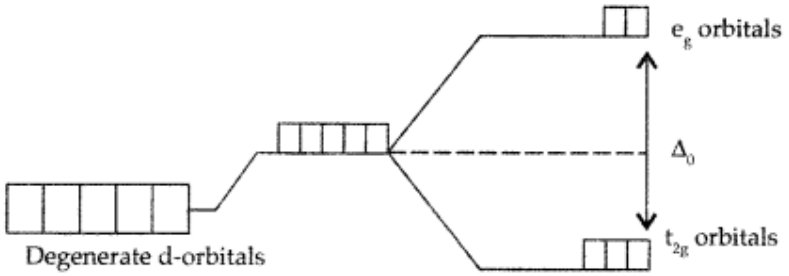
Giving a suitable example for each, explain the following :
(i) Crystal field splitting
(ii) Linkage isomerism
(iii) Ambidentate ligand
Answer:
(i) Crystal field splitting: It is the splitting of the degenerate energy levels due to the presence of ligands. When ligand approaches a transition metal ion, the degenerate d-orbitals split into two sets, one with lower energy and the other with higher energy. This is known as crystal field splitting and the difference between the lower energy set and higher energy set is known as crystal field splitting energy (CFSE)



Splitting of d-orbitals in an octahedral complex

Example : $3d^5$ of Mn^{2+}
(ii) Linkage isomerism: When more than one atom in an ambidentate ligand is linked with central metal ion to form two types of complexes, then the formed isomers are called linkage isomers and the phenomenon is called linkage isomerism.
$[Cr(H_2O)_5(NCS)]^{2+}$ Pentaaquathiocyanate chromium (III) ion
$[Cr(H_2O)_5(NCS)]^{2+}$
Pentaaquaisothiocyanate chromium (III) ion

(iii) Ambidentate ligand: The monodentate ligands with more than one coordinating atoms is known as ambidentate ligand. Monodentate ligands have only one atom capable of binding to a central metal atom or ion. For example, the nitrate ion NO_2^- can bind to the central metal atom/ion at either the nitrogen atom or one of the oxygen atoms.
Example : — SCN thiocyanate, — NCS isothiocyanate

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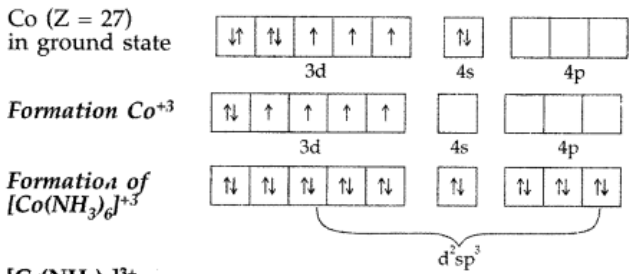
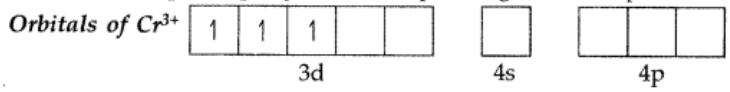
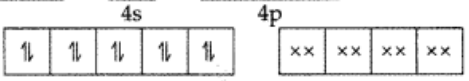
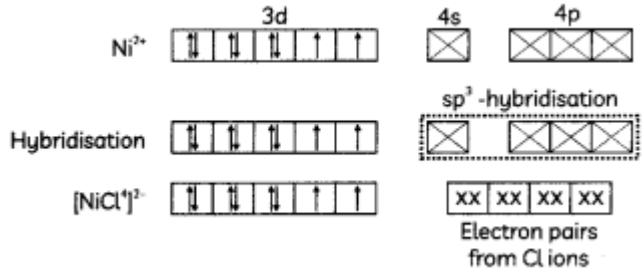
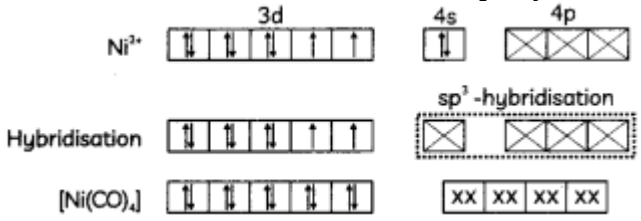
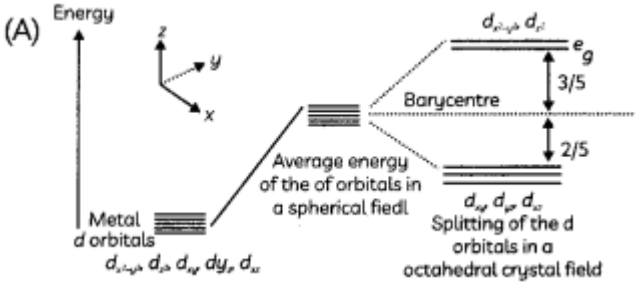
Compare the following complexes with respect to structural shapes of units, magnetic behaviour and hybrid orbitals involved in units :
$[Co(NH_3)_6]^{+3}$, $[Cr(NH_3)_6]^{3+}$, $Ni(CO)_4$
(At. nos. : Co = 27, Cr = 24, Ni = 28)
Answer:
(i) $[Co(NH_3)_6]^{+3}$ → Octahedral shape, d^2sp^3 hybridisation, diamagnetic
Formation of $[Co(NH_2O)_6]^{+3}$ → oxidation state of Co is +3.



(ii) $[Cr(NH_3)_6]^{3+}$
Octahedral shape, d^2sp^3 hybridisation paramagnetic (3 unpaired electrons)



	d^2sp^3 hybridised orbitals of Cr^{3+}  d^2sp^3 hybrids containing 6 pairs of electrons from 6 NH_3 molecules (*iii*) **$[Ni(CO)_4]$** Tetrahedral shape, sp^3 hybridisation, diamagnetic (no unpaired electrons) *Orbitals of Ni*  *sp^3 hybridised orbitals of Ni*  sp^3 hybrids containing 4 pairs of electrons from 4 CO molecules	
15	**Explain the following :** **(i) Low spin octahedral complexes of nickel are not known.** **(ii) The π-complexes are known for transition elements only.** **(iii) CO is a stronger ligand than NTL, for many metals.** Answer: (i) The electronic configuration of Ni is [Ar] 3d8 4s2 which shows that it can only form two types of complexes i.e. square planar (dsp2) in presence of strong ligand and tetrahedral (sp3) in presence of weak ligand. There are four empty orbitals in Ni while octahedral complexes require six empty orbitals. (ii) Due to presence of empty d-orbitals in transition metals, they can accept electron pairs from ligands containing π electrons and hence can form ic-bonding complexes. Example : ligands like C_5H_5, C_6H_6 etc. (iii) Due to greater magnitude of Δ_0, CO produces strong fields which cause more splitting of d-orbitals and moreover it is also able to form π bond due to back bonding.	
16	A) **On the basis of crystal field theory, write the electronic configuration for d^4 ion is $\Delta_0 < P$.** Answer: $t_{2g}^3\ e_g^1$ $\Delta_0 < P$, the configuration will be t_{2g}, e_g and it is in the case of weak field Ligands and high spin complex will be formed. (B) **Write the hybridization and shape of $[Ni(CN)_4]^{2-}$. (Atomic number of Ni = 28)** Answer: dsp2, square planar. Related Theory: The Crystal Field Stabilization Energy (CFSE) derived from the splitting of the d orbital energies is greater for square planar arrangement. In a tetrahedral arrangement, no pair of ligands is pointing at one specific d orbital. Thus, for first-row atoms such as Ni^{2+} (a efi species), tetrahedral arrangement will be pre-ferred if the ligands are large and weak-field. If the ligands are small (more rod-like) and are strong-field, the planar arrangement will be preferred. (C) **Which of the following is more stable complex and why?** $[Co(NH_3)_6]^{3+}$ and $[Co(en)_3]^{3+}$ (3) Answer: $[Co(en)_3]^{3+}$ is more stable than $[Co(NH_3)_6]^{3+}$ as $[Co(en)_3]^{3+}$ is a metal chelate due to presence of bidentate ligand ethylene diamine ligand. Metal chelates are more stable than complexes containing only monodentate ligands.	

	Related Theory: When a ligand attaches to the metal ion in a manner that forms a ring, then the metal- li-gand association is found to be more stable. In other words, complexes containing chelate rings are more stable than complexes without rings. This is known as the chelate effect.	
17	**(A) Give one chemical test as evidence to show that $[Co(NH_3)_5Cl]\ S0_4$ and $[CO(NH_3)_5(S0_4)]Cl$ are ionisation isomers.** **(B) $[NiCl_4]^{2-}$ is paramagnetic while $[Ni(CO)_4]$ is diamagnetic, though both are tetrahedral. Why? (Atomic number of Ni = 28)** **OR** **(A) Draw figure to show the splitting of d orbitals in an octahedral crystal field.** **(B) What will be the correct order for the wavelengths of absorption in the visible region for the following:** **$[Ni(N0_2)_6]^{4-}$, $[Ni(NH_3)_6]^{2+}$, $[Ni(H_20)_6]^{2-}$** **(3)** Answer: (A) When $[Co(NH_3)_5(S0_4)]Cl$ is treated with silver nitrate solution, a white precipitate of AgCl is formed. But $[Co(NH_3)_5Cl]\ S0_4$ does not give white ppt with AgN03 solution. $[Co(NH_3)_5S0_4]Cl + AgN0_3 \rightarrow AgCl$ (White ppt) $[CO(NH_3)_5\ Cl]S0_4 + AgN0_3 \rightarrow$ No white ppt (B) In $[NiCl_4]^{2-}$ complexion, nickel is in +2 oxidation state and the configuration is 3d8. Since the molecule is tetrahedral, it involves sp^3 hybridisation as shown below:  The molecule is paramagnetic because it contains two unpaired electrons. In $[Ni(CO)_4]$, nickel is in 0 oxidation state and has the configuration $4s^2\ 3d^4$ or $3d^{10}$. The molecule is tetrahedral and involves sp^3-hybridisation as given below:  Each CO donates a pair of electrons forming four Ni-CO bonds. The compound is diamagnetic since it contains no unpaired electron. OR  The splitting of the d orbitals in an octahedral field takes place in such a way that dx^2-y^2,	

	dz^2 experience a rise in energy and form the eg level, while dxy dzy and dzx experience a fall in energy and form the t_{2g} level (B) The wavelengths of absorption in the visible region will be in the order: $[Ni(N0_2)_6]^{4-} > [Ni(NH_3)_6]^{2+} > [Ni(H_20)_6]^{2-}$ Explanation: The central metal ion in all three complexes is the same. Therefore, absorption in the visible region depends on the ligands. The order in which the CFSE values of the ligands increases in the spectrochemical series is as follows: $H_2O < NH_3 < NO_2^-$ Thus, the amount of crystal-field splitting observed will be in the following order: $\Delta_0(H_2O) < \Delta_0(NH_3) < \Delta_0(N0_2)$ (More the energy, less the wavelength)	
18	**3** **Read the passage given below and answer the following questions :** Iron forms many complexes in its +2 and +3 oxidation states such as $[Fe(H_2O)_6]^{2+}$ (*A*); $[Fe(CN)_6]^{4-}$ (*B*); $[Fe(H_2O)_6]^{3+}$ (*C*); $[Fe(CN)_6]^{3-}$ (*D*), etc., They exhibit, different magnetic properties and undergo different hybridisation of iron. **The following questions are multiple choice questions. Choose the most appropriate answer :** **(i)** Which of the following statements is correct? (a) (*B*) is paramagnetic while (*C*) is diamagnetic. (b) Both (*B*) and (*D*) are outer orbital complexes. (c) Both (*A*) and (*C*) are paramagnetic. (d) (*A*) is outer orbital complex and (*C*) is inner orbital complex. **(ii)** The complex having maximum magnetic moment is (a) (*A*) (b) (*B*) (c) (*C*) (d) (*D*) **OR** Which of the following does not represent correct configuration of the *d*-orbitals in the given complexes? (a) (*A*) : $t_{2g}^4 e_g^2$ (b) (*B*) : $t_{2g}^6 e_g^0$ (c) (*C*) : $t_{2g}^4 e_g^1$ (d) (*D*) : $t_{2g}^5 e_g^0$ **(iii)** The spin only magnetic moment of complexes (*A*), (*B*), (*C*) and (*D*) are respectively (in BM) (a) $2\sqrt{6}, 0, \sqrt{35}, \sqrt{3}$ (b) $0, 2\sqrt{6}, \sqrt{35}, \sqrt{3}$ (c) $\sqrt{15}, 2\sqrt{6}, \sqrt{3}, 0$ (d) $\sqrt{3}, \sqrt{8}, 0, \sqrt{15}$ **(iv)** Which of the given complexes are outer orbital complexes? (a) (*A*) and (*B*) only (b) (*B*) and (*C*) only (c) (*A*) and (*C*) only (d) (*B*) and (*D*) only	

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Read the passage given below and answer the following questions :

Metal carbonyl is an example of coordination compounds in which carbon monoxide (CO) acts as ligand. These are also called homoleptic carbonyls. These compounds contain both σ and π character. Some carbonyls have metal-metal bonds. The reactivity of metal carbonyls is due to (i) the metal centre and (ii) the CO ligands. CO is capable of accepting an appreciable amount of electron density from the metal atom into their empty π or π^* orbitals. These types of ligands are called π-accepter or π-acid ligands. These interactions increases the Δ_o value.

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

(i) What is the oxidation state of metal in $[Mn_2(CO)_{10}]$?

(a) +1 (b) −1 (c) +2 (d) 0

(ii) Among the following metal carbonyls, the C – O bond order is lowest in

(a) $[Mn(CO)_6]^+$ (b) $[Fe(CO)_5]$ (c) $[Cr(CO)_6]$ (d) $[V(CO)_6]^-$

OR

Which of the following can be reduced easily?

(a) $V(CO)_6$ (b) $Mo(CO)_6$ (c) $[Co(CO)_4]^-$ (d) $Fe(CO)_5$

(iii) The oxidation state of cobalt in $K[Co(CO)_4]$ is

(a) +1 (b) +3 (c) −1 (d) 0

(iv) Structure of decacarbonyl manganese is

(a) trigonal bipyramidial (b) octahedral (c) tetrahedral (d) square pyramidal.

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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.

a **Assertion :** $[Fe(CN)_6]^{3-}$ has d^2sp^3 type hybridisation.
Reason : $[Fe(CN)_6]^{3-}$ ion shows magnetic moment corresponding to two unpaired electrons.

b **Assertion :** The ligands nitro and nitrito are called ambidentate ligands.
Reason : An ambidentate ligand can attach to metal through two different atoms.

c **Assertion :** Thiocarbonyl is a neutral ligand.
Reason : Thiocarbonyl has three donor atoms but behaves as a bidentate ligand.

d **Assertion :** The ligand N_3^- is named as nitride.
Reason : N_3^- is derived from HN_3.

e **Assertion :** $[CrCl_2(H_2O)_4]NO_3$ is dichlorotetraaquachromium(III) nitrate.
Reason : In writing the name of the complex cation is written first followed by the anion.

CHAPTER 10

HALOALKANES AND HALOARENES

GIST OF THE LESSON

a) Compounds containing halogen atom bonded to sp^3 hybridized carbon atom:

i) Alkyl halides or Haloalkane (R-X): They form a homologous series represented by the formula $C_nH_{2n+1}X$.

R-X can be primary (1^0) R-CH_2-X, secondary (2^0) R_2CH-X or Tertiary (3^0) R_3C-X

Examples: Primary: CH_3Cl, CH_3-CH_2-Br

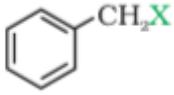
Secondary: $(CH_3)_2CH$ Br

Tertiary : $(CH_3)_3C$-Cl

ii) Allylic halides : Halogen atom is bonded to ***sp³***carbon which in turn is bonded to ***sp²***carbon of an aliphatic chain/alicyclic chain.

Example: $CH_2 = \underset{sp^2}{CH}\text{-}\underset{sp^3}{CH_2}\text{-}Cl$

iii) Benzylic halides: Halogen is bonded to ***sp³***carbon which in turn is bonded to ***sp²***carbon of an aromatic ring.

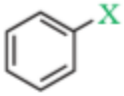


b) Compounds containing halogen atom bonded to sp^2 hybridized carbon atom:

i) Vinylic halides: Halogen atom is bonded to sp^2 carbon atom of an aliphatic /alicyclic chain

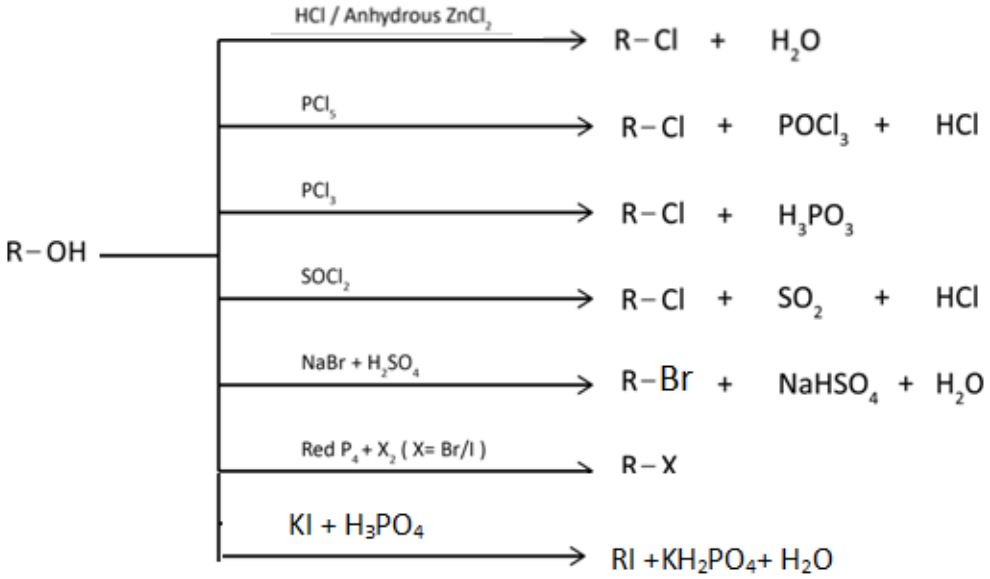
Example: CH_2=CH-Cl,

ii) Aryl halides: Halogen is bonded to ***sp²*** carbon of an aromatic ring. Halogen is bonded to ***sp²***carbon of an aromatic ring.



METHOD OF PREPARATION OF ALKYL HALIDES

a) From alcohols



b) From Alkenes

i) By addition of HX (Markovnikov'srule)

eg: CH_3-CH=CH_2 + HCl ⟶ CH_3-CH(Cl)- CH_3

(major product)

Anti Markownikov's rule for HBr addition in presence of Benzoyl peroxide

CH_3- CH=CH_2 + HBr —(Benzoyl peroxide)→ CH_3-CH_2-CH_2-Br(major product)

ii) By addition of halogen

CH_2=CH_2 + Br_2 —(CCl_4)→ Br-CH_2-CH_2-Br

(Test for unsaturation since the reddish brown colour of Br_2 is discharged)

c) By halogen exchange reactions

i) Finkelstein reaction

Acetone

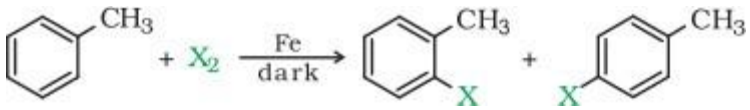
R-X (X= Cl or Br) + NaI ⟶ R-I + NaX

ii) Swarts reaction

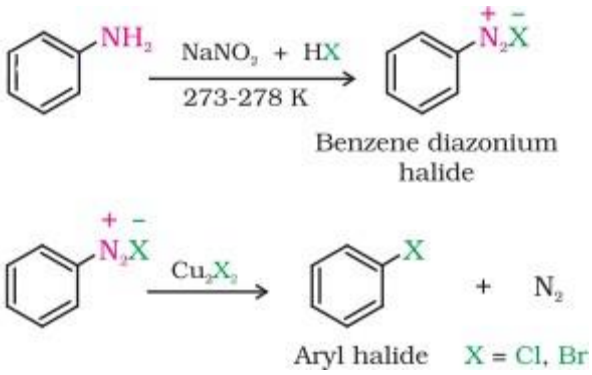
R-X (X= Cl or Br) + AgF ⟶ R-F+ AgF

PREPARATION OF ARYLHALIDES

a) By electrophilic substitution



b) By Sandmeyers reaction



Physical properties of alkyl halides

Melting and boiling points

1. Boiling points of alkyl halides are higher than those of the hydrocarbons of comparable molecular mass, due to stronger intermolecular force (dipole–dipole interaction and Vander Waal's forces) in alkyl halides.

For the same alkyl group, the boiling points of alkyl halides increase in the order R-Cl <R-Br< R-I

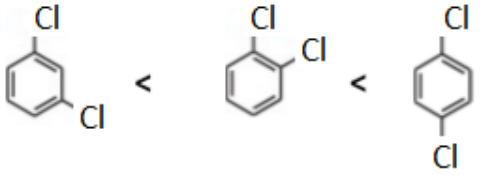
2. The boiling points of isomeric halo alkanes decrease with increase in branching, because the surface area decreases as the branching increases and hence the intermolecular force decreases.

Eg: The boiling points of various isomers of butyl bromide follow the order $1^o > 2^o > 3^o$

$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}Br > CH_3\text{-}CH_2\text{-}CH(Br)\text{-}CH_3 > CH_3\text{-}C(Br)(CH_3) - CH_3$

3. Among the isomers of dichloro benzene, the para isomer has the highest melting point.

This is due to the symmetry of para isomer that fits into the crystal lattice better as compared to ortho and meta isomers. Melting points of dichloro benzene follow the order:



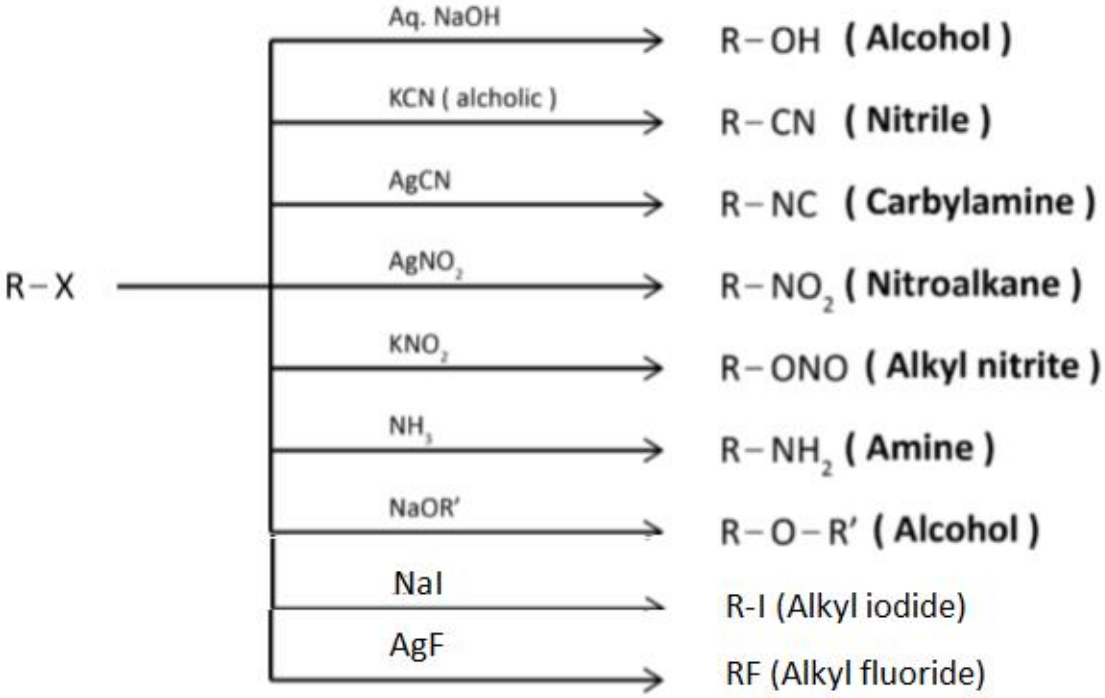
Solubility : Halo alkanes are sparingly soluble in water, because they can't form hydrogen bond with water. However they are highly soluble in organic solvents

Reactions of Halo alkanes

a) Nucleophilic substitution reactions

Due to polar nature of C-X bond carbon atom gets a partial positive charge. As a result, a nucleophile can attack this carbon atom and causes the departure of the halogen atom as halide ion. This type of reaction in which a stronger nucleophile replaces weaker nucleophile is called nucleophilic substitution reaction.

Examples



Ambident nucleophiles: These are nucleophiles which possess two nucleophilic centre's through which they can attack

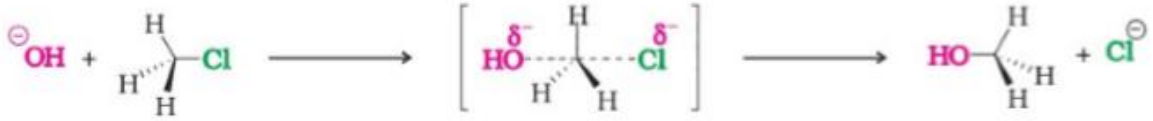
Eg: CN^- and NC^-

NO_2^- and ONO^- etc.

MECHANISM OF NUCLEOPHILIC SUBSTITUTION

a) **Substitution nucleophilic bimolecular (SN^2)** In this mechanism the rate of the reaction depends upon the concentration of both the reactants (nucleophile and alkyl halide)

Eg:



Transition state

The incoming nucleophile (-OH) interacts with alkyl halide (CH_3-Cl) causing carbon –halogen bond (C-Cl) to break while forming a new carbon – OH bond. These two processes takes place in a single step and no intermediate is formed. The presence of bulky alkyl groups around the carbon bearing the halogen atom will hinder the approach of the incoming nucleophile. Hence the rate of reaction decreases.

Thus the order of reactivity of alkyl halides in SN^2 reaction is

Primary(1^0) > secondary(2^0) > tertiary(3^0)

Stereo chemical impact of S_N2 mechanism

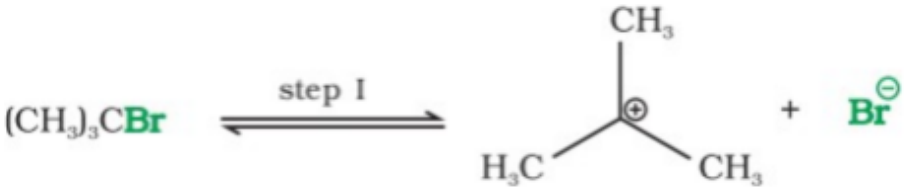
Since the incoming nucleophile is attacking the carbon atom from the rear side (opposite) of the leaving group (halogen) the configuration (3D arrangement) of the product formed will be opposite of the alkyl halide. This is known as inversion of configuration.

If the alkyl halide is optically active (dextro or laevo rotatory), the optical activity of the product formed will be inverted, ie, dextro will become laevo and vice versa.

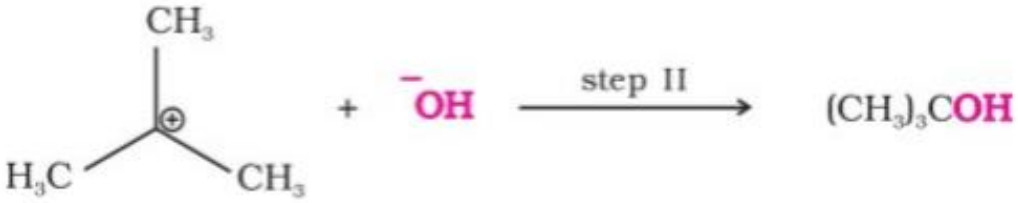
b) Substitution nucleophilic unimolecular (S_N1) In this mechanism.

The rate of reaction depends upon the concentration of only one reactant, ie the alkyl halide. It occurs in two steps

Step 1: The polarized carbon-halogen (C-X) bond undergoes slow cleavage to produce a carbocation and a halide ion.



As the stability of carbocation increases, the rate of reaction also increases



SN^1 reactions are generally carried out in polar protic solvents like water, alcohol etc.

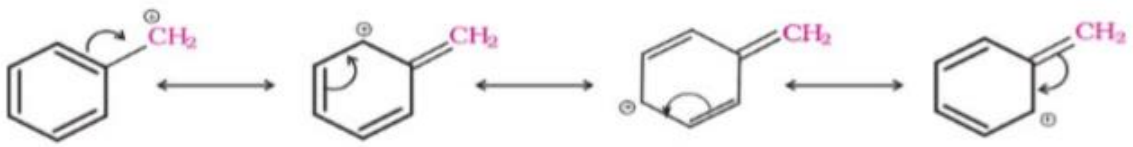
Since the reactivity in SN^1 mechanism depends on the stability of the intermediate, the rate of the reaction follows the order :

Primary(1^0) < secondary(2^0) < tertiary(3^0)

Allylic and benzylic halides show high reactivity towards the SN^1 mechanism due to the stability of allylic and benzylic carbocation intermediates through resonance

Resonance in allylic carbocation

Resonance in Benzylic carbocation



For the same alkyl group, the order of reactivity in both mechanisms is

R-I > R-Br > R-Cl > R-F

Stereo chemical impact of SN^1 mechanism

In S_N^1 mechanism, 50% of the products will have the same configuration as that of the alkyl halide (retention) and remaining 50% will have opposite configuration (inversion). Therefore the resultant mixture is optically inactive and is called as racemic mixture and the process is known as racemisation.

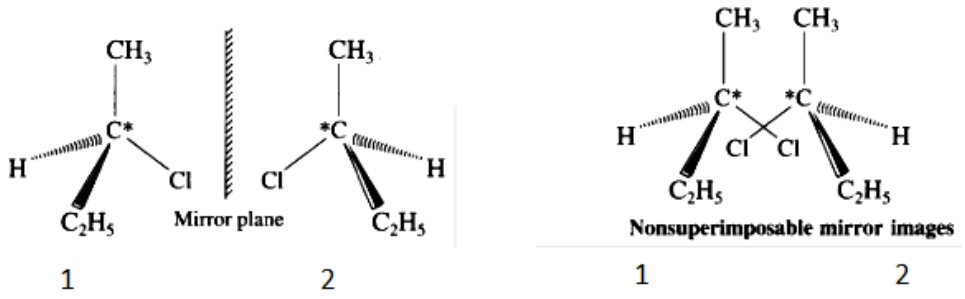
OPTICAL ACTIVITY

The ability of a compound to rotate the plane of a plane polarised light, when passed through the solution of the compound is known as optical activity. The compound which can rotate the plane of the plane polarised light towards clockwise direction is called dextrorotatory (d or +) and which rotate towards anticlockwise direction is called laevorotatory (l or -)

Reason for optical activity :

The molecular asymmetry is responsible for optical activity. Molecular asymmetry arises when the molecule does not possess any elements of symmetry like plane of symmetry, centre of symmetry, axis of symmetry etc. An organic compound shows molecular asymmetry when it has at least one asymmetric carbon atom ie the carbon atom that is bonded to 4 different atoms/groups.

Example of an asymmetric compound is 2-Chlorobutane. It has one asymmetric (Chiral) carbon atom (C_2). The two configurations are



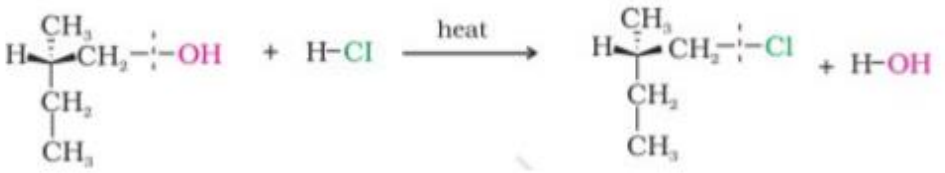
Compounds (1) and (2) are related to each other as object and it's non-superimposable mirror image. Such a pair of molecules is known as enantiomers or chiral molecules. If one form is dextro rotatory (d) then the other will be laevorotatory (l).

Racemic mixture or Racemic modification :

A mixture containing the two enantiomers of a compound (d and l) in equal proportions, which is optically inactive due to cancellation of the optical rotation of one enantiomers by the other , is called

racemic mixture denoted as 'dl' or (±). The process of conversion of an enantiomers into a racemic mixture is known as racemisation.

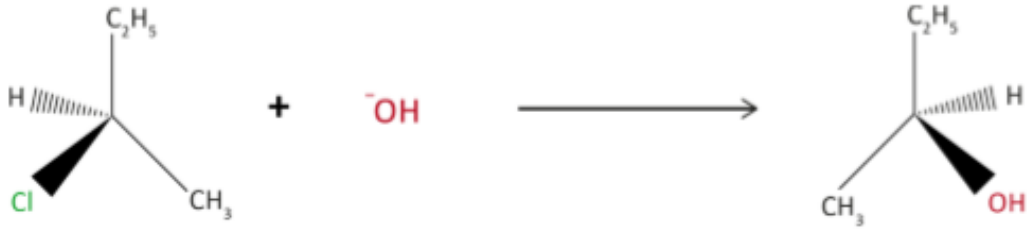
Retention: Retention of configuration is the preservation of configuration around an asymmetric carbon atom during a chemical reaction. This will happen when no bonds around the asymmetric carbon atom are broken



(-) 2-Methylbutan-1-ol (-) 1- Chloro-2-methylbutane

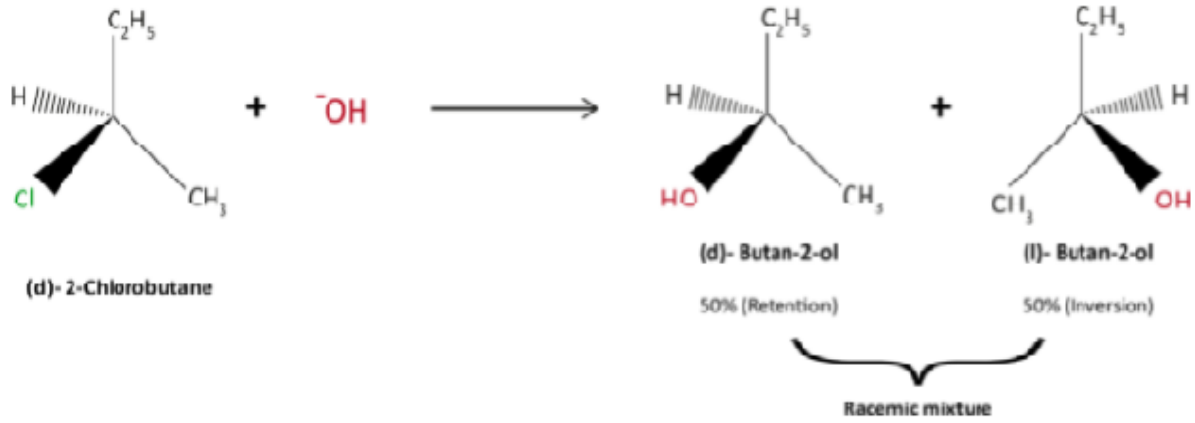
Inversion: During a chemical reaction, if a bond around an asymmetric carbon atom is broken and a new bond is formed so that the configuration of the new compound formed is opposite of the initial compound. These results in inversion of optical rotation ie dextro rotatory reactant molecule will become laevo rotatory product and vice versa.

During SN^2 reaction inversion takes place



(d)- 2-Chlorobutane (l)- Butan-2-ol

During S_N^1 reaction 50% of the products will retain the configuration of the reactant and remaining 50% of the products will undergo inversion. So the resultant product will be racemic mixture and optically inactive. Example S_N^1 mechanism



(d)- 2-Chlorobutane (d)- Butan-2-ol (l)- Butan-2-ol

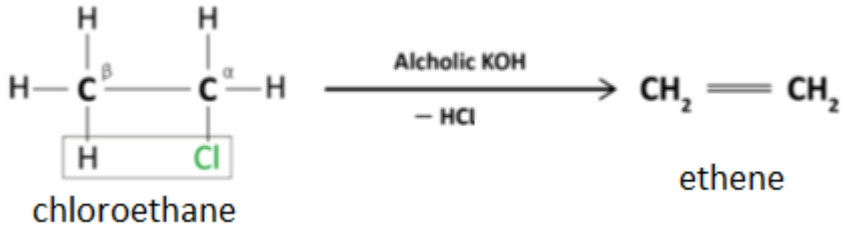
50% (Retention) 50% (Inversion)

Racemic mixture

Comparison between S_N1 and S_N2 reaction mechanisms

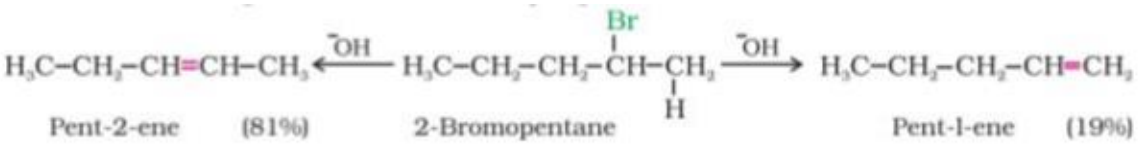
Reaction Parameters	S_N1	S_N2
Molecularity	It is unimolecular nucleophilic substitution reaction.	It is bimolecular nucleophilic substitution reaction.
Order	It is first ordered reaction Rate =k [Nu]	It is second ordered reaction. Rate = k [Nu][RX]
Alkyl halide structure	Tertiary> secondary >> primary > Methyl	Methyl > primary>secondary>>Tertiary
Nucleophile	Rate of reaction is independent of concentration of nucleophile.	Rate of reaction depends upon concentration of nucleophile.
	Attacks from both sides of carbonium ion	Attacks from backside of the substrate
Intermediate	The intermediate formed is carbocation	Five membered intermediate is formed
Mechanism	It is taking place in two step	It is a single step reaction
Stereochemistry	In this reaction racemisation takes place (Both retention and inversion)	In this reaction, 100% inversion takes place.

β- Elimination reactions in alkyl halides



If there is a possibility of more than one alkene formation due to availability of more than one β-hydrogen atom, the major alkene is formed according to to Zaitsev rule. This rule states that "In dehydrohalogenation reactions, the preferred product is that alkene which has the greater number of alkyl groups attached to the doubly bonded carbon atoms**.**

Example



Reaction with metals:

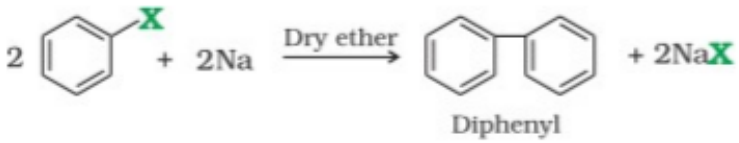
Alkyl halides react with Magnesium in dry ether medium and form alkyl magnesium halides known as 'Grignard Reagent'

Eg : CH_3-CH_2-Br + Mg(Dry ether medium)→ CH_3-CH_2-MgBr

Grignard reagents should be prepared under anhydrous conditions, because they react with water (or any other protic solvents like alcohol) and form the corresponding hydrocarbon.

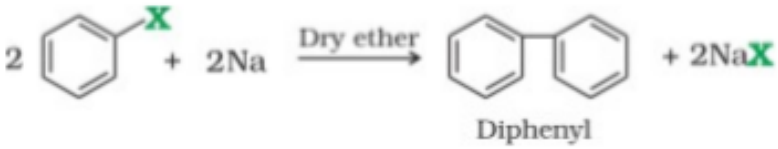
R-MgX + H_2O → R-H + Mg(OH)X

Fittig reaction



Diphenyl

Wurtz-Fittig reaction



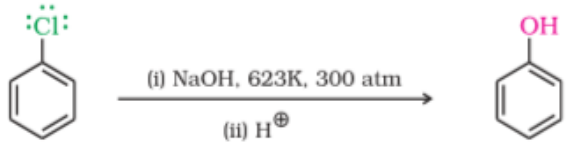
Diphenyl

Nucleophilic substitution in Aryl halides

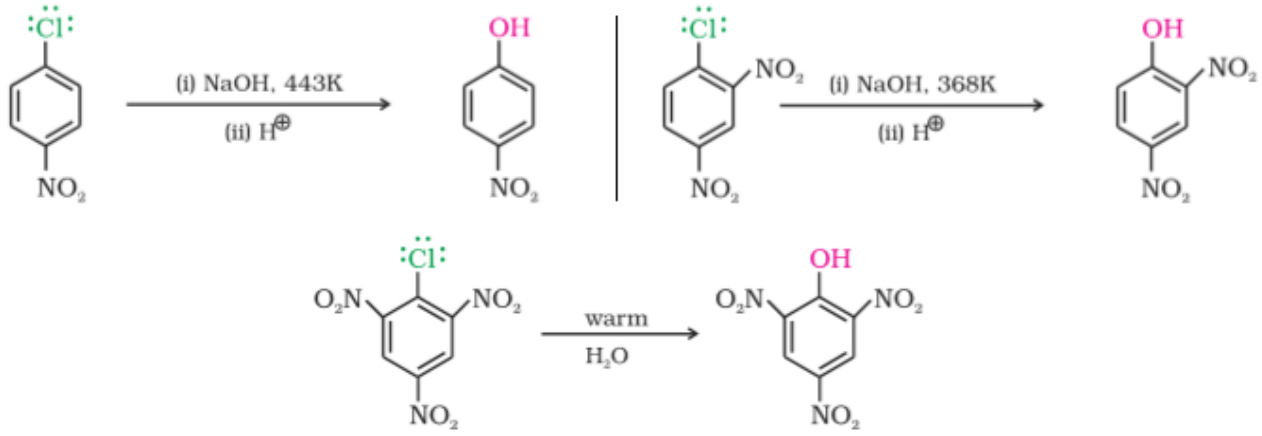
Aryl halides are extremely less reactive towards nucleophilic substitution due to the following reasons.

1. C-X bond acquires a partial double bond character due to resonance and hence the cleavage of C-X bond becomes difficult. (draw resonance structure)
2. The C-X bond is shorter due to greater electro negativity of sp^2 carbon
3. The phenyl carbocation formed during S_N1 reaction is highly unstable
4. Due to electron rich arenes, there is greater electron-electron repulsion when an electrophile approaches the aryl halide. However under drastic conditions aryl halides undergo nucleophilic substitution.

However under drastic conditions aryl halides undergo nucleophilic substitution



The presence of – I groups like –NO_2 at ortho/para positions in aryl halides increases the reactivity



There is no effect on reactivity when the –I groups are present at meta position

Electrophilic substitution reactions in aryl halides

Due to resonance in aryl halides, the electron density increases at ortho/para positions.

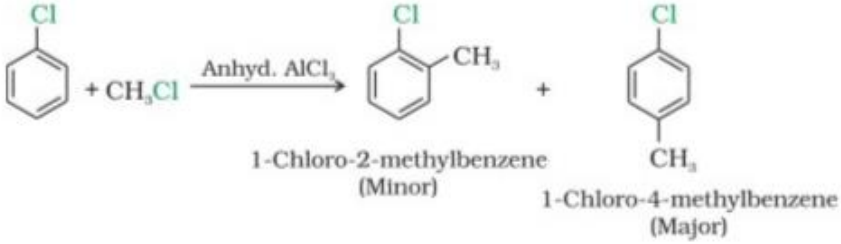
Halogenation:

Nitration

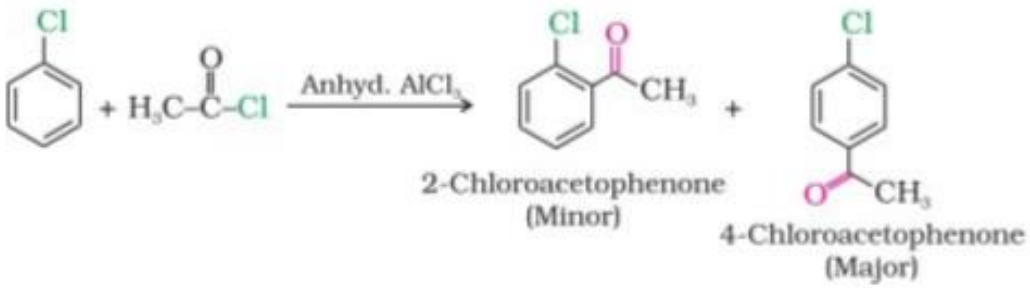
Sulphonation

Friedel craft's reaction

a) Alkylation



b)Acylation



Polyhalogen compounds

The hydrocarbons or any carbon compounds containing more than one halogen atom (group 17 elements of the modern periodic table) are known as ***polyhalogen compounds.***

1. Dichloromethane CH_2Cl_2.

Dichloromethane is a geminal organic compound and is also called Methylene chloride or Methylene dichloride. The majority of Methylene dichloride in the environment is due to industrial emissions. Dichloromethane is used as a solvent in food technology.,aerosol formulations., a solvent in the manufacturing of pharmaceutical products., degreasing agent.

2. Trichloromethane (Chloroform) $CHCl_3$.

Chloroform is an organic chemical compound initially employed as an ideal anesthetic.

It is a colourless, sweet-smelling dense liquid produced on a large scale.

Used as an anaesthetic in dentistry during root canal procedures. utilised in the past as an extraction dissolvable for fats, greases, oils, and different items; as a laundry spot,as an indirect food additive in food packaging materials for adhesive components and as a component of food contact materials.

3. Tetra chloromethane (Carbon Tetrachloride) CCl_4.

It is a colourless liquid with a "sweet" smell that can be detected at low levels. It is used in the manufacturing of refrigerants, as a cleaning agent and was also used as a fire extinguisher. When carbon tetrachloride is released into the air, it rises in the atmosphere and depletes the ozone layer. Depletion of the ozone layer is believed to increase human exposure to ultraviolet rays, leading to increased skin cancer, eye diseases and disorders, and possible disruption of the immune system

4. Iodoform CHI_3

Iodoform which is also called triiodomethane is a yellow crystalline solid. It is insoluble in water but soluble in solvents like ethanol, chloroform, and ether.It is hydrolyzed to give sodium methanoate (sodium formate) when treated with an aqueous sodium hydroxide solution.

Iodoform was used earlier as an antiseptic but the antiseptic properties are due to the liberation of free iodine and not due to the iodoform itself. Due to its objectionable smell, it has been replaced by other formulations containing iodine.

5. Freons (CFCs) :Freons are the chlorofluorocarbon compounds of methane and ethane. The chlorofluorocarbon compounds containing carbon, fluorine, and chlorine. They are extremely stable, unreactive, non-toxic, non-corrosive and easily liquefiable gases.

Freon 12 or R-12 (CCl_2F_2) is one of the most common representatives of this group. It is manufactured from tetra chloromethane by Swarts reaction.

These are usually produced for aerosol propellants, refrigeration and air conditioning purposes.

6. DDT (*p, p'*-Dichlorodiphenyltrichloroethane)

It is a colourless, crystalline, tasteless and almost odourless organochloride known for its insecticidal effect. It is effective against the mosquito that spreads malaria and lice that carry typhus.But due to the ill effects of DDT such as chemical instability and fat solubility, it got banned in many countries.

ASSERTION-REASON TYPE OF QUESTIONS

The question given below consist of an assertion and a reason use the following key to choose appropriate answer

a) Both assertion and reason are correct and reason is the correct explanation of the assertion
b) Both assertion and reason are correct and reason is not the correct explanation of the assertion
c) Assertion is correct but reason is incorrect
d) Assertion is wrong Reason is correct.

1) **Assertion**: Alkyl halides are insoluble in water
Reason: Energy is required to break H bonds in water

2) **Assertion**: Para chloro-benzene is having higher melting point than other two isomers
Reason: Due to symmetry molecule is well fit in to the lattice.

3) **Assertion:** Tertiary alkyl halides are least reactive in S_N2 reactions
Reason: Steric hindrance is minimum in tertiary Alkyl halides

4) **Assertion**: Only achiral molecules when undergo substitution, optical rotation changes
Reason: When molecule and its mirror images are non superimposable, they show opticalactivity.

5) **Assertion**: Alkyl iodides are more reactive towards nucleophilic substitution reaction
Reason: C-I bond is stronger than any other carbon halogen bond

6) **Assertion:** The reaction of Arenes and iodine is carried out in presence of HIO_4
Reason: HIO_4 Oxidises HI formed during the reaction to I_2 and prevents backward reaction.

7) **Assertion**: During Finkelstein reaction alkyl chloride is treated with NaI in presence of Acetone
Reason: Acetone is a very good organic solvent

8) **Assertion**: Boiling points of alkyl iodides are lower than that of Alkyl chlorides
Reason: Vander force is more in alkyl iodides due to large size of iodine

9) **Assertion:** Among isomeric alkyl halides straight chain alkyl halides have highest boiling point
Reason: Dispersion force is minimum in branched chain alkyl halides.

10) **Assertion**: Alkyl halides mainly form alkyl cyanides when treated with AgCN
Reason: Due to covalent nature of AgCN attack takes place through Nitrogen.

11) **Assertion**: Alkyl halides forms Nitriles when treated with KCN
Reason: CN^- is an ambident nucleophile

12) **Assertion:** In Mono haloarenes further electrophilic substitution takes place at ortho and para position.
Reason: The lone pair of electrons on Cl is in conjugation with benzene ring, increasingelectron density at ortho and para position...

13) **Assertion**: Nitration of chloro benzene leads to the formation of Meta nitro chlorobenzene.
Reason: NO_2 group is Meta directing towards electrophilic substitution reaction.

14) **Assertion**: Allyl halides react faster in S_N1 reaction
Reason: Allyl cations are stabilized by resonance

15) **Assertion**: Among different halogens alkyl chlorides are more reactive than iodides towards substitution reaction
Reason: C-Cl bond is stronger than C-I bond

16) **Assertion**: Hydrolysis of (-) 2-bromo octane Proceeds with the inversion of configuration
Reason: This reaction proceeds via the formation of carbocation.

17) **Assertion**: Benzyl halides react faster in S_N1 reaction
Reason: Benzyl cations formed is stabilized by resonance.

18) **Assertion**: When 2-bromo butane is treated with alcoholic KOH But-1-ene is the major product
Reason: During dehydrohalogenation reactions more alkylated alkene is the major product.

19 **Assertion**: During the reaction between Tertiary butyl bromide and C_2H_5ONa Alkene is the major product.
Reason: In presence of strong base Elimination competes over substitution.

20) **Assertion**: It is necessary to avoid even traces of water from Grignard reagent.
Reason: Grignard reagent is used in preparing alcohols

21) **Assertion:** It is difficult to break C-X bond in alkyl halides
Reason: C-X bond in aryl halides have partial double character

22) **Assertion**: Propene when treated with HBr form 1- bromo propane as the major product
Reason: During the addition of HBr a secondary carbocation is formed.

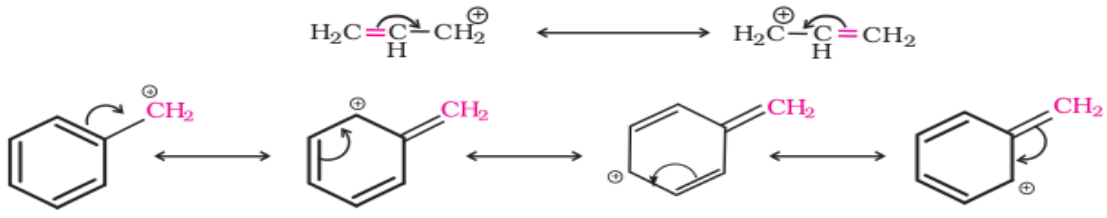
23) **Assertion**: The presence of NO_2 group at ortho position of aryl halides increases reactivity ofhaloarenes towards nucleophilic substitution reaction
Reason: Presence of NO_2 group at ortho and para position of aryl halides reduces the electron density in benzene and hence facilitates the attack.

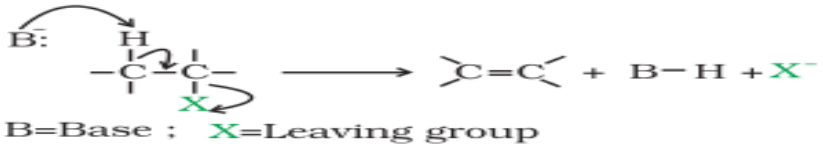
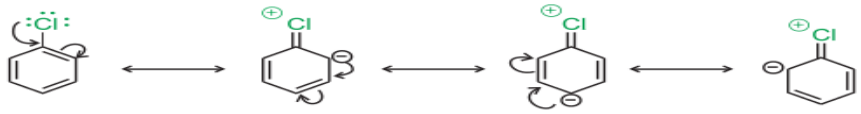
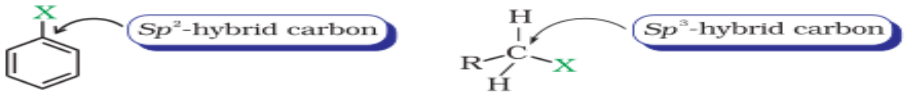
24) **Assertion**: Alkyl halides are more reactive towards nucleophilic substitution reaction comparedto aryl halides
Reason: In alkyl halides halogen is connected to sp^3 hybridised carbon.

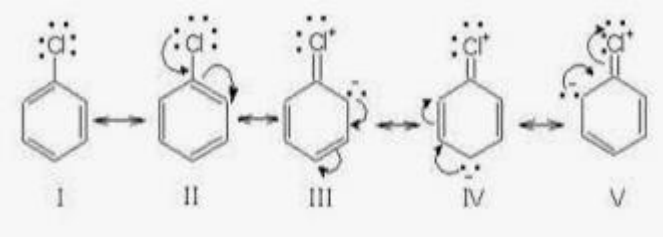
25) **Assertion**: S_N^1 reaction are generally carried out in presence polar protic solvents such as water
Reason: The energy needed to break C-X bond is obtained through solvation of halide ion with proton of protic solvent.

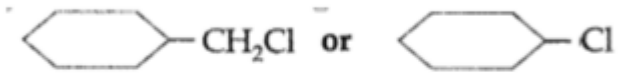
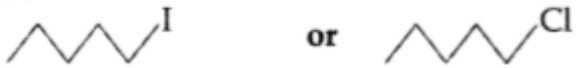
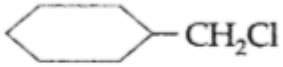
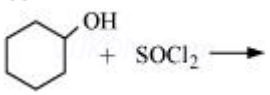
ANSWER KEY

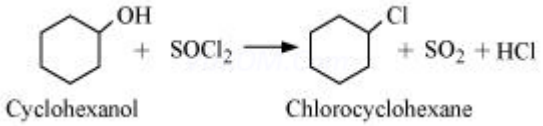
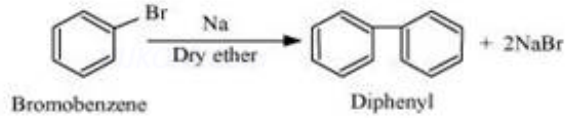
1) b 2) a 3) c 4) d 5) c 6) a 7) b 8) d 9) b 10) d 11) b 12) a 13) d 14) a 15) d 16) c 17) a 18) d 19) a 20) b 21) d 22) d 23) a 24) b 25) a

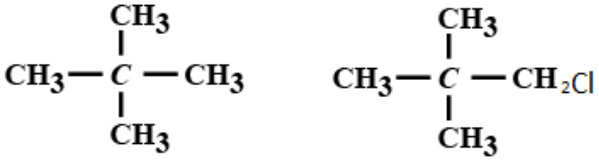
SHORT ANSWER TYPE QUESTIONS		
1	**Why the boiling points of chlorides, bromides and iodides are considerably higher than those of the hydrocarbons of comparable molecular mass?** Due to greater polarity as well as higher molecular mass as compared to the parent hydrocarbon, the intermolecular forces of attraction (dipole-dipole and van der Waals) are stronger in the halogen derivatives	1
2	**The para-isomers of isomeric dihalobenzenes are high melting as compared to their ortho- and meta-isomers.** It is due to symmetry of para-isomers that fits in crystal lattice better as compared to ortho or meta isomer.	1
3	**Haloalkanes react with KCN to form alkyl cyanides as main product while AgCN forms isocyanides as the chief product. Explain.** KCN is predominantly ionic and provides cyanide ions in solution. Both carbon and nitrogen atoms are in a position to donate electron pairs. The attack takes place mainly through carbon 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 isocyanides as the main product.	1
4	**Allylic and benzylic halides show high reactivity towards the S_N1 reaction. Explain The carbocation thus formed gets stabilised through resonance** 	1
5	**Grignard reagents should be prepared under anhydrous conditions. Why?** Grignard reagents are highly reactive and react with any source of proton to give hydrocarbons. $RMgX + H_2O \rightarrow RH + Mg(OH)X$ It is therefore necessary to avoid even traces of moisture from a Grignard reagent	1
6	**What are elimination reactions?**	1

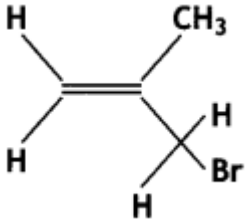
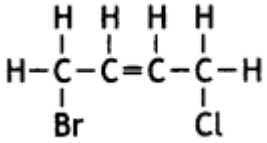
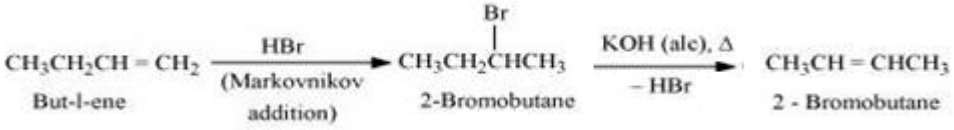
	Ans: When a haloalkane with β-hydrogen atom is heated with alcoholic solution of potassium hydroxide, an alkene is formed as a product. There is elimination of hydrogen atom from β-carbon and a halogen atom from the α-carbon atom . Since β-hydrogen atom is involved in elimination, it is often called β-elimination.  B=Base ; X=Leaving group	
7	**What are chiral and achiral molecules** The objects which are non- superimposable on their mirror image are said to be chiral and this property is known as chirality. The objects, which are, superimposable on their mirror images are called achiral	2
8	**What do you mean by racemic mixture and racemization**? A mixture containing two enantiomers in equal proportions is known as racemic mixture. It will have zero optical rotation, as the rotation due to one isomer will be cancelled by the rotation due to the other isomer. The process of conversion of enantiomers into a racemic mixture is known as racemisation	2
9	**Aryl halides are extremely less reactive towards nucleophilic substitution reactions. Why**? i) Resonance effect In haloarenes, the electron pairs on halogen atom are in conjugation with π-electrons of the ring.C—Cl bond acquires a partial double bond character due to resonance and the bond cleavage in haloarene is difficult.  **ii) Difference in hybridisation of carbon atom in C—X bond** In case of haloarene the sp^2 hybridized 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, haloarene are less reactive than haloalkane 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 stabilized by resonance and therefore, S_N1 mechanism	2

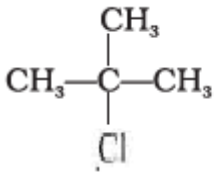
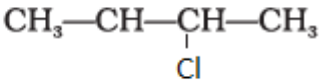
	is ruled out. (iv) Because of the possible repulsion, it is less likely for the electron rich nucleophile to approach electron rich arenes.	
10	**Electrophilic substitution reactions in haloarenes occur slowly and require more drastic conditions as compared to those in benzene. Why?**  • Due to resonance, the electron density increases more at ortho- and para-positions than at meta-positions. • Further, 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	2
11	**Cl is an electron withdrawing group but it is ortho, para- directing in electrophilic aromatic substitution reactions. Why?** • Chlorine withdraws electrons through inductive effect and releases electrons through resonance. • Through inductive effect, chlorine destabilizes the intermediate carbocation and through resonance, halogen tends to stabilize the carbocation and the effect is more pronounced at ortho- and para- positions. • 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.	2
11	**Give chemical tests to distinguish between** **(a) Benzyl chloride & chloro benzene** **(b) Vinyl iodide and ethyl iodide** Ans: (a) On adding NaOH solution & aqueous $AgNO_3$, Benzyl chloride gives white precipitate of AgCl, while chlorobenzene does not react at room temperature. (b) On adding NaOH solution & aqueous $AgNO_3$, ethyl iodide gives yellow precipitate of Agl, while vinyl iodide does not react .	2
12	**What do you mean by retention of configuration and inversion of configuration?** Ans:	2

	Retention of configuration is the preservation of integrity of the spatial arrangement of bonds to an asymmetric centre during a chemical reaction or transformation. Here the optical rotation of the reactant and product are the same **Inversion of configuration** is the inversion of the spatial arrangement of bonds to an asymmetric centre during a chemical reaction or transformation. Here the optical rotation of the reactant and product are different	
13	**Which one of the two compounds reacts faster by S_N2 reaction?** (a)  (b)  Ans: (a)  (b) 	2
14	**Among the isomeric alkyl halides of molecular formula C_4H_9Cl, identify** **(a) The optically active isomer** **(b) The most reactive halide towards S_N1** **(c) The isomer with lowest boiling point** Ans: draw the structure and find out the isomer (a) sec- Butyl chloride $CH_3CH(Cl)CH_2CH_3$ (b) tert- Butyl chloride $(CH_3)_3$ C Cl (c) tert- Butyl chloride $(CH_3)_3$ C Cl	3
15	**Complete the reactions:** (a) $CH_3CH_2Br + AgCN \rightarrow$ Dry ether (b) $CH_3CH_2Br + Na \rightarrow$. c)  Ans: (a) $CH_3CH_2Br + AgCN \rightarrow CH_3CH_2NC + AgCl$	3

	(b) $CH_3CH_2Br + Na \xrightarrow{\text{Dry ether}} CH_3CH_2\ CH_2CH_3 + NaBr$ (c)  Cyclohexanol Chlorocyclohexane	
16	**Write short notes on a) Finkelstein reaction b) Swarts reactions c) Fittig reaction** Ans: a) Finkelstein reaction: Alkyl chlorides or bromides when treated with NaI in dry acetone, alkyl iodides are formed. This reaction is known as Finkelstein reaction. $R\text{-}X + NaI \xrightarrow{\text{Dry acetone}} R\text{-}I + NaX$ (where X = Cl, Br) b) Swarts reaction: This method is used for the preparation of alkyl fluorides. Here alkyl chloride or bromide is treated with a metallic fluoride like AgF, Hg_2F_2, CoF_2 or SbF_3, to get alkyl fluoride. $R\text{-}X + AgF \rightarrow R\text{-}F + AgX$ (where X = Cl or Br) $2\ R\text{-}X + CoF_2 \rightarrow 2\ R\text{-}F + CoX_2$ c) Aryl halide on treatment with sodium metal in presence of ether gives diphenyl and is called Fittig reaction  Bromobenzene Diphenyl	3
17	**a) State i) Zaitsev (Saytzeff) rule** **ii)Markownikoff's rule** b) **What happens when methyl chloride is treated with KCN.** Ans: a) i) Zaitsev (Saytzeff) rule. The rule states that "in dehydrohalogenation reactions, if there is possibility of formation of more than one alkene the preferred product is that alkene which contains greater number of alkyl groups attached to the doubly bonded carbon atoms." ii)Markownikoff's rule. The rule states that "when an unsymmetrical reagent is added to an unsymmetrical alkene, the positive part of the addendum (adding molecule) goes and attaches to the double bonded carbon containing more number of	3

	hydrogen and the negative part of the addendum gets attached to the double bonded carbon containing lesser number of hydrogen atoms b) When methyl chloride is treated with KCN, it undergoes a substitution reaction to give methyl cyanide. $CH_3Cl + KCN \rightarrow CH_3CN + KCl$	
18	**Give reasons** **a) Chloroform is stored in amber coloured bottle.** **b) Wurtz reaction cannot be used to prepare alkanes containing odd the number of carbon atom.** c) **Sulphuric acid not used during the reaction of alcohols with KI** Ans: a) Chloroform is slowly oxidised by air in the presence of light to an extremely poisonous gas, carbonyl chloride (COCl2), also known as phosgene. $2CHCl_3 + O_2 \xrightarrow{\text{light}} 2COCl_2 + HCl$ b) Wurtz reaction not preferred for the preparation of alkane containing an odd number of carbon atoms **due to the formation of a number of products**. When two different types of alkyl halides are taken, a mixture of three alkanes with odd and even numbers of carbon atoms are obtained. c) In the presence of sulphuric acid(H_2SO_4), KI produces HI $2KI + H_2SO_4 \longrightarrow 2KHSO_4 + 2HI$ Since H_2SO_4 is an oxidizing agent, it oxidizes HI produced in the reaction to I_2) $2HI + H_2SO_4 \longrightarrow I_2 + SO_2 + H_2O$ Henceit will not produce alkyl iodides	3
19	**A hydrocarbon alkane (A), having molecular mass 72g/mol gives only one mono-chlorination product. Identify the hydrocarbon. and write the mono chlorinated product** **Ans:** Since it is an alkane, its formula is C_nH_{2n+2} ∴ 12n+2n+2=72 n = 5 **(A)** has the molecular formula C_5H_{12} The isomer of pentane which yield single monochloro derivative should have all the 12 hydrogen's equivalent. Neopentane (2,2 - dimethyl propane) is the only possibility. The monochlorinated product is neopentyl chloride (1-chloro-2,,2-dimethyl propane)  Neopentane neopentyl chloride	3

20	**a) Write the IUPAC name of the following compound**  **b) Write the structure of 1-Bromo-4- chlorobut-2-ene** **c) How will you bring about the following conversion?** **But-1-ene to but-2-ene** Ans: a) 3-Bromo- 2-methylpropene b)  c)  	3

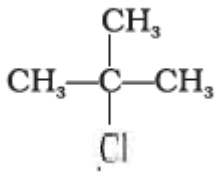
	LONG ANSWER TYPE OF QUESTIONS	
1	a) **Compound (A) with molecular formula C_4H_9Cl is treated with aq. NaOH solution. The rate of this reaction depends upon the concentration of the compound 'A' only. When an optically active isomer 'B' of this compound was treated with aq. NaOH solution, the rate of reaction was found to be dependent on concentration of compound an NaOH both.** **(i) Write down the structural formula of both compounds 'A' and 'B'.** **(ii) Out of these two compounds, which one will be converted to the product with inverted configuration.** **(iii) which one will undergo racemisation on treatment with aq. NaOH.** b) **Arrange each set of compounds in order of increasing boiling points.** **(i) Bromo methane, Bromoform, Chloromethane, Dibromo methane.** **(ii) 1-Chloropropane, Isopropyl chloride, 1-Chlorobutane.** Ans:a) i)  A  B	5

ii)Alkyl halides on treatment with aq. KOH gives alcohol as the major product.

$C_4H_9Cl + NaOH(aq) \rightarrow C_4H_9OH + NaCl$

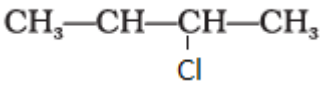
In the case of compound .A. rate of reaction depends upon the concentration of .A. only, the reaction proceeds through the S_N1 mechanism as the alkyl halide is a tertiary alkyl halide.

A should be

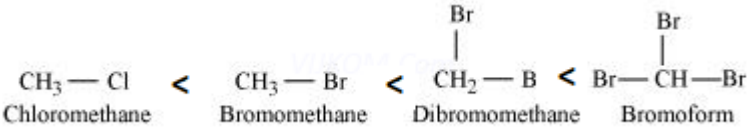


iii)In the case of compound .B. which is an optically active isomer of .A., rate of reaction depends upon the concentration of .B. as well as NaOH. Therefore, the reaction occurs by SN^2 mechanism which is favoured by 1^o and 2° alkyl halides.

The compound B is

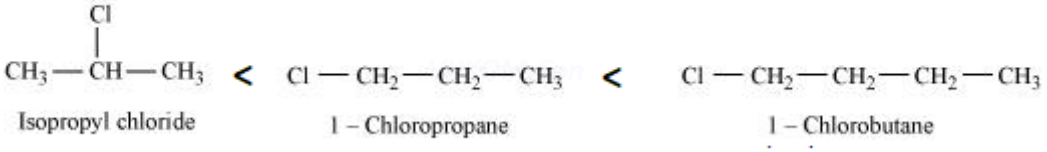


b) i)



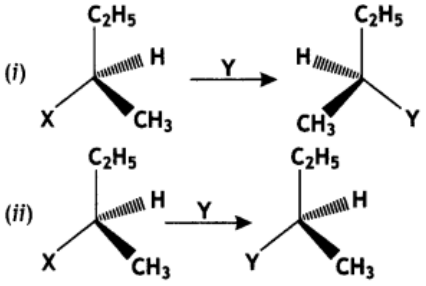
For alkyl halides containing the same alkyl group, the boiling point increases with an increase in the atomic mass of the halogen atom and the no. of halogen atom

(ii)



Straight chain compound are having more boiling point than branched compound because of more van der waals force of attraction.

2 a) Which of the following two reactions is S_N2 and why? 5



b) How will you distinguish the presence butane and butane

c) How would you carry out the following conversions?

i) Benzyl chloride to benzyl alcohol

ii) Aniline to bromobenzene

iii) Benzene to 4-bromonitrobenzene

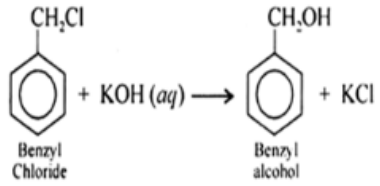
Answer:

a) Reaction (i) is SN^2 because it proceeds by inversion of configuration

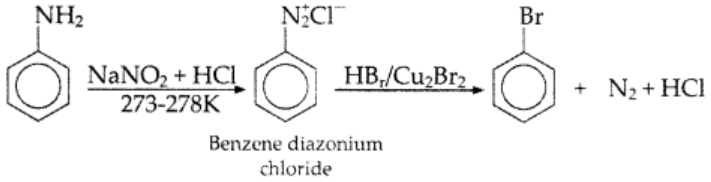
b)

Unsaturated compounds gives addition reaction with Br_2 water and decolourise it but saturated ccmpounds does not give addition reactions. Hence they can be distinguish by flame test as well as by bromine water test.Br_2 water is a brown coloured liquid.. Butene being an unsaturated compound decolourises bromime water but not butane.

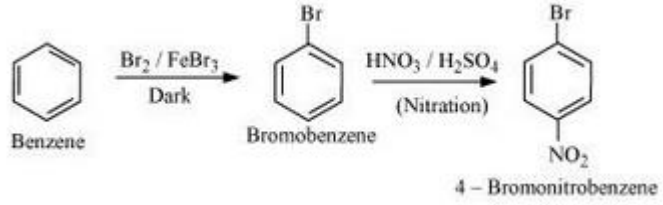
c) i)



ii)



iii)

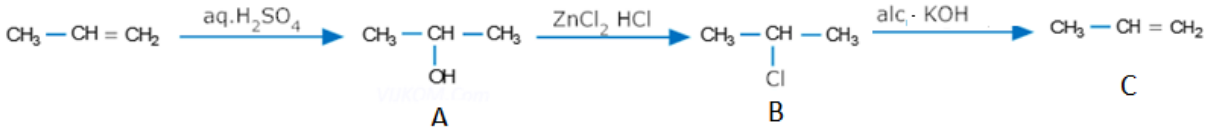


3 **a)An organic compound 'A' having molecular formula C_3H_6 on treatment with aqueous sulphuric acid given' B' which on treatment with Lucas reagent gives 'C'. The compound 'C' on treatment with ethanolic KOH gives back on compound 'A'. Identify A, B, & C.**

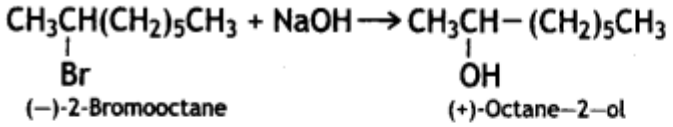
b) Propose the mechanism of the reaction taking place when

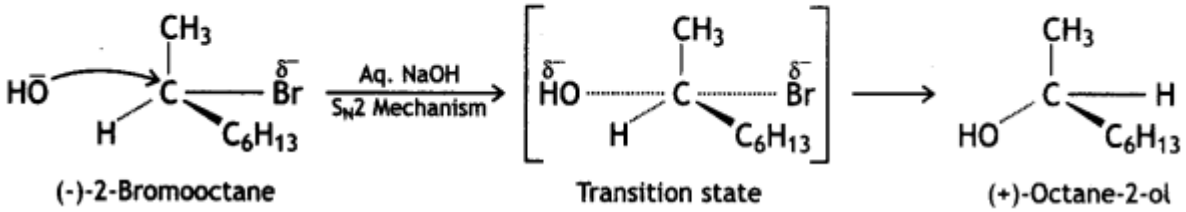
(i) (-) – 2 – Bromooctane reacts with sodium hydroxide to form (+) – octane-2-ol.

Ans. a)



b)

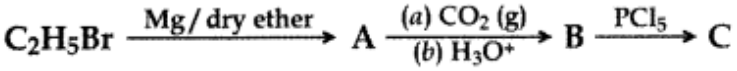




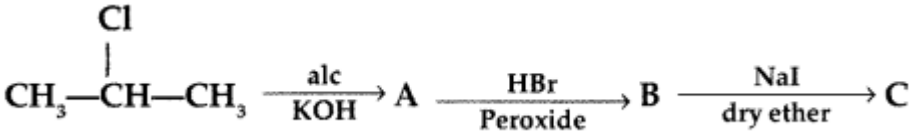
(-)-2-Bromooctane

4 a) **Write structures of compounds A, B and C in each of the following reactions**:

i)



ii)



b) Give reasons for the following:

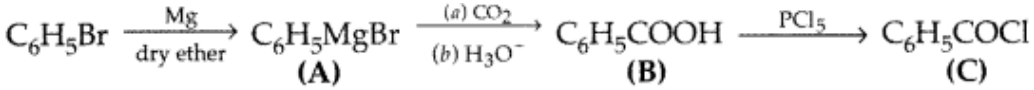
(i) Benzyl chloride is highly reactive towards the S_N^1 reaction.

(ii) 2-bromobutane is optically active but 1-bromobutane is optically inactive.

(iii) Electrophilic reactions in haloarenes occur slowly.

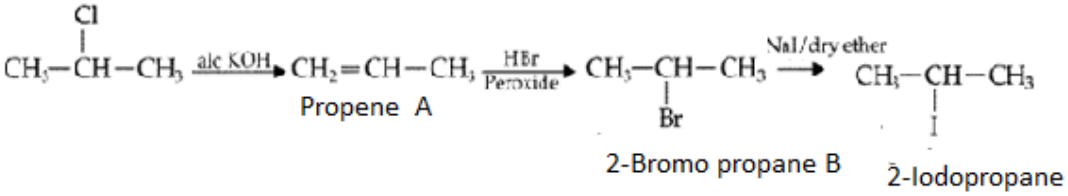
Ans:

a) i)



A = Phenylmagnesium bromide
B = Benzoic acid
C = Benzoyl chloride

ii)



b) (i) Benzyl carbonium ion is stabilized by resonance.
(ii) 2-Bromobutane is chiral, therefore, optically active, whereas 1 -chlorobutane is not chiral, therefore optically inactive.
(iii) It is due to —I effect of halogens, it deactivates benzene ring towards electrophilic substitution reactions.

5

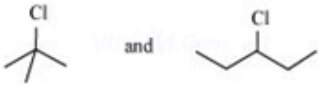
a) Give reason

i) **Dextro- and laevorotatory isomers of Butan-2-ol difficult to separate by fractional distillation**

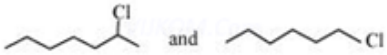
ii) **(±) 2 – Butanol is optically inactive.**

b) **In the following pairs of compounds which compound undergoes S_N1 reactions**

(i)



(ii)



c) **How will convert propene to propyne**

Ans:

a) **i)** Dextro- and laevorotatory isomers of butan-2-ol are enantiomers of each other and both have the same boiling point. Hence, these cannot be separated by fractional distillation

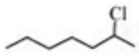
ii)(±) 2 – Butanol represents a racemic mixture of (+) 2-butanol and (-) 2-butanol which rotate the plane polarized light in different directions but to an equal extent. Therefore, the (±) compound is optically inactive

b)

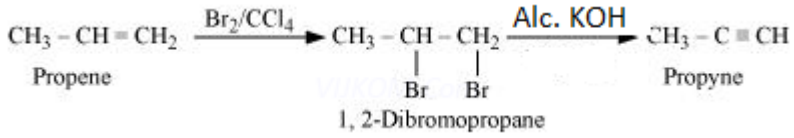
Ans. (i)

2 – Chloro – 2 – methylpropane (3°)
(I)

(ii)



c)



Propene

1, 2-Dibromopropane

Propyne

CASE BASED QUESTIONS

Case i) Read the following passage and answer the questions given below.

Alkyl halides are best prepared from alcohols, on treating with Hydrogen halides, phosphorus halides or thionyl chloride. Thionyl chloride is preferred because other two products are escapable gases. The reaction of primary secondary and tertiary alcohols with HCl need a catalyst $ZnCl_2$. With tertiary alcohol the reaction is conducted by shaking with Con. HCl at room

temperature. Tertiary alcohols are more reactive. The above methods are not applicable for the preparation of Aryl halides because the carbon oxygen bond in phenols has a partial double bond character and is difficult to break being stronger than a single bond

A statement of assertion is followed by a statement of reason. Mark the correct choice from the options given below :

(a) Both assertion and reason are true and reason is the correct explanation of assertion.
(b) Both assertion and reason are true but reason is not the correct explanation of assertion.
(c) Assertion is true but reason is false.
(d) Assertion is false but reason is true

1) **Assertion**: Thionyl chloride is the best reagent to convert alcohols to Alkyl chlorides
Reason: With Thionyl chloride alkyl chloride is the only product formed.
2) **Assertion**: Primary secondary and tertiary alcohols can be distinguished using Lucas test
Reason: Tertiary alcohols immediately form turbidity due to the formation of alkyl halides.
3) **Assertion**: Primary alcohols react fast with HCl and forms alkyl halide at room temperature.
Reason: Alkyl halides are insoluble in water.
4) **Assertion**: Aryl halides can be prepared by treating phenols with halogen acid
Reason: In phenol C-O bond is having partial double bond character.

Case ii) Read the following passage and answer the questions given below.

S_N^1 reactions are generally carried out in presence of protic solvents. Like acetic acid. The reaction between a tertiary alkyl halide and nucleophile follows the first order kinetics. The rate of reaction depends on the concentration of alkyl halide .it occurs in two steps. In first step step C-X bond undergoes cleavage to form carbocation, it is then attacked by nucleophile in second step which is very fast. The energy needed for breaking C-X bond is obtained through solvationof halide ion with proton of protic solvent. Greater the stability of carbocation, Greater will be itsease of formation and faster will be its rate of reaction. In the case of optically active alkyl halide S_N1 reaction is accompanied by Racemisation. The carbocation formed in step one is sp^2 hybridised. Which is triagonal planar. The attack of nucleophile may be accomplished from either side to give a mixture of products.

5) **Assertion:** S_N2 reaction takes place in presence of protic solvent.
Reason: The energy is released by the solvation of halide ion with proton.

6) **Assertion**. The rate of S_N^1 reaction depends only on the concentration of alkyl halide.

Reason: Formation of carbocation is slow step and slow step determines the rate of reaction.

7) **Assertion**: Tertiary alkyl halides reacts faster in S_N^1 reaction

Reason. Tertiary carbocations are more stable and formed at faster rate.

8) **Assertion**: During S_N^1 reaction of an optically active alkyl halide Racemisation takes place

Reason. Racemic mixture consists of equal amount of dextro and leavo isomer.

9) **Assertion:** Attack of nucleophile to carbon of carbocation takes place through either sideforming two isomers with opposite configuration.
Reason: Carbocation is sp^3 hybridised and have triogonal planar geometry

10) **Assertion**: - In S_N1 reaction second step is very fast and reversible.

Reason: - The carbocation formed is highly unstable and highly reactive.

OR

Read the passage given below and answer the following questions:

Nucleophilic substitution reactions are of two types; substitution nucleophilic bimolecular (S_N2) and substitution nucleophilic unimolecular (S_N1) depending on molecules taking part in determining the rate of reaction. Reactivity of alkyl halide towards S_N1 and S_N2 reactions depends on various factors such as steric hindrance, stability of intermediate or transition state and polarity of solvent. S_N2 reaction mechanism is favoured mostly by primary alkyl halide then secondary and then tertiary. This order is reversed in case of S_N1 reactions.

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

(i) Which of the following is most reactive towards nucleophilic substitution reaction?

(a) C_6H_5Cl **(b)** $CH_2=CHCl$ **(c)** $ClCH_2CH=CH_2$ **(d)** $CH_3CH=CHCl$

(ii) Isopropyl chloride undergoes hydrolysis by

(a) $S_N1$mechanism **(b) $S_N2$mechanism** **(c) S_N1 and $S_N2$mechanism** **(d) neither S_N1 and $S_N2$mechanism**

(iii) The most reactive nucleophile among the following is

(a) CH_3O^- **(b) $C_6H_5O^-$** **(c) $(CH_3)_2CHO^-$** **(d) $(CH_3)_3CO^-$**

(iv) Tertiary alkyl halides are practically inert to substitution by $S_N2$mechanism because of

(a) insolubility **(b) instability** **(c) inductive effect** **(d) stearic hindrance.**

ANSWER KEY

1)c 2) b 3) d 4) d 5) d 6) a 7) a 8) b 9) c 10) d

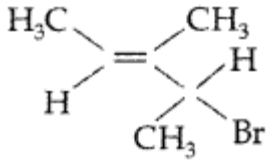
OR

i) C ii)C iii)A iv)D

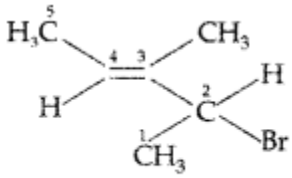
CBSE BOARD QUESTIONS

1. Question 2.

Give the IUPAC name of the following compound :



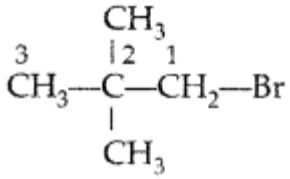
Answer:



IUPAC name : *2-Bromo-3-methylpent-3-ene*

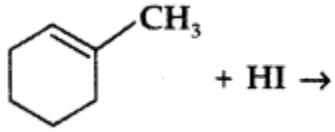
2. **Write the IUPAC name of the following compound : $(CH_3)_3$ CCH_2Br**

Answer:

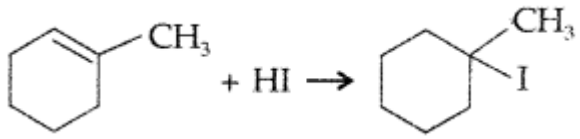


IUPAC name : 1-bromo-2, 2-dimethyl propane

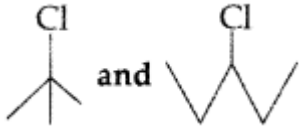
3. **Draw the structure of major monohalogen product formed in the following reaction**



Answer:



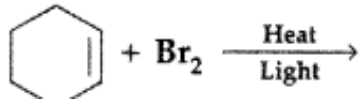
4. **In the following pair of compounds, which will react faster by S_N1 mechanism and why?**



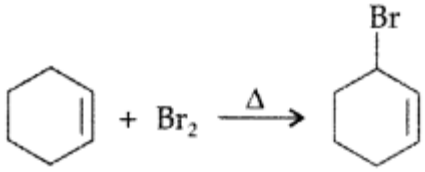
Answer:

reacts faster by S_N1 mechanism as it is a tertiary halide and it produces a stable tertiary carbocation.

5. **Draw the structure of major monohalogen product in the following reaction**



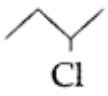
Answer:



6. **Arrange the following in increasing order of boiling point:**
(i) $CH_3CH_2CH_2CH_2Br$
(ii) $(CH_3)_3.Br$
(iii) $(CH_3)_2C.Br$
Answer:
$(CH_3)_2C.Br < (CH_3)_2.CHCH_2.Br < CH_3CH_2CH_2CH_2Br$

7. **Identify the chiral molecule in the following pair : (All India 2014)**

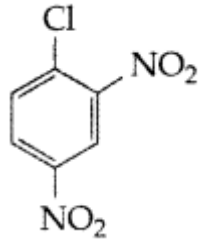
Answer:



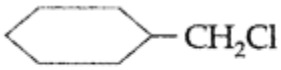
(2-Chlorobutane) is a chiral molecule.

8. **Write the structure of 2, 4-dinitrochlorobenzene.**

Answer:



9. **Which one in the following pairs of substances undergoes S_N2 substitution reaction faster and why?**

(*i*)  **or** 

(*ii*)  **or** 

Answer:

(*ii*)  (*i*)  CH_2Cl is a primary halide and grou therefore undergoes S_N2 reaction faster. undergoes S_N2 reaction faster.

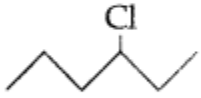
10. **Which one in the following pairs undergoes S_N1 substitution reaction faster and why?**

(*i*)  **or** 

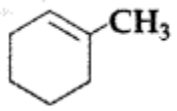
(*ii*)  **or** 

Answer:

(*i*)  (3° alkyl halide) reacts faster than  (2° alkyl halide) due to greater stability of 3° carbocations over 2° carbocation.

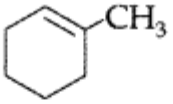
(*ii*) As  is a secondary alkyl halide which reacts faster in S_N1 reaction than 1° alkyl halide  due to greater stability of 2° carbocations over 1° carbocations.

11. **Complete the following reaction equations**

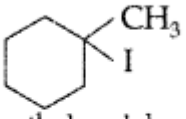
(*i*)  + HI ⟶

(*ii*) $CH_3CH_2CH = CH_2 + HBr \rightarrow$

Answer:

(*i*)  + HI $\xrightarrow{\text{Mark.addn.}}$

1-Methyl-1-cyclohexene



1-Iodo-1-methyl cyclohexane

(*ii*) $CH_3CH_2CH = CH_2 + HBr \xrightarrow{\text{Mark.addn.}}$

1-Butene

$CH_3—CH_2\underset{\displaystyle Br}{\underset{|}{C}}H—CH_3$

2-Bromobutane

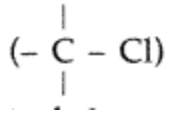
12. **Account for the following:**

(i) The C – Cl bond length in chlorobenzene is shorter than that in CH_3 – Cl.

(ii) Chloroform is stored in closed dark brown bottles.

Answer:

(i) In haloalkanes, the halogen atom is attached



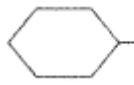
to sp^3-hybridized carbon while in haloarenes it is attached to sp^2 -hybridized carbon whose size is smaller than sp^3 orbital carbon. Therefore C – Cl bond in chloro-benzene is shorter than alkyl chloride.

(ii) $CHCl_3$ is stored in dark coloured bottles to cut off light because $CHCl_3$is slowly oxidised by air in presence of light to form an extremely poisonous gas, carbonyl chloride, popularly known as phosgene.

$$2CHCl_3 + O_2 \xrightarrow{\text{Light}} 2O = C\begin{matrix}Cl\\Cl\end{matrix} + 2HClZ$$

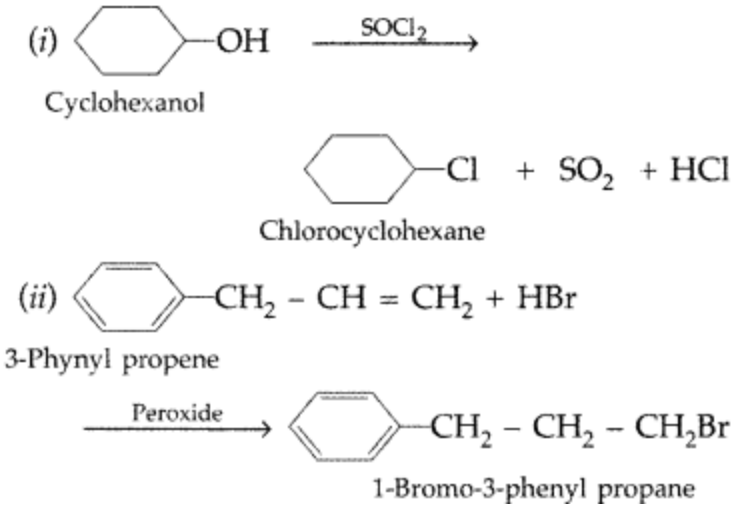
Choloform — Phosgene or Carbonyl chloride

13. **Draw the structure of major monohalo product in each of the following reactions**

(*i*)  $\xrightarrow{SOCl_2}$

(*ii*)  $CH_2 - CH = CH_2 + HBr \xrightarrow{\text{Peroxide}}$

Answer:



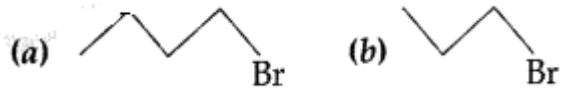
14. **Which compound in each of the following pairs will react faster in S_N2 reaction with —OH? (i) CH_3Br or CH_3I (ii) $(CH_3)_3$ CCl or CH_3Cl**

Answer:

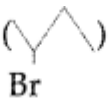
(i) CH_3I: Because Iodide is better leaving group than bromide.

(ii) CH_3Cl : Carbon atom leaving group is less hindered.

15. **Which alkyl halide from the following pair is (i) Chiral and (ii) undergoes S_N2 reaction faster**?



Answer:

(i) 2-bromobutane () is a chiral compound and 1 Bromo Butane undergoes S_N2 reaction faster.

16. **How will you carry out the following conversions :**

(i) 2-Bromopropane to 1-bromopropane

(ii) Benzene to p-chloronitrobenzene

Answer:

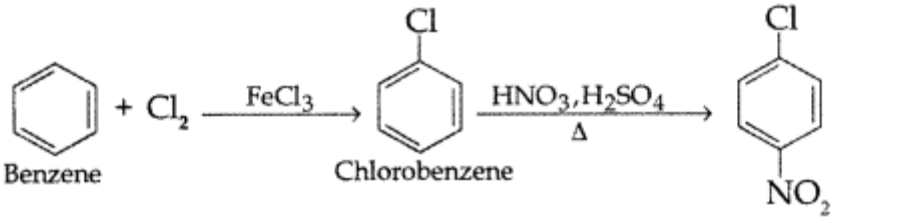
(*i*) $CH_3CH(Br)CH_3$ + alc. KOH ⟶ $CH_3CH{=}CH_2$ + KBr + H_2O

2-Bromopropane → Propene

Propene —(Peroxide + HBr)→ $CH_3CH_2CH_2Br$

1-Bromopropane

(*ii*) **Benzene to p-chloronitrobenzene**



Benzene → Chlorobenzene → p-chloronitrobenzene

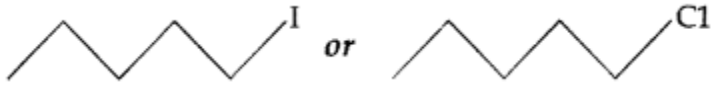
17. **Answer the following questions**

(i) What is meant by chirality of a compound? Give an example.

(ii) Which one of the following compounds is more easily hydrolyzed by KOH and why?

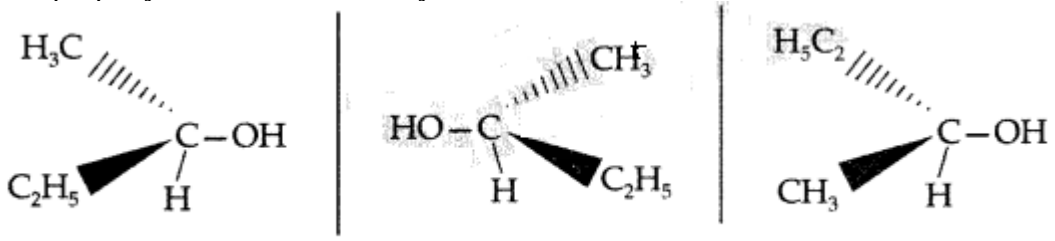
$CH_3CHClCH_2CH_3$ or $CH_3CH_2CH_2Cl$

(iii) Which one undergoes S_N2 substitution reaction faster and why?



Answer:

(i) Chirality : The objects which are non-superimposable on their mirror image are said to be chiral and this property is known as chirality for Butan-2-ol



A B C

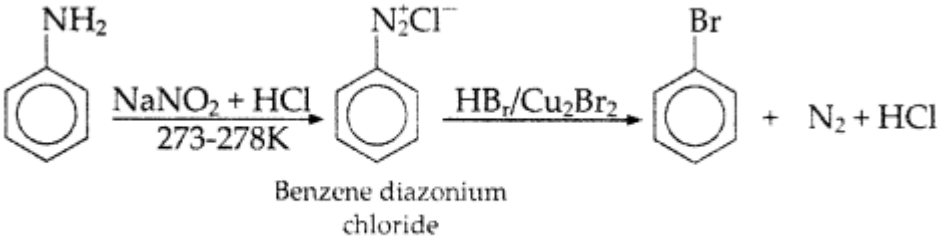
C is non-superimposable on its mirror image A.

(*ii*) $CH_3-\underset{\underset{Cl}{|}}{CH}-CH_2-CH_3$ is more easily hydrolysed by KOH as it forms II° carbocation where $CH_3CH_2CH_2Cl$ will form I° carbocation. II° carbocation is more stable than I°.

(iii) As I is a better leaving group because of its large size, it will be released at a faster rate in the presence of incoming nucleophile.

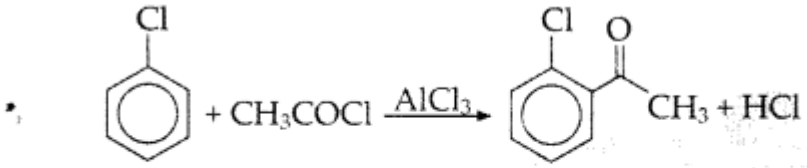
Therefore  will undergo S_N2 substitution reaction faster.

18. **How can the following conversions be carried out :**
(i) Aniline to bromobenzene
(ii) Chlorobenzene to 2-chloroacetophenone
(iii) Chloroethane to butane
Answer:
(i) Aniline to bromobenzene



Benzene diazonium chloride

(*ii*) Chlorobenzene to 2-chloroacetophenone



(*iii*) Chloroethane to butane

$$2CH_3CH_2Cl + 2Na \xrightarrow{\text{Dry ether}} CH_3CH_2{-}CH_2{-}CH_3 + 2NaCl$$

19. **Write structures of compounds A, B and C in each of the following reactions**

$$C_2H_5Br \xrightarrow{Mg/\text{dry ether}} A \xrightarrow[(b)\ H_3O^+]{(a)\ CO_2\ (g)} B \xrightarrow{PCl_5} C$$

Answer:

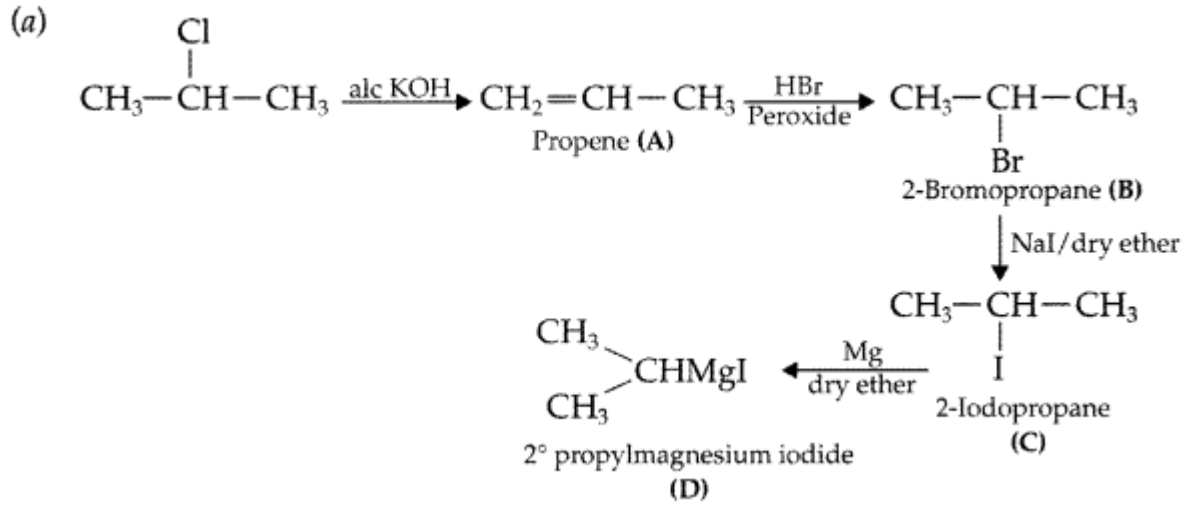
$$C_6H_5Br \xrightarrow[\text{dry ether}]{Mg} \underset{\textbf{(A)}}{C_6H_5MgBr} \xrightarrow[(b)\ H_3O^-]{(a)\ CO_2} \underset{\textbf{(B)}}{C_6H_5COOH} \xrightarrow{PCl_5} \underset{\textbf{(C)}}{C_6H_5COCl}$$

A = Phenylmagnesium bromide
B = Benzoic acid
C = Benzoyl chloride

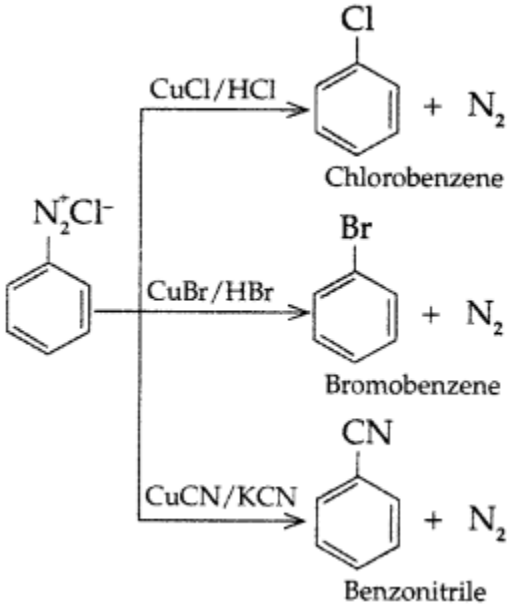
20. **a) Write the structural formula of A, B, C and D in the following sequence of reaction:**

$$CH_3{-}\underset{\displaystyle Cl}{\underset{|}{CH}}{-}CH_3 \xrightarrow[KOH]{alc} A \xrightarrow[Peroxide]{HBr} B \xrightarrow[\text{dry ether}]{NaI} C \xrightarrow[\text{dry ether}]{Mg} D$$

(b) **Illustrate Sandmeyer's reaction with the help of a suitable example.**
Answer:



(b) Sandmeyer's reaction: The substitution of diazo group of benzene diazonium chloride by Chloro, Bromo and Cyano group with the help of solution of CuCl dissolved in HC1, CuBr/HBr and CuCN/KCN respectively is known as Sandmeyer's reaction.



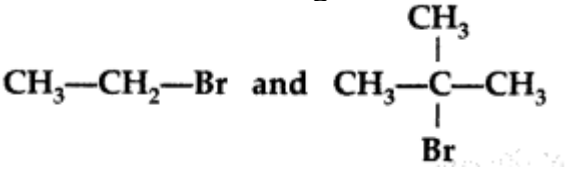
21. **Predict the order of reactivity of four isomeric bromobutanes in S_N1 reaction.**
Answer:

$$CH_3CH_2CH_2CH_2Br < (CH_3)_2CHCH_2Br < CH_3\underset{\underset{Br}{|}}{CH}CH_2CH_3 < (CH_3)_3CBr$$

22. **Predict the order of reactivity of the following compounds in S_N1 reaction :**
$C_6H_5CH_2Br$, $C_6H_5C(CH_3)(C_6H_5)Br$, $C_6H_5CH(C_6H_5)Br$, $C_6H_5CH(CH_3)Br$

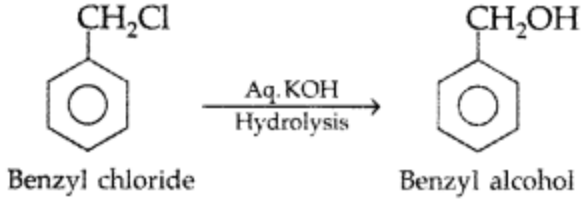
Answer:
$C_6H_5C(CH_3)(C_6H_5)Br > C_6H_5CH(C_6H_5)Br > C_6H_5CH(CH_3)Br > C_6H_5CH_2Br$

23. **Which would undergo S_N2 reaction faster in the following pair and why?**

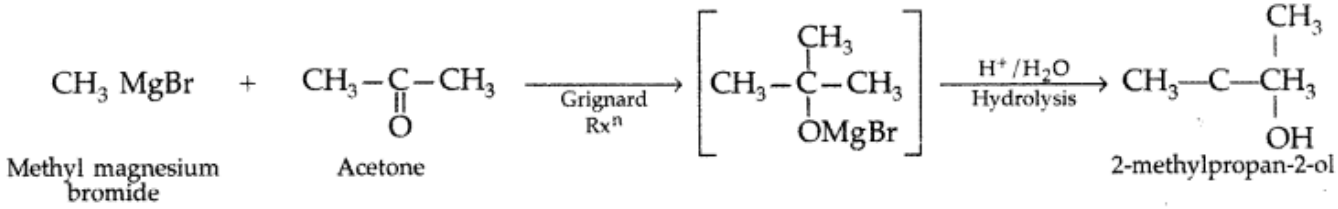


Answer:
CH_3CH_2Br reacts faster because it is a primary halide (1° halide).

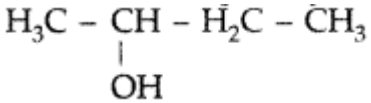
24. **How are the following conversions carried out?**
(i) Benzyl chloride to benzyl alcohol,
(ii) Methyl magnesium bromide to 2-methyl- propan-2-ol.
Answer:
(i) Benzyl chloride to benzyl alcohol



(ii) Methyl magnesium bromide to 2-methylpropan-2-ol

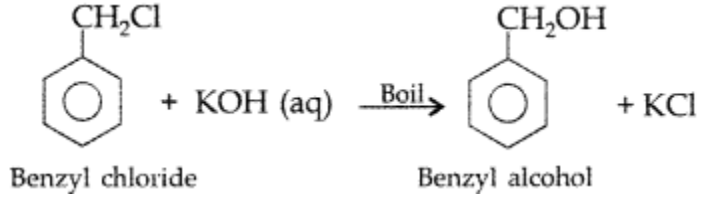


25**. (a) Why does p-dichlorobenzene have a higher m.p. than its o- and m-isomers?**
(b) Why is (±)-Butan-2-ol optically inactive?
Answer:
(a) p-isomers are comparetively more symmetrical and fit closely in the crystal lattice, thus require more heat to break these strong forces of attraction. Therefore higher melting point than o- and m-isomers.
(b) (±)-Butan-2-ol is optically inactive because in racemic mix one type of rotation is cancelled by other.



26. **Give chemical tests to distinguish between the following pairs of compounds :**
(a) Benzyl chloride and Chlorobenzene
(b) Chloroform and Carbon tetrachloride
Answer:

(a) Chlorobenzene and Benzyl chloride :
Benzyl chloride is more reactive than chlorobenzene towards nucleophillic substitution reactions, therefore, benzyl chloride on boiling with aqueous KOH produces benzyl alcohol and KCl.



The reaction mixture on acidification with dil. HNO_3 followed by treatment with $AgNO_3$ solution produces white ppt. of AgCl due to formation of KCl

$$KCl + AgNO_3 \longrightarrow \underset{\text{white ppt.}}{AgCl\downarrow} + KNO_3$$

But chlorobenzene does not undergo hydrolysis under these mild conditions to give phenol and KCl.
(b) Chloroform and Carbon tetrachloride
By Carbylamine test: CCl_4 does not give this reaction but chloroform gives this reaction and produces offensive smell of phenyl isocyanide.

$$\underset{\text{Chloroform}}{CHCl_3} + \underset{\text{Aniline}}{C_6H_5NH_2} + 3KOH\ (alc.) \xrightarrow{\Delta}$$

$$\underset{\text{Phenyl isocyanide}}{C_6H_5N} \rightrightarrows C + 3KCl + 3H_2O$$

27. **Account for the following :**
(a) The dipole moment of chlorobenzene is lower than that of cyclohexyl chloride.
(b) Alkyl halides, though polar, are immiscible with water.
(c) Grignard's reagents should be prepared under anhydrous conditions.
Answer:
(a) Electron pairs of Cl atom are in conjugation with n electrons of the benzene ring so C-Cl bond in chlorobenzene
acquires some double bond character while C-Cl bond in cyclohexyl chloride is a pure single bond.
C – Cl bond in chlorobenzene is shorter than in cyclohexyl chloride. Since dipole moment is a product of charge and distance, so chlorobenzene has lower dipole moment than cyclohexyl chloride.

(b) Alkyl halides are polar molecules, therefore, their molecules are held together by dipole-dipole attraction. The molecules of H_2O are held together by H-bonds. Since the new forces of attraction between water and alkyl halide molecules are weaker than the forces of attraction already existing between alkyl halide- alkyl halide molecules and water- water molecules, therefore, alkyl halides are immiscible with water.

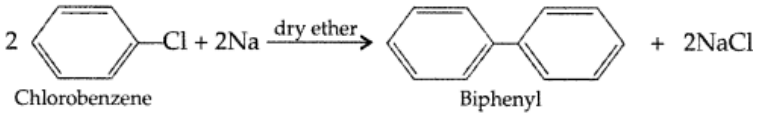
(c) Grignard's reagents are very reactive. They react with alcohol, water, amines etc. to form corresponding hydrocarbon.
R-MgX + HOH → RH + Mg(OH)X
Therefore, Grignard's reagents must be prepared under anhydrous conditions.

28. **Give reasons :**
(a) n-Butyl bromide has higher boiling point than f-butyl bromide.

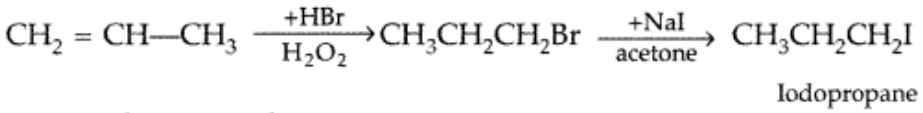
(b) Racemic mixture is optically inactive.
(c) The presence of nitro group (-NO_2) at o/p positions increases the reactivity of haloarenes towards nucleophilic substitution reactions.
Answer:
(a) n-Butyl bromide has higher boiling point than f-butyl bromide because it has larger surface area hence have more Van der Waals' forces.
(b) Rotation due to one enantiomer is cancelled by another enantiomer.
(c) The presence of nitro group (-NO_2) at ortho and para positions withdraws the electron density' from benzene ring and thus facilitating the attack of nucleophile.

29. **a) Account for the following :**
(i) Electrophilic substitution reactions in haloarenes occur slowly.
(ii) Haloalkanes, though polar, are insoluble in water.
(b) Arrange the following compounds in increasing order of reactivity towards S_N2 displacement: 2-Bromo-2-Methylbutane, 1-Bromopentane, 2-Bromopentane (Comptt. All India 2017)
Answer:
(a) (i) Due to -I effect of halogen atom, it withdraws electrons from the benzene ring and thus ring gets deactivated.
(ii) They fail to form hydrogen bonds with water. More energy is required to break hydrogen bonds in water and less energy is released when new attractions are set up.
(b) 2-Bromo-2-Methylbutane < 2-Bromopentane < 1-Bromopentane

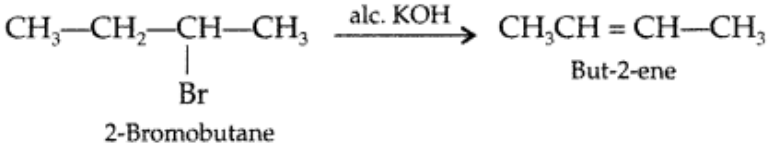
30. **How do you convert:**
(i) Chlorobenzene to biphenyl
(ii) Propene to 1-iodopropane
(iii) 2-bromobutane to but-2-ene
Answer:
(i) Chlorobenzene to biphenyl (Fittig reaction)



(*ii*) **Propene to 1-iodopropane**



(*iii*) **2-Bromobutane to but-2-ene**



CHAPTER 11

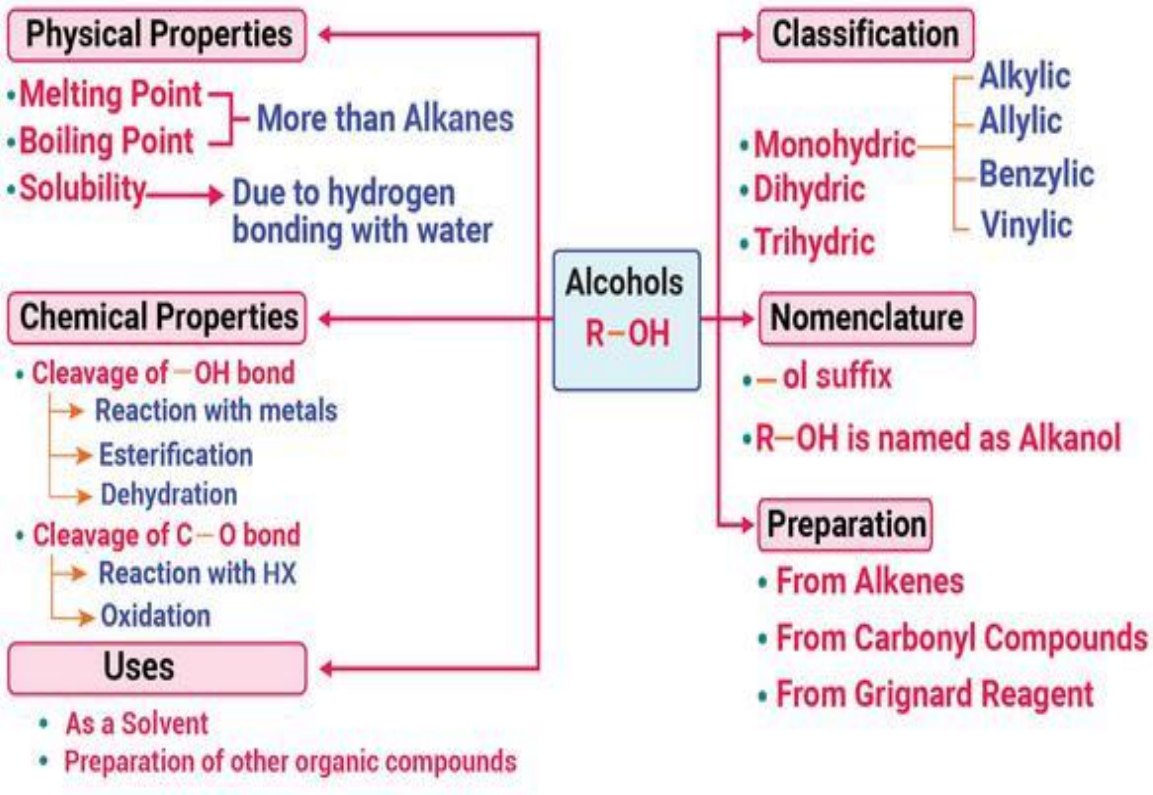
ALCOHOLS, PHENOLS AND ETHERS

GIST OF THE LESSON

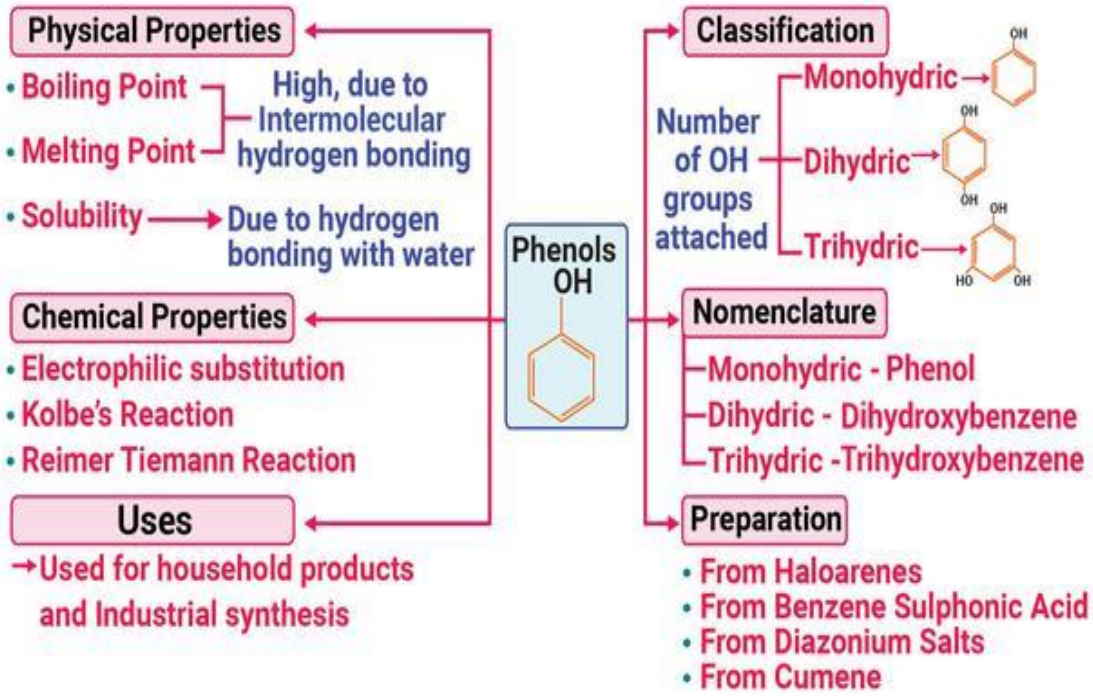
1. Introduction to alcohols, phenols and ethers
2. Classification: Alcohols— Mono, Di, Tri or Polyhydric alcohols & Phenols— Mono, Di and tri hydric phenols.
3. Classification of Ethers.
4. Nomenclature of Alcohols, phenols & Ethers: Common name &IUPAC name.
5. Structures of Functional Groups.
6. Methods of preparations of Alcohols , Phenols & Ethers
7. Mechanism of Hydration of alkenes & Dehydration of alcohols.
8. Physical Properties of Alcohols, Phenols & Ethers.
9. Chemical Reactions of Alcohols, Phenols & Ethers.
10. Acidity of Alcohols & Phenols:
11. Reactions of Phenols with special reference to Kolbe's reaction, Reimer-Tiemann reaction.
12. Some Commercially Important Alcohols: Methanol & Ethanol.
13. Preparation of Ethers with special reference to Williamson synthesis.
14. Reactions of ethers with special reference to Friedel-Crafts reaction.

CONCEPT MAPPING

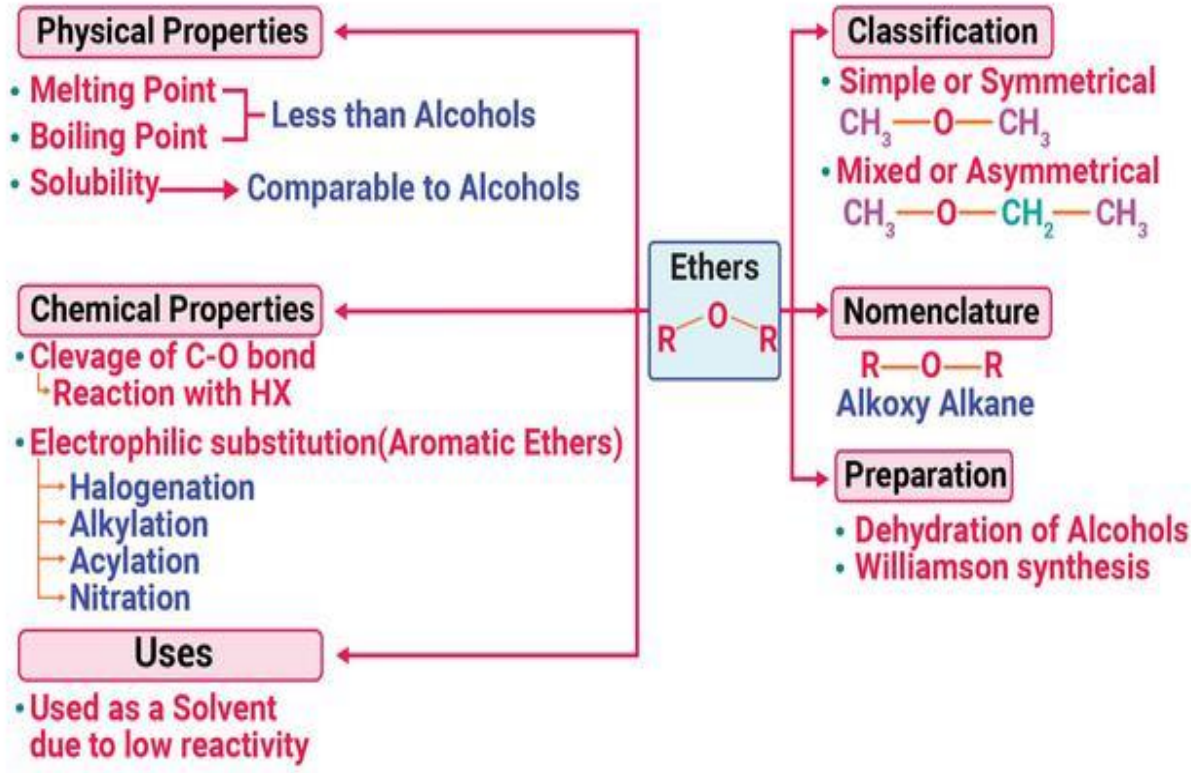
ALCOHOLS



PHENOLS



ETHERS



MULTIPLE CHOICE QUESTIONS

1. **Which of the following is a secondary alcohol?**

a) 2-methylbutan-2-ol b) 3-methylbutan-1-ol c) 2-methylbutan-1-ol d) 3- methylbutan-2-ol

2. **Reaction between acetone and methylmagnesiumchloride followed by hydrolysis will give :**

a) Isobutylalcohol b) Isopropyl alcohol c) sec-butyl alcohol d) tert-butyl alcohol

3. **When salicylic acid is heated with Zn dust , what will be the main product ?**

a) Benzene b) phenol c) Toluene d) Benzoic acid

4. **To prepare butan-2-ol using CH_3MgI, what other chemical would you choose ?**

a) Propanal b) Ethanal c) Ethanol d) Propan-2-ol

5. **Which of the following cannot be made by using Williamson's synthesis ?**

a) Methoxy benzene b) tert-butyl ethyl ether c) allyl methyl ether d) Ditert-butyl ether

6. **Heating of phenyl methyl ether with HI produces**

a) Iodobenzene b) phenol c) benzene c) ethyl chloride

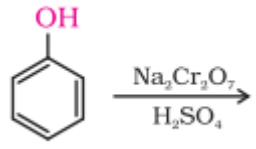
7. **Which of the following will not be soluble in $NaHCO_3$**

a) 2,4,6 trinitrophenol b) Benzoic acid c) o- Nitrophenol d) Benzene sulphonic acid

8. **Which of the following reagents may be used to distinguish between phenol and benzoic acid ?**

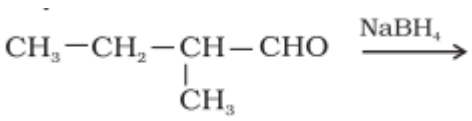
a) Neutral $FeCl_3$ b) Aqueous NaOH c) Tollen's reagent d) Molisch reagent

9. **Identify the product of the following reaction :**



a) Benzaldehyde b) Benzene c) Benzoquinone d) Benzoic acid

10. **Identify the product of the following reaction :**



a) 2-methylbutan-1-ol b) 2- methylbutanoic acid c) 2- methylbutane d) 2-methylbutan-2-ol

ASSERTION REASON TYPE QUESTIONS

For questions given below two statements are given- one labelled Assertion (A) and the other labelled as Reason (R). Select the correct answer from the codes (A) , (B) , (C) and (D) as given below :

(A) Bothe 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

11. **Assertion** (A) : The carbon-oxygen bond length in phenol is slightly less than that in methanol.

Reason (R) : The carbon –oxygen bond in phenol has partial double bond character due to + R effect

12. **Assertion** (A) : Aldehydes are reduced to primary alcohols by using $LiAlH_4$

Reason (R) : $LiAlH_4$ is a strong reducing agent

13. **Assertion** (A) : The acid strength of primary alcohol is more than secondary alcohol

Reason (R) : + I effect decreases the acid character

14. **Assertion** (A) : o- nitrophenol has lower boiling point than p-nitrophenol

Reason (R) : o-nitrophenol possess intramolecular hydrogen bonding while p-nitrophenolhas intermolecular hydrogen bonding

15. **Assertion** (A) : t-Butyl methyl ether on treatment with HI at 373K gives a mixture of methyliodide and tert-butyl alcohol

Reason (R) : The reaction occurs by S_N^1 mechanism

ANSWER KEY

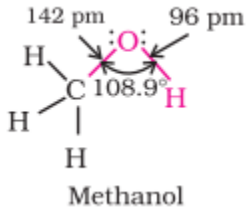
Q1.	Q2.	Q3	Q4.	Q5.
D	D	D	A	D
Q6.	Q7.	Q8.	Q9.	Q10.
B	B	A	C	A
Q11.	Q12.	Q13.	Q14.	Q15.
A	A	A	A	D

SHORT ANSWER TYPE QUESTIONS

1. **How simple or symmetrical is different from mixed or unsymmetrical?**
   Ethers are classified as simple or symmetrical, if the alkyl or aryl groups attached to the oxygen atom are the same, and mixed or unsymmetrical, if the two groups are different. Diethyl ether, $C_2H_5OC_2H_5$, is symmetrical ether whereas $C_2H_5OCH_3$ and $C_2H_5OC_6H_5$ are unsymmetrical ethers.

2. **Give a chemical test to distinguish between the following pairs of compounds: Methanol and phenol**
   Phenol gives a violet colouration with $FeCl_3$ solution while methane does not.

3. **The bond angle**  **in alcohol is slightly less than the tetrahedral bond angle. Give reason?**
   The bond angle in alcohols is slightly less than the tetrahedral angle (109°-28′). It is due to the repulsion between the unshared electron pairs of oxygen.



Methanol

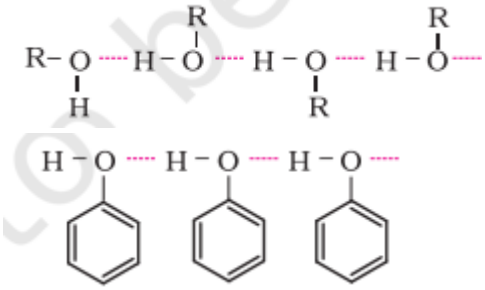
4. **The carbon– oxygen bond length (136 pm) in phenol is slightly less than that in methanol. Give reason?**
   The carbon– oxygen bond length (136 pm) in phenol is slightly less than that in methanol. This is due to
   (i) partial double bond character on account of the conjugation of unshared electron pair of oxygen with the aromatic ring and
   (ii) sp^2 hybridised state of carbon to which oxygen is attached.

5. **Why the bond angle in ether is slightly greater than the tetrahedral angle?**
   In ethers, the four electron pairs, i.e., the two bond pairs and two lone pairs of electrons on oxygen are arranged approximately in a tetrahedral arrangement. The bond angle is slightly greater than the tetrahedral angle due to the repulsive interaction between the two bulky (–R) groups.

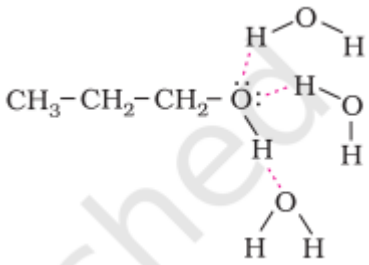
6. **Why the boiling point of 2- Methylpropan-2-ol is less than that of butanol?**
   The boiling points of alcohols and phenols increase with increase in the number of carbon atoms (increase in van der Waals forces). In alcohols, the boiling points decrease with increase of branching in carbon chain (because of decrease in van der Waals forces with decrease in surface area).

7. **Why the boiling points of alcohols and phenols are higher in comparison to other classes of compounds, namely hydrocarbons, ethers, haloalkanes and haloarenes of comparable molecular masses?**
   Boiling points of alcohols and phenols are higher in comparison to other classes of compounds,

namely hydrocarbons, ethers, haloalkanes and haloarenes of comparable molecular masses. The high boiling points of alcohols and phenols are mainly due to the presence of intermolecular hydrogen bonding in them which is lacking in ethers and hydrocarbons.



8. **Several of the lower molecular mass alcohols are miscible with water in all proportions. Give reasons?**
   Solubility of alcohols and phenols in water is due to their ability to form hydrogen bonds with water molecules as shown. The solubility decreases with increase in size of alkyl/aryl (hydrophobic) groups.



9. **Arrange the following sets of compounds in order of their increasing boiling points:**
   (a) Pentan-1-ol, butan-1-ol, butan-2-ol, ethanol, propan-1-ol, and methanol.
   (b) Pentan-1-ol, n-butane, pentanal, ethoxyethane.
   (a) Methanol, ethanol, propan-1-ol, butan-2-ol, butan-1-ol, pentan-1-ol.
   (b) n-Butane, ethoxyethane, pentanal and pentan-1-ol.

10. **Why alcohols act as Bronsted bases?**
    Alcohols act as Bronsted bases. It is due to the presence of unshared electron pairs on oxygen, which makes them proton acceptors.

11. **Why p-Nitro phenol is more acidic than Cresols?**
    In substituted phenols, the presence of electron withdrawing groups such as nitro group enhances the acidic strength of phenol. This effect is more pronounced when such a group is present at ortho and para positions. It is due to the effective delocalization of negative charge in phenoxide ion when substituent is at ortho or para position.
    On the other hand, electron releasing groups, such as alkyl groups, in general, do not favour the formation of phenoxide ion resulting in decrease in acid strength.

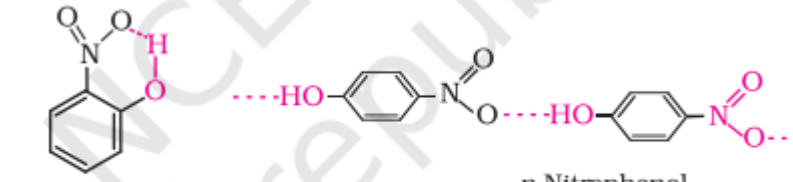
12. **Arrange the following compounds in increasing order of their acid strength:**
    Propan-1-ol, 2, 4, 6-trinitrophenol, 3-nitrophenol, 3, 5-dinitrophenol, phenol, 4-methylphenol.

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

13. **How primary, secondary and tertiary alcohols are distinguished by Lucas reagent test?**
Alcohols react with hydrogen halides to form alkyl halides.

$ROH + HX \rightarrow R\text{–}X + H_2O$ The difference in reactivity of three classes of alcohols with HCl distinguishes them from one another (Lucas test). Alcohols are soluble in Lucas reagent (conc. HCl and $ZnCl_2$) while their halides are immiscible and produce turbidity in solution. In case of tertiary alcohols, turbidity is produced immediately as they form the halides easily. Primary alcohols do not produce turbidity at room temperature.

14. **Why o-Nitro phenol is steam volatile while p-nitro phenol is less volatile?**
The ortho and para isomers can be separated by steam distillation. o-Nitrophenol is steam volatile due to intramolecular hydrogen bonding while p-nitrophenol is less volatile due to intermolecular hydrogen bonding which causes the association of molecules.



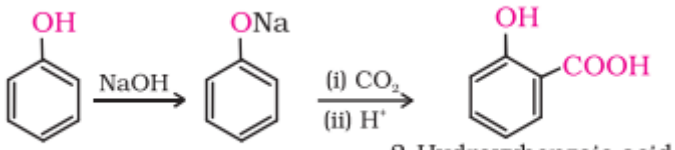
o-Nitrophenol (Intramolecular H-bonding)

p-Nitrophenol (Intermolecular H-bonding)

15. **How will you convert phenol into ortho hydroxybenzoic acid?**

Or

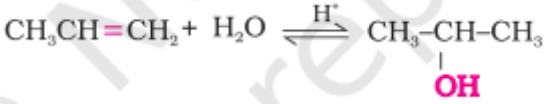
Explain Kolbe's reaction.
Phenoxide ion generated by treating phenol with sodium hydroxide is even more reactive than phenol towards electrophilic aromatic substitution. Hence, it undergoes electrophilic substitution with carbon dioxide, a weak electrophile. Ortho hydroxybenzoic acid is formed as the main reaction product.



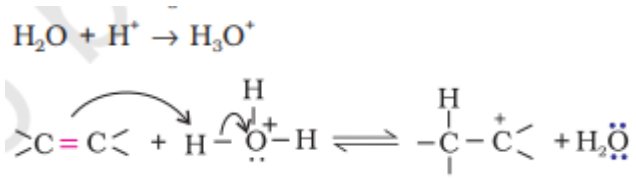
2-Hydroxybenzoic acid (Salicylic acid)

LONG ANSWER TYPE QUESTIONS

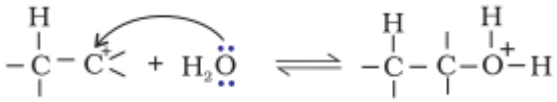
16. Explain the mechanism of hydration of alkene to alcohol?
Alkenes react with water in the presence of acid as catalyst to form alcohols. In case of unsymmetrical alkenes, the addition reaction takes place in accordance with Markovnikov's rule.



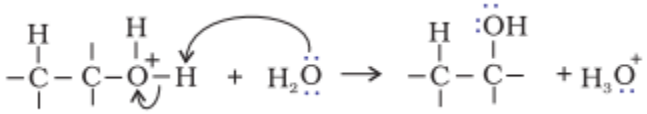
Mechanism The mechanism of the reaction involves the following three steps:
Step 1: Protonation of alkene to form carbocation by electrophilic attack of H_3O^+



Step 2: Nucleophilic attack of water on carbocation.



Step 3: Deprotonation to form an alcohol.



17. Give the structures and IUPAC names of the products expected from the following reactions:

(a) Catalytic reduction of butanal.

(b) Hydration of propene in the presence of dilute sulphuric acid.

(c) Reaction of propanone with methyl magnesium bromide followed by hydrolysis.

(a) $CH_3-CH_2-CH_2-CH_2-OH$

Butan-1-ol

(b) $CH_3-\underset{\underset{OH}{|}}{CH}-CH_3$

Propan-2-ol

(c) $CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH$

2-Methylpropan-2-ol

18. How are the following conversions carried out?

i) Propene to propan -2-ol

ii)Benzyl chloride to Benzyl alcohol

iii) anisole to parabromo anisol

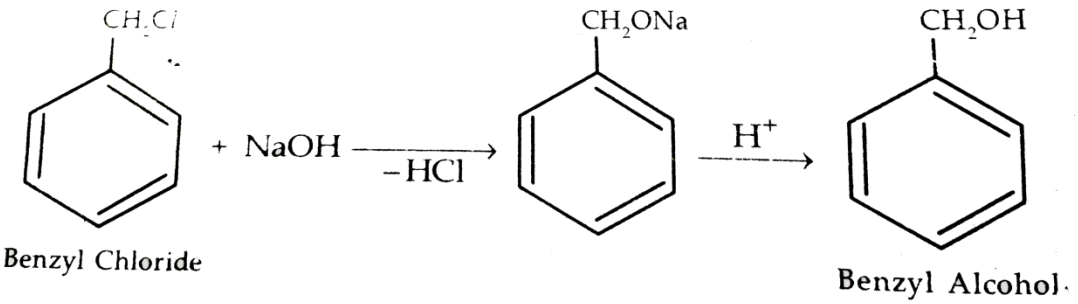
(i) $\underset{\text{Propene}}{CH_3-CH=CH_2} + \underset{\text{Sulphuric acid}}{H-OSO_3H(\text{Conc.})} \longrightarrow CH_3-\underset{\underset{OSO_3H}{|}}{CH}-CH_3$

Isopropyl Hydrogen Sulphate

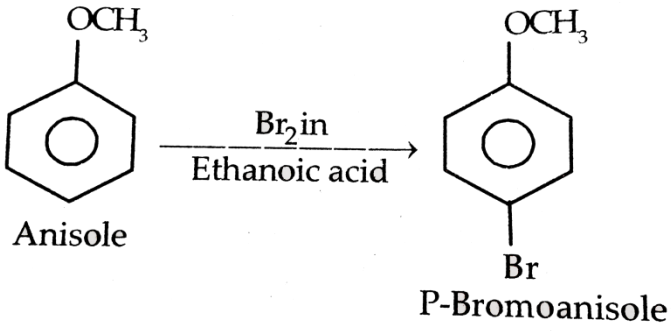
$\xrightarrow[-H_2SO_4]{H_2O\,\Delta} CH_3-\underset{\underset{OH}{|}}{CH}-CH_3$

Propan – 2 – ol

(ii)

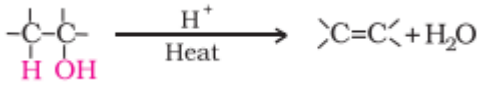


(iii)



19. Explain the mechanism of dehydration of alcohol to alkene?

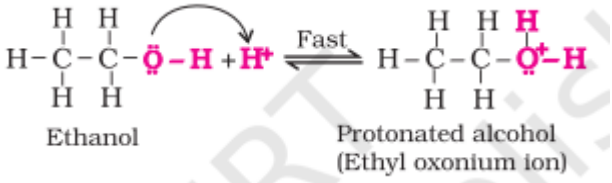
Alcohols undergo dehydration (removal of a molecule of water) to form alkenes on treating with a protic acid e.g., concentrated H2SO4 or H3PO4 , or catalysts such as anhydrous zinc chloride or alumina.



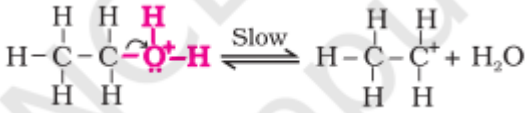
The mechanism of dehydration of ethanol involves the following steps:

Mechanism

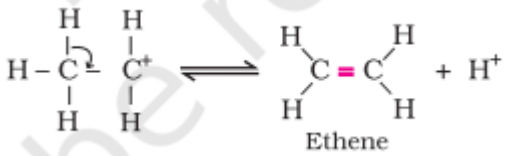
Step 1: Formation of protonated alcohol.



Step 2: Formation of carbocation: It is the slowest step and hence, the rate determining step of the reaction.



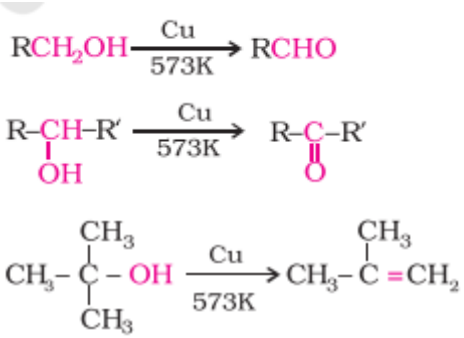
Step 3: Formation of ethene by elimination of a proton.



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.

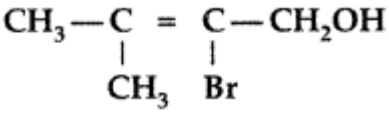
20. **What happens when alcohol vapours are passed over heated copper silver catalyst?**

When the vapours of a primary or a secondary alcohol are passed over heated copper at 573 K, dehydrogenation takes place and an aldehyde or a ketone is formed while tertiary alcohols undergo dehydration.

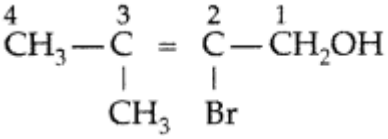


CBSE BOARD QUESTIONS

1. **Give the IUPAC name of the following compound :**



Answer:



2-Bromo-3-methylbut-2-ene-1-ol

2.**Ortho nitrophenol has lower boiling point than p-nitrophenol. Why?**

Answer:

Ortho-nitrophenol has lower boiling point due to formation of intramolecular H-bonding whereas p-nitrophenol forms intermolecular H-bonding.

3.**The C-O bond is much shorter in phenol than in ethanol. Give reason.**

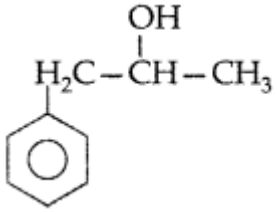
Answer:

Carbon of C-O bond of phenol is Sp^2 hybridised, so it acquires a partial double bond character but in ethanol it is Sp^3 hybridised and a single bond. Double bond is shorter than a single bond.

4.**Write the structure of the molecule of a compound whose IUPAC name is 1-phenylpropan-2-ol.**

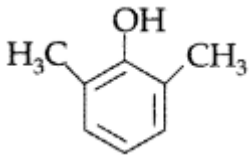
Answer:

1-phenylpropan-2-ol

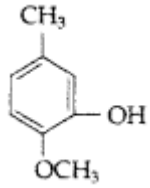


5.**Draw the structure of 2, 6-Dimethylphenol.**

Ans.



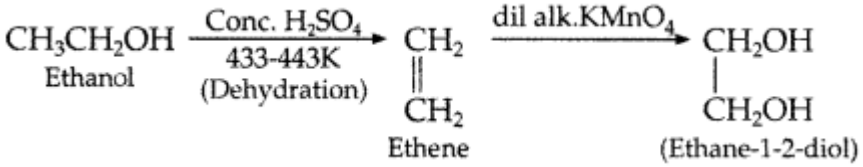
6.**Write IUPAC name of**



Answer:
IUPAC name : 2-Methoxy-5-methyl phenol

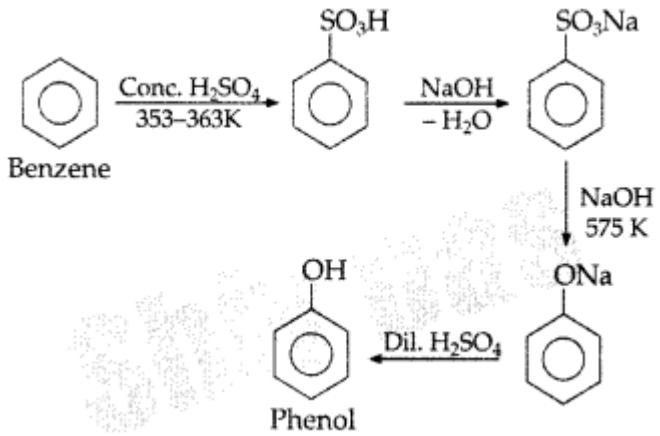
7. **Of the two hydroxy organic compounds ROH and R'OH, the first one is basic and other is acidic in behaviour. How is R different from R'?**
Answer: When R = alkyl, ROH behaves as a bronsted base and when R' = aryl, R'OH behaves as a bronsted acid

8. **How would you obtain ethane-1, 2-diol from ethanol?**
Answer:



9. **Give a chemical test to distinguish between 2-Pentanol and 3-Pentanol.**
Answer:
2-pentanol gives Iodoform test with yellow ppt. of Iodoform while 3-pentanol does not give this test.

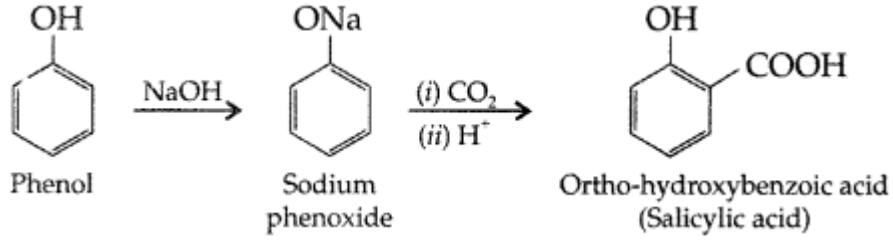
10. **How would you obtain phenol from benzene?**
Answer



11. **Write the chemical reaction to explain Kolbe's reaction.**

Answer:

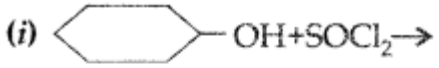
Kolbe's reaction : Phenol reacts with CO_2 in presence of sodium hydroxide (NaOH) produces sodium phenoxide which on treatment with CO_2 followed by acidification produces salicylic acid

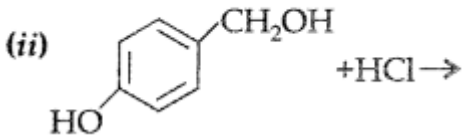


12. **How would you obtain acetophenone from phenol?**

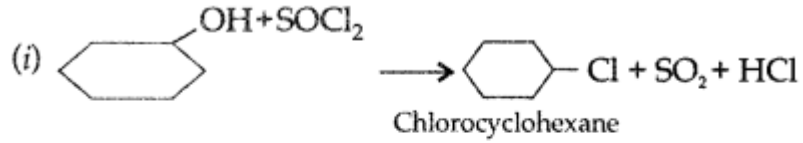
Answer:

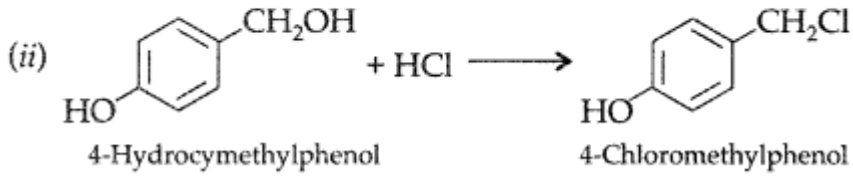
13.Complete the following reaction equations :





Answer:





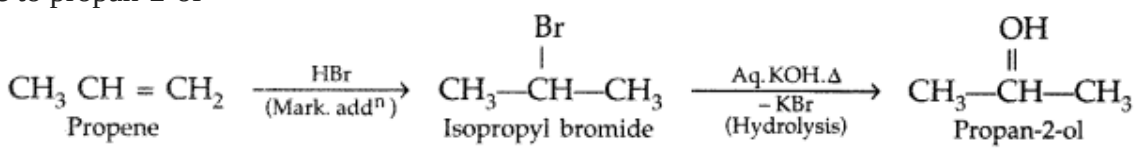
14.**How are the following conversions carried out?**

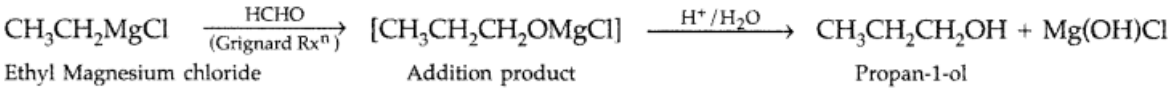
(i) **Propene to propan-2-ol**

(ii) Ethylmagnesium chloride to propan-1-ol.

Answer:

(i) Propene to propan-2-ol

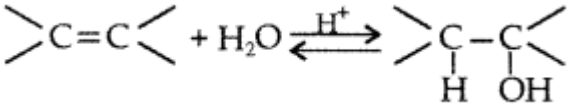




15.**Explain the mechanism of acid catalysed hydration of an alkene to form corresponding alcohol.**

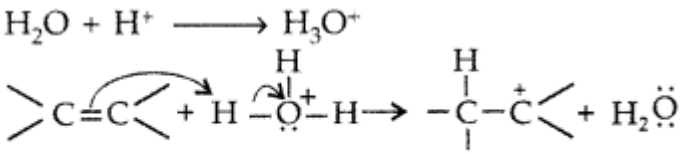
Answer:

Acid catalysed hydration : Alkenes react with water in the presence of acid as catalyst to form alcohols

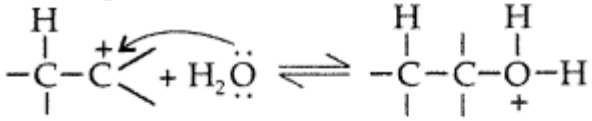


Mechanism : It involves three steps :

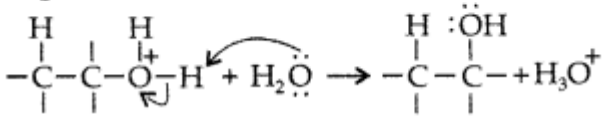
(i) Protonation of alkene to form carbocation by electrophilic attack of H_3O^+



(*ii*) Nucleophilic attack of water on carbocation



(*iii*) Deprotonation to form an alcohol



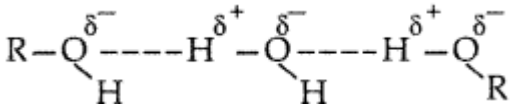
16.**Explain the following behaviours :**

(i) Alcohols are more soluble in water than the hydrocarbons of comparable molecular masses.

(ii) Ortho-nitrophenol is more acidic than ortho-methoxyphenol. (All India 2012)

Answer:

(i) Alcohols can form H-bonds with water and break the H-bonds already existing between water molecules. So they are soluble in water.



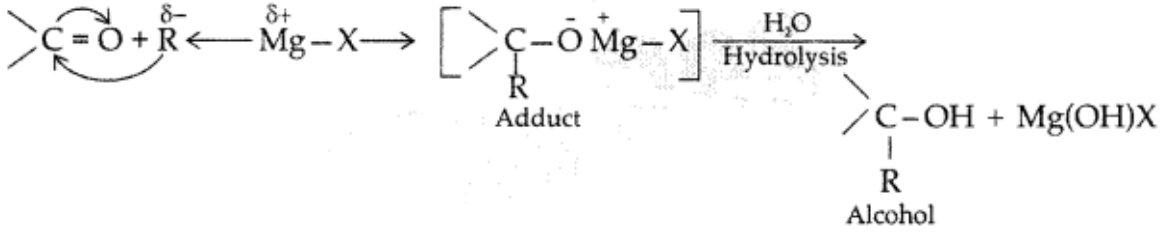
On the other hand, hydrocarbons cannot form H-bonds with water and hence are insoluble in water.

(ii) Due to strong – R and -1 effect of the – NO_2 group, electron density in the – OH bond decreases and hence the loss of a proton becomes easier. Moreover O-nitrophenoxide ion is stabilized by resonance, 1 thereby making O-nitrophenol a stronger acid.

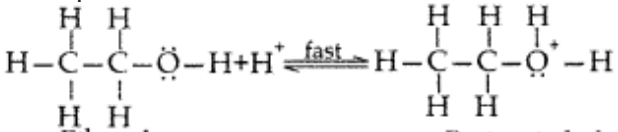
In O-methoxyphenol, due to + R effect of the – OCH_3 group the electron density in the

O – H bond increases thereby making the loss of proton difficult. Furthermore, the O-methoxyphenoxide ion left after the loss of a proton is destabilized by resonance because the two negative charges repel each other. So O-methoxyphenol is a weaker acid.

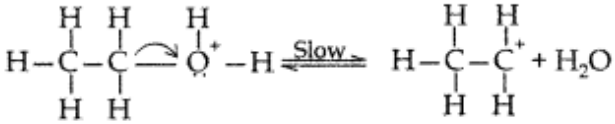
17.**Explain the mechanism of the following reactions :**
(i) Addition of Grignard's reagent to the carbonyl group of a compound forming an adduct followed by hydrolysis.
(ii) Acid catalysed dehydration of an alcohol forming an alkene.
(iii) Acid catalysed hydration of an alkene forming an alcohol. (Delhi 2009)
Answer:
(i) Carbonyl group undergoes nucleophillic addition reaction with Grignard reagent to form an adduct which undergoes hydrolysis to give alcohol in the following manner:



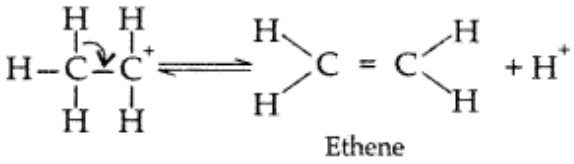
(ii) The mechanism of dehydration of ethanol involves the following steps :
Mechanism : It involves the following three steps :
Step 1 : Formation of protonated alcohol



Step 2 : Formation of Carbocation : It is the slowest and rate determining step.

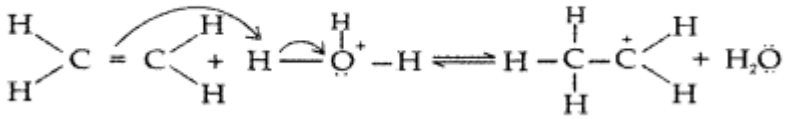


Step 3 : Formation of ethene by elimination of a proton



(iii) Acid catalysed hydration : Alkenes react with water in the presence of acid as catalyst to form alcohols. Mechanism : It involves the following three steps :
Step 1 : Protonation of alkene to form carbocation by electrophilic attack of H $3O^+$

$$H_2O + H^+ \rightarrow H_3O^+$$

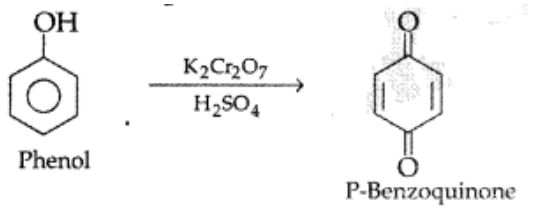


18. **Explain the following observations :**
(i) The boiling point of ethanol is higher than that of methoxymethane.
(ii) Phenol is more acidic than ethanol.
(iii) o- and p-nitrophenols are more acidic than phenol. (All India 2009)
Answer:
(i) Due to presence of intermolecular H-bonding, associated molecules are formed, hence ethanol has high boiling point while methoxymethane does not have intermolecular H-bonding.
(ii) Phenol on losing H^+ ion forms phenoxide ion, and ethanol on losing H^+ ion forms ethoxide ion.

Phenoxide ion is more stable than ethoxide ion as phenoxide ion exists in resonance structure. Due to this phenol is more acidic than ethanol.
(iii) Both o- and p-nitrophenols contain the NO_2 group which is an electron withdrawing group. Due to -R and -I effect of the $-NO_2$ group, electron density in the OH bond of substituted phenol decreases and hence the loss of proton becomes easy and therefore more acidic.

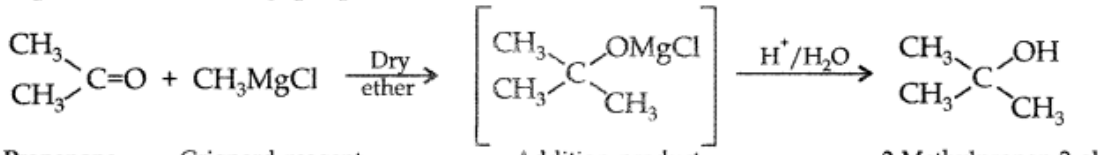
19. **How would you convert the following :**
(i) Phenol to benzoquinone
(ii) Propanone to 2-methylpropan-2-ol
(iii) Propene to propan-2-ol

Ans:



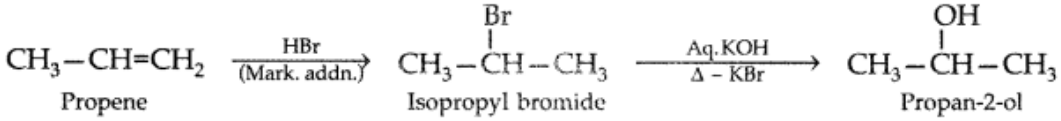
Phenol P-Benzoquinone

(*ii*) **Propanone to 2-methylpropan-2-ol**



Propanone Grignard reagent Addition product 2-Methylpropan-2-ol

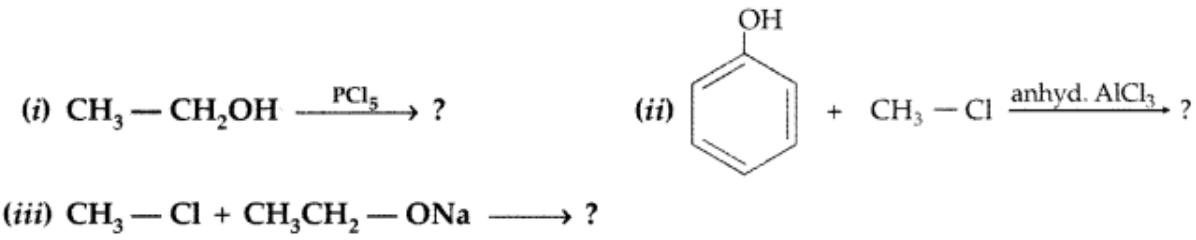
(*iii*) **Propene to propan-2-ol**



Propene Isopropyl bromide Propan-2-ol

20. **Give reasons for the following :**
(i) Phenol is more acidic than methanol.
(ii) The C—O—H bond angle in alcohols is slightly less than the tetrahedral angle (190°28′).
(iii) $(CH_3)_3C$—O—CH_3 on reaction with HI gives $(CH_3)_3C$—I and CH_3—OH as the main products and not $(CH_3)_3C$—OH and CH_3—I. (All India 2015)
Answer:
(i) Phenol is more acidic than methanol because in phenol, phenoxide ion formed is more stabilized by resonance than phenol. There is no resonance in methanol.
(ii) The C—O—H bond angle in alcohols is slightly less than tetrahedral angle due to repulsion between the lone pairs of electrons of oxygen.
(iii) $(CH_3)_3C^+$ is 3° carbo-cation which is more stable than CH_3^+ for S_N1 reaction.

21. **Write the major product in the following equations**

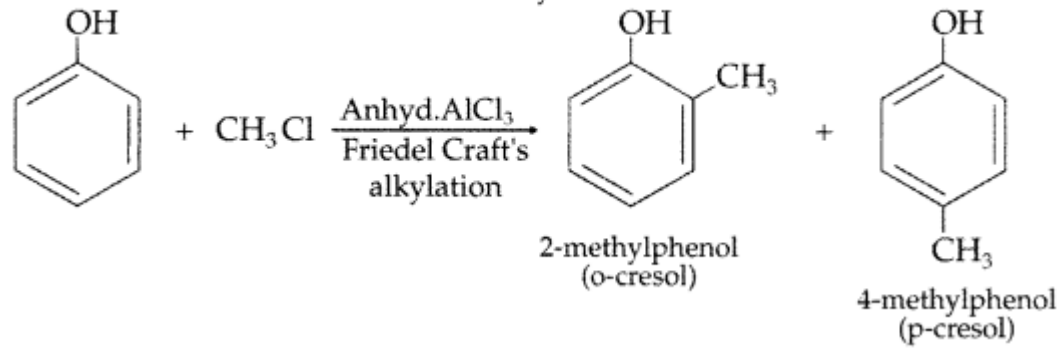


,

Ans:

(*i*) $CH_3 - CH_2OH + PCl_5 \longrightarrow CH_3CH_2Cl + POCl_3 + HCl$

Ethanol — Ethyl chloride

(*ii*) 

2-methylphenol (o-cresol)

4-methylphenol (p-cresol)

(*iii*) Williamson's ether synthesis :

$CH_3Cl + CH_3CH_2ONa \longrightarrow CH_3CH_2O - CH_3 + NaCl$

Methyl chloride — Sodium ethoxide — Methoxy ethane

ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

(GIST OF THE LESSON)

1. Aldehydes and ketones, are commonly called as carbonyl compounds.

2. In Rosenmund's reduction, poisoning of Pd with $BaSO_4$ prevent reduction of R – CHO to R – CH_2OH.

3. In the reaction of toluene with CrO_3 , acetic anhydride is used to protect benzaldehyde by forming benzylidene- diacetates to avoid its oxidation to benzoic acid.

4. Order of reactivity of aldehydes and ketones towards nucleophilic addition is :

(i) HCHO > CH_3 CHO > CH_3CH_2CHO.

(ii) HCHO > RCHO > R CO R.

(iii) Ar-CHO > Ar -COR > Ar -CO -Ar.

5. Benzaldehyde reduces Tollens' reagent but it does not reduce Fehling's and Benedict's solution.

6. Aldehydes and ketones with at least one α−H atom get condensed in presence of a base. This is known as Aldol condensation.

7. Aldol condensation involves carbanion as intermediate.

8. Aldehydes with no α−H atoms undergo Cannizzaro's reaction.

9. Ketones react with dihydric alcohols to form cyclic ketals.

10. Monocarboxylic acids having (C12−C18) carbon atoms, are called fatty acids.

11. Boiling points of carboxylic acids is greater than corresponding alcohols.

12. Presence of EWGs (electron withdrawing groups) enhances the acidic character of carboxylic acids.

13. −COOH group is m-directing in electrophilic substitution reactions.

14. Compounds containing three or more– CHO group are named as carbaldehydes

15. Formaldehydes cannot be prepared by Rosenmund's reduction reaction since formyl chloride is unstable at room temperature.

16. Benzaldehyde is less reactive than aliphatic aldehydes towards nucleophilic addition reaction.

17. Aromatic ketones are less reactive, they do not react with $NaHSO_3$.

18. In the reaction of aldehydes and ketones with ammonia derivatives, the medium should be slightly acidic (pH=4.5). In highly acidic medium, ammonia derivatives being acidic, form salts and do not act as nucleophile .

19. Ketones do not give Tollen's test and Fehling's solution test.

20. Only CH3CHO and all methyl ketones give Iodoform test.

21. A stronger acid has higher pKb but lower pKa.

22. Benzoic acid is a stronger acid than acetic acid.

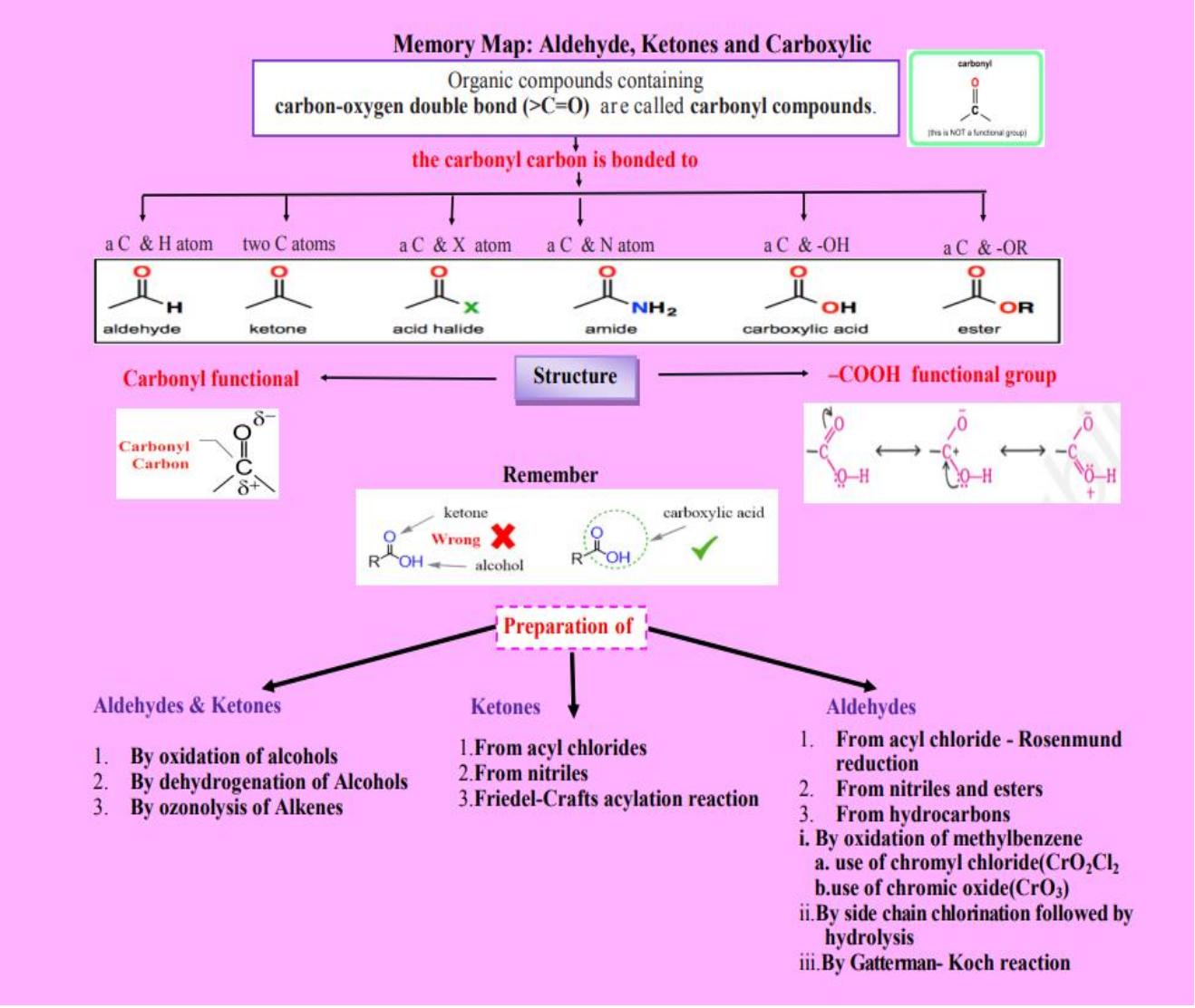
23 -CHO and–COOH group, attached to benzene ring, are deactivating and m-directing.

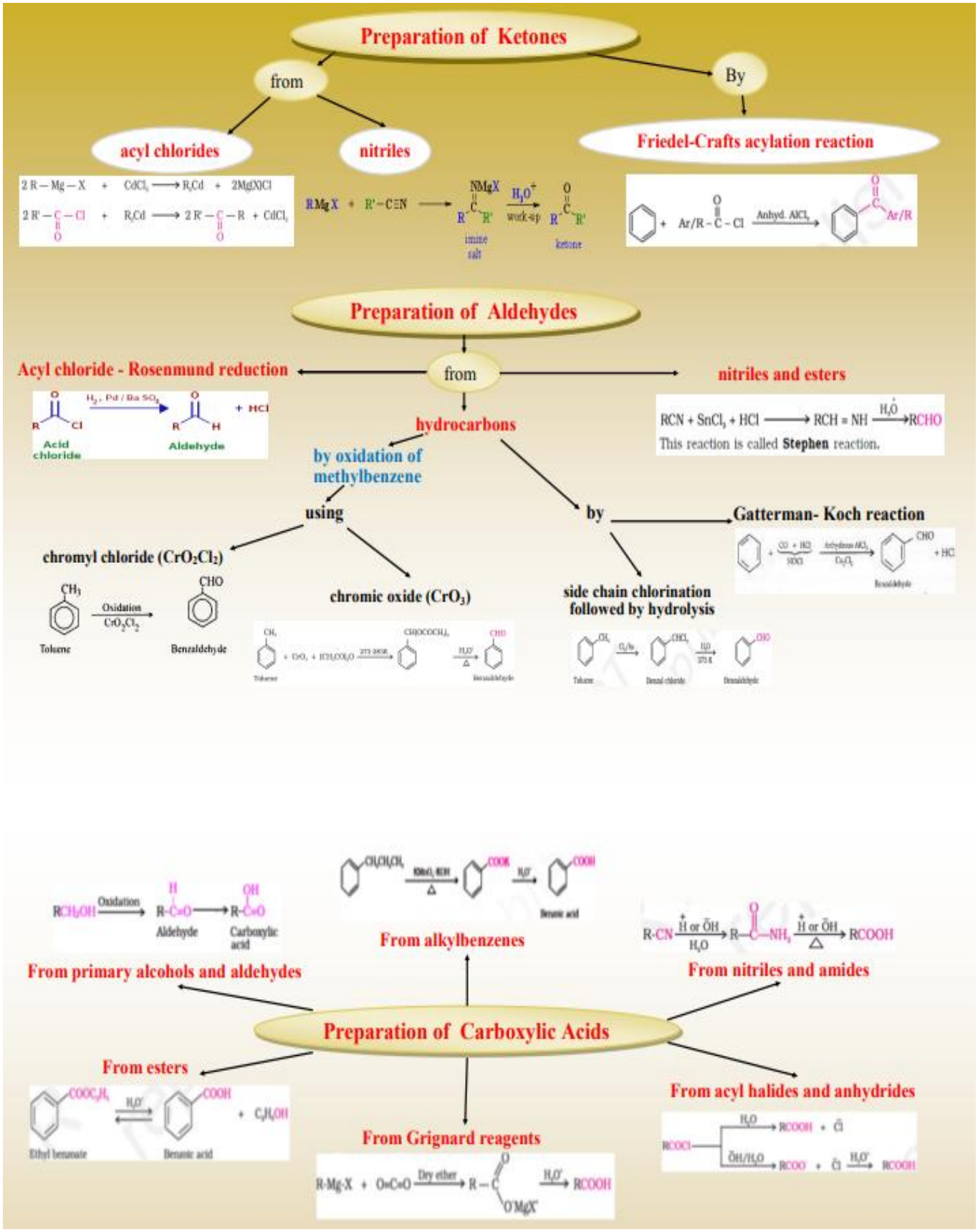
24. Methanoic acid decolourise the pink colour of acidified KMnO4 solution but acetic acid does not.

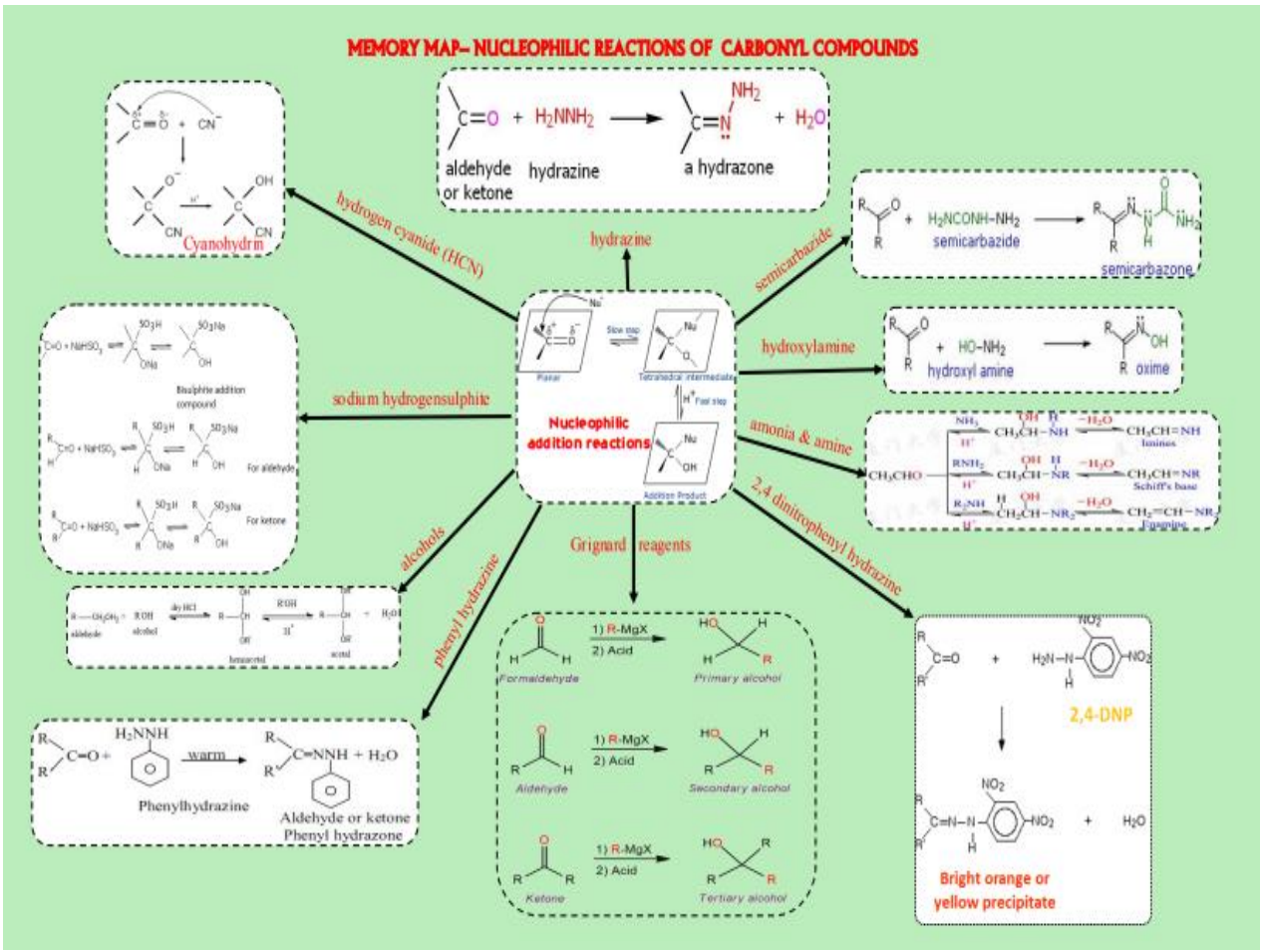
25. A 40% aqueous solution of formaldehyde is known as formalin and is used to preserve biological specimens, and to prepare Bakelite.

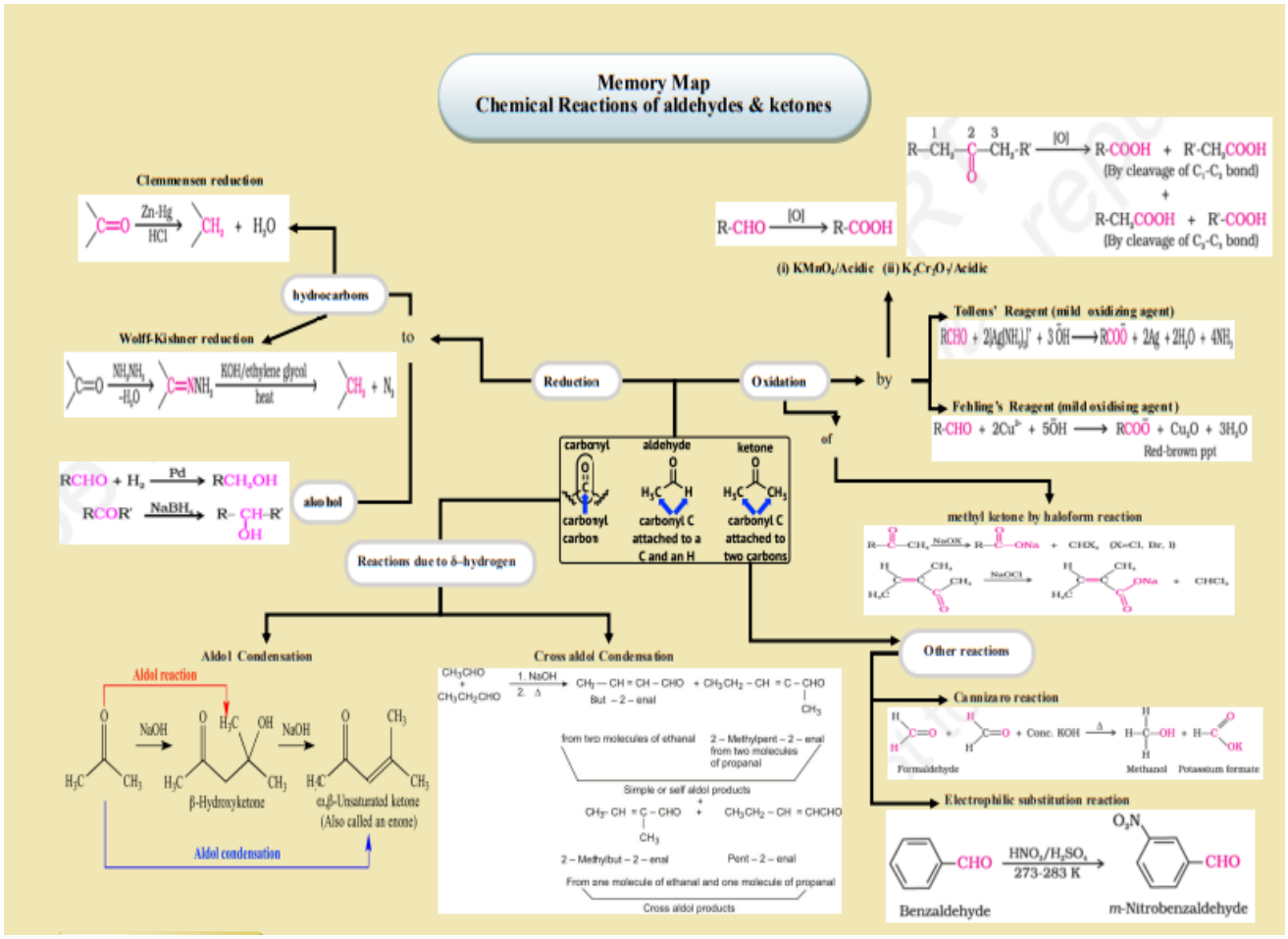
26. Benzaldehyde is used in perfumery and in dye industries.

MIND MAPPING




Preparation of Ketones
from
By
acyl chlorides
nitriles
Friedel-Crafts acylation reaction
imine salt
ketone
Preparation of Aldehydes
Acyl chloride - Rosenmund reduction
from
nitriles and esters
Acid chloride
Aldehyde
hydrocarbons
This reaction is called Stephen reaction.
by oxidation of methylbenzene
using
by
Gatterman- Koch reaction
chromyl chloride (CrO_2Cl_2)
chromic oxide (CrO_3)
side chain chlorination followed by hydrolysis
Toluene
Benzaldehyde
Oxidation
Preparation of Carboxylic Acids
From primary alcohols and aldehydes
From alkylbenzenes
From nitriles and amides
From esters
From acyl halides and anhydrides
From Grignard reagents
Ethyl benzoate
Benzoic acid
Aldehyde
Carboxylic acid


MEMORY MAP– NUCLEOPHILIC REACTIONS OF CARBONYL COMPOUNDS
aldehyde or ketone
hydrazine
a hydrazone
Cyanohydrin
hydrogen cyanide (HCN)
hydrazine
semicarbazide
semicarbazone
hydroxylamine
hydroxyl amine
oxime
sodium hydrogensulphite
Nucleophilic addition reactions
ammonia & amine
alcohols
Grignard reagents
phenyl hydrazine
2,4 dinitrophenyl hydrazine
Phenylhydrazine
warm
Aldehyde or ketone
Phenyl hydrazone
Formaldehyde
Primary alcohol
Aldehyde
Secondary alcohol
Ketone
Tertiary alcohol
2,4-DNP
Bright orange or yellow precipitate



SHORT ANSWER QUESTIONS (2 MARKS)

Q1. Aldehydes and Ketones have lower boiling points than corresponding alcohols. Why?

ANS. The boiling points of aldehydes and ketones are lower than that of corresponding alcohols due to absence of intermolecular H–bonding in aldehydes and ketones.

Q2. Account for the following :

CH3CHO is more reactive than CH3COCH3 towards reaction with HCN.

Ans. It is a nucleophilic addition reaction, in which CN – acts as a nucleophile. CH3CHO undergoes nucleophilic addition reactions faster than CH3COCH3 as in CH3COCH3 there are two electron releasing methyl groups attached to the carbonyl carbon that hinders the approach of nucleophile to carbonyl carbon and reduce the electrophilicity of the carbonyl group while in CH3CHO, there is only one methyl group attached to carbonyl carbon.

Q3. What is Tollens' reagent? Write one usefulness of this reagent.

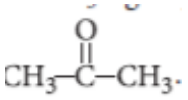
ANS. Tollens' reagent is an ammoniacal silver nitrate solution. Tollens' reagent is used to test an aldehyde Both aliphatic and aromatic aldehydes reduce Tollens 'reagent and give silver mirror.

Q4. The aldehydes and ketones undergo a number of addition reactions. Explain.

ANS: Aldehydes and ketones undergo a number of addition reactions as both possess the carbonyl functional group which reacts with a number of nucleophiles such as HCN, NaHSO3, alcohols,ammonia derivatives and Grignard reagents.

Q5.A and B are two functional isomers of compound C2H6O. On heating with NaOH and I_2, isomer B forms yellow precipitate of iodoform whereas isomer A does not form any precipitate. Write the formulae of A and B .

ANS: Formula of compounds A and B = C3H6O & B forms yellow precipitate of iodoform. Hence,

B must contain —COCH3 group Therefore, compound 'B' must be  .

A does not give iodoform test and it is functional isomer of B thus, it may be CH3CH2CHO.

Q6**.** Arrange the following compounds in increasing order of their boiling points.

CH3CHO, CH3CH2OH, CH3OCH3 , CH3CH2CH3

Ans. The molecular masses of the given compounds are in the range 44 to 46. CH3CH2OH undergoes extensive intermolecular H-bonding, resulting in the association of molecules. Therefore, it has the highest boiling point and is more polar than CH3OCH3 and so CH3CHO has stronger intermolecular dipole - dipole attraction than CH3OCH3 and so CH3CH2CH3 has only weak van der Waals force. Thus, the arrangement of the given compounds in the increasing order of their boiling points is given by:

CH3CH2CH3<CH3OCH3<CH3CHO<CH3CH2OH

Q7. Give chemical tests to distinguish between :Benzoic acid and Phenol

ANS. Phenol and benzoic acid can be distinguished by their reactions with sodium bicarbonate solution. Benzoic acid will give effervescence with NaHCO3 but phenol will not react.

Q8. Account for the following :Cl -CH2COOH is a stronger acid than CH3COOH.

ANS. Chloroacetic acid has lower pKa value than acetic acid; 'Cl' in chloroacetic acid shows

–I effect, it creates less electron density on oxygen of carboxylic acid. thus, release of proton becomes easier. In case of acetic acid, the state of affair is just opposite. Hence, chloroacetic acid is stronger than acetic.

Q9. Monochloroethanoic acid has a higher pKa value than dichloroethane acid.Why?

ANS: The strength of an acid is indicated by pKa value, where, pKa = – log Ka

Since monochloroethanoic acid is weaker than dichloroethanoic acid , it has lower value of

dissociation constant Ka. ,therefore, it has higher value of pKa.

Q10. Ethanoic acid is a weaker acid than benzoic acid. Explain.

ANS: The —COOH group in benzoic acid is attached to sp2 - carbon of the phenyl ring and is more acidic than acetic acid in which —COOH group is attached to sp3 – carbon atom of CH3 group. So, benzoic acid is stronger than acetic or acetic acid is weaker acid than benzoic acid.

Q11. Arrange the following in order of increasing reactivity towards nucleophilic addition reaction Ethanal, propanal, propanone, butanone .

Ans: Due to steric hindrance & +I effect, the reactivity towards nucleophilic addition reaction decreases. So order is butanone< propanone < propanal < ethanol.

SHORT ANSWER QUESTIONS (3 MARKS)

Q12.. Account for the following

(i) Higher carboxylic acid are insoluble in water. Why?

(ii) Why p-nitro benzoic acid has higher Ka value than benzoic acid?

(iii) The boiling points of aldehydes and ketones are lower than that of the corresponding acids.

Ans: (i)Due to increased hydrophobic part, H-bonding does not take place. So higher carboxylic acid are insoluble in water.

Ans(ii): Higher the Ka value, stronger is the acid. Nitro group has –R as well as –I effect which makes the O-H more polar hence p-nitro benzoic acid is stronger acid. (The conjugate base gets stabilised through delocalisation of the negative charge by inductive and /or resonance effects). So it has higher Ka value

.(iii) The boiling points of aldehydes and ketones are lower than that of the corresponding acids due to intermolecular hydrogen bonding in carboxylic acids

Q.13. Account for the following :

(i) Oxidation of toluene to C6H5CHO with CrO3 is carried out in presence of acetic anhydride.

(ii) Melting point of an acid with even number is higher than those of its neighbours with odd number of carbon atoms.

(iii) Aromatic acids are solid while most of aliphatic acids are liquids.

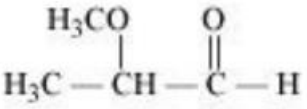
Ans. (i) Oxidation of toluene to C6H5CHO with CrO3 is carried out in presence of acetic anhydride. to prevent further oxidation of C6H5CHO to benzoic acid.

(ii) Acids with even number of carbon atoms fit into crystal lattice. Hence melting point of an acid with even number is higher than those of its neighbours with odd number of carbon atoms. (iii)Aromatic acids have higher molecular weight and strong Van der Waals force of attraction as compared to aliphatic acids so they are solids

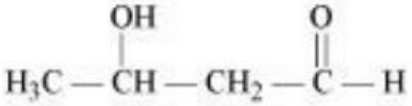
Q14. Write the structures of the following compounds.

(i) α-Methoxy propionaldehyde
(ii) 3-Hydroxybutanal
(iii) 2-Hydroxycyclopentanecarbaldehyde

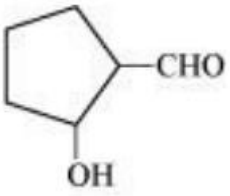
Ans. (i)



(ii)



(iii)



Q15.(i). Why does solubility decrease with increasing molecular mass in carboxylic acid?

(ii) Why PCC cannot oxidize methanol to methanoic acid while KMnO4 can? .

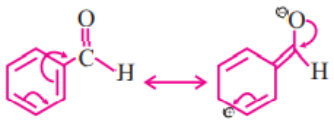
(iii) Benzaldehyde is less reactive in nucleophilic addition reactions than propanal ? Why?

Ans. (i) Solubility decrease with increasing molecular mass in carboxylic acid as with increase of molecular mass size the hydrophobic carbon chain length increases.

(ii) PCC (pyridinium chlorochromate)is a mild oxidizing agent and can oxidize methanol to methanal only, while KMnO4 is strong oxidizing agent which oxidizes it to methanoic acid.

(iii)Carbon atom of carbonyl is C6H5CHO is less reactive than that of propanal.

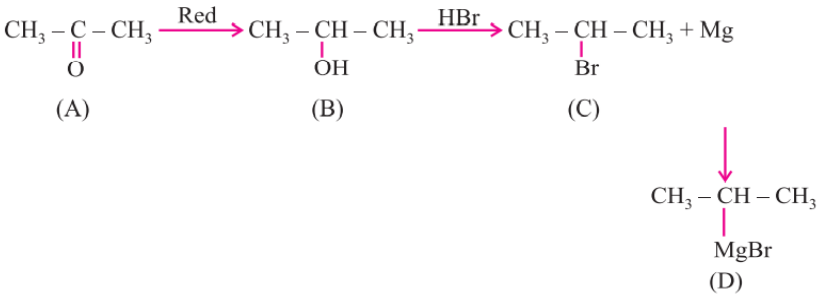
C6H5CHO less polar due to resonance

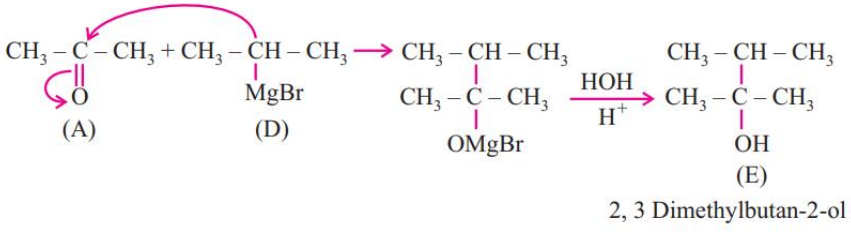


LONG ANSWER TYPE QUESTIONS (5 Marks)

Q. 16. An organic compound ‘A’ (C3H6O) is resistant to oxidation but forms compound ‘B’ (C3H8O) 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





Q. 17. Give reasons for the following :

(i) C6H5COOH is weaker than formic acid.

(ii) HCOOH and CH3COOH are differentiated by Tollen's reagent.

(iii) R – COOH do not give characteristic reaction of > C = O.

(iv) Carboxylic acids are stronger acids than phenols.

(v) Acid amides are weakly basic in nature.

Ans. (i) Due to instability of carboxylate anion due to conjugation, C6H5COOH is weaker than formic acic

(ii) Presence of H—C(=O)— group

CH3COOH do not give Tollens's test.

(iii) > C = O group is sterically hindered in carboxylic acid, hence do not give characteristic reaction of > C = O.

(iv) Carboxylic acids are stronger acids than phenols due to the dispersal of –ve charge on carboxylate ions than phenoxide ion.

(v)Acid amides are basic due to lone pair of electrons on nitrogen atom.

Q. 18. (a) Write the chemical equation for the reaction involved in cannizzaro reaction.

(b) Draw the structure of semicarbazone of ethanal.

(c) Why pka of F-CH2 COOH is lower than that of Cl–CH2 COOH

(d)Write the product in the following reaction

CH3CH=CHCH2CN - (i) DIBAL-H(ii)H2O →

(e) How can you distinguish between propanal and propanone?

Ans. (a) $HCHO + HCHO \xrightarrow{\text{Conc. NaOH}} HCOONa + CH_3OH$

(b) $CH_3CH = N–NHCONH_2$

(c) Stronger –I effect of fluorine makes $F\text{-}CH_2COOH$ to be stronger acid than $Cl–CH_2COOH$ and less pka

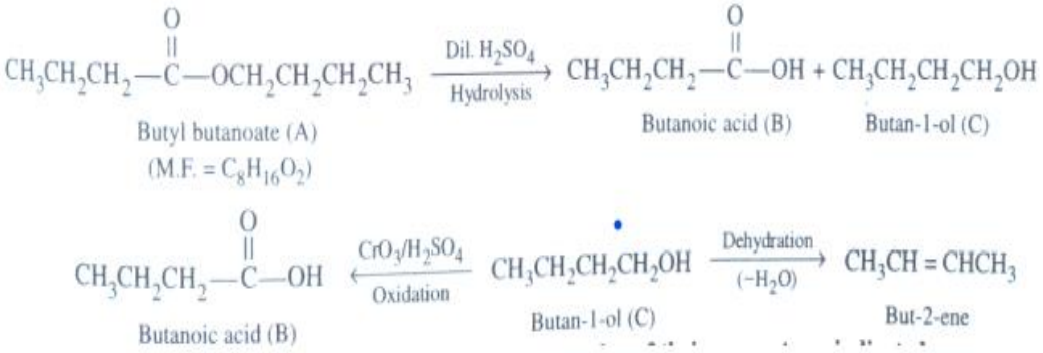
(d) $CH_3CH = CHCH_2CHO$

(e) Silver mirror formed on adding ammonical silver nitrate to propanal and not with propanone.

Q19.An organic compound A (molecular formula C8H16O2) was hydrolysed with dil. Sulphuric acid to give carboxylic acid (B) & alcohol (C). C on oxidation with chromic acid produced B. C on dehydration gives but-2-ene as the major product. Write the equation for the reactions involved.

Ans: i)A is ester as it produces carboxylic acid & alcohol

. ii) Alcohol on oxidation produces B Carboxylic acid, it means both have same number of carbons . iii) C alcohol on dehydration produces but-2-ene, it means C must be 1-butanol. B must be butanoic acid. So compound A must be CH3CH2CH2COOCH2CH2CH2CH3



Q20.Which of the following compounds would undergo aldol condensation, which the Cannizzaro reaction and which neither? Write the structures of the expected products of aldol condensation and Cannizzaro reaction.

(i) Methanal (ii) 2-Methylpentanal (iii) Benzaldehyde (iv) Benzophenone

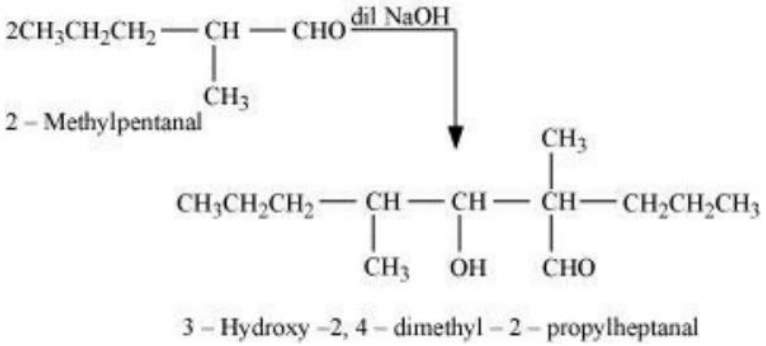
ANS: Aldehydes and ketones having at least one α-hydrogen undergo aldol condensation. The compounds (ii) 2-methylpentanal contain one or more α-hydrogen atoms. Therefore, it undergoes aldol condensation.

Aldehydes having no α-hydrogen atoms undergo Cannizzaro reactions. The compounds (i) Methanal, (iii) Benzaldehyde and do not have any α-hydrogen. Therefore, these undergo cannizzaro reactions.

Compound (iv) Benzophenone is a ketone having no α-hydrogen atom . Hence, this compound do not undergo either aldol condensation or cannizzaro reactions.

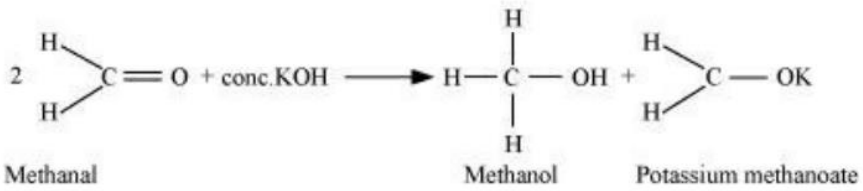
Aldol condensation

(ii)

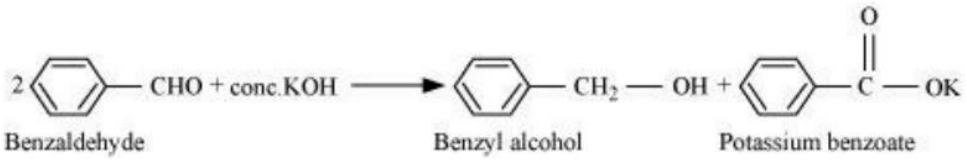


Cannizzaro reaction

(i)



(iii)



Q.21 Describe the following a) (i) Acetylation (ii) Cannizzaro reaction

b) Give plausible explanation for each of the following:

(i) Cyclohexanone forms cyanohydrin in good yield but 2, 2, 6 trimethylcyclohexanone does not.

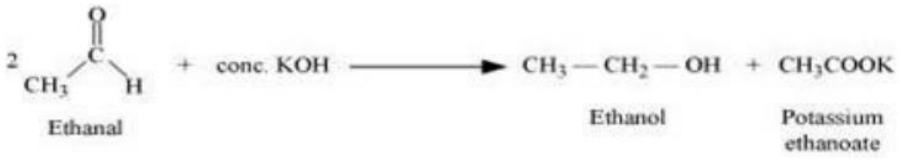
(ii) There are two - groups in semicarbazide. However, only one is involved in the formation of semi carbazones.

(iii) During the preparation of esters from a carboxylic acid and an alcohol in the presence of an acid catalyst, the water or the ester should be removed as soon as it is formed.

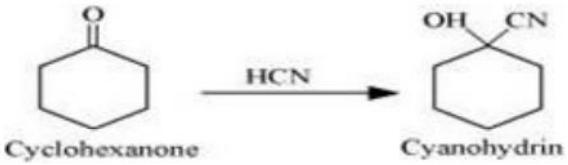
ANS a)(i)Acetylation: The introduction of an acetyl functional group into an organic compound is known as acetylation. It is usually carried out in the presence of a base such as pyridine, dimethylaniline, etc. This process involves the substitution of an acetyl group for an active hydrogen atom. Acetyl chloride and acetic anhydride are commonly used as acetylating agents. For example, acetylation of ethanol produces ethyl acetate.

For example, acetylation of ethanol produces ethyl acetate.

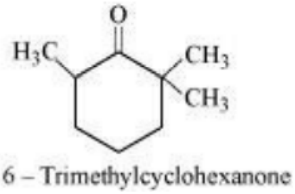
(ii) Cannizzaro reaction: The self oxidation-reduction (disproportionation) reaction of aldehydes having no α-hydrogens on treatment with concentrated alkalis is known as the Cannizzaro reaction. In this reaction, two molecules of aldehydes participate where one is reduced to alcohol and the other is oxidized to carboxylic acid. For example, when ethanol is treated with concentrated potassium hydroxide, ethanol and potassium ethanoate are produced



Ans.b) (i)Cyclohexanones form cyanohydrins according to the following equation.

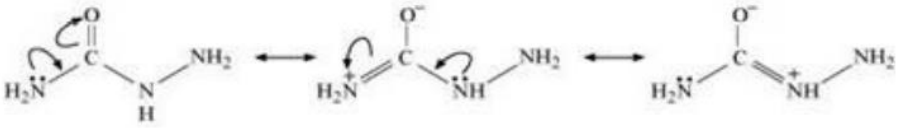


In this case, the nucleophile CN - can easily attack without any steric hindrance. However, in the case of 2, 2, 6 trimethylcydohexanone, methyl groups at α-positions offer steric hindrances and as a result, CN - cannot attack effectively thus, it does not form cyanohydrin in good yield as compared to cyclohexanone which does not have steric hindrance. For this reason, it does not form a cyanohydrin.



2, 2, 6 – Trimethylcyclohexanone

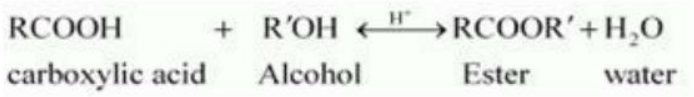
(ii)Semi carbazide undergoes resonance involving only one of the two - groups, which is attached directly to the carbonyl-carbon atom. The lone pair on NH2 attached to carbonyl group is involved in resonance and hence not available for reaction.



Therefore, the electron density on - group involved in the resonance also decreases. As a result, it cannot act as a nucleophile. Since the other - group is not involved in resonance; it can act as a nucleophile and can attack carbonyl-carbon atoms of aldehydes and ketones to produce semi carbazones.

(iii) Ester along with water is formed reversibly from a carboxylic acid and an alcohol in presence of an acid. If either water or ester is not removed as soon as it is formed, then it reacts to give back the reactants as the reaction is reversible. Therefore, to shift the equilibrium in the forward direction i.e., to produce

more ester, either of the two should be removed. The ester formed does not get hydrolysed easily.



MULTIPLE CHOICE QUESTIONS

1. Carbonyl compounds undergo nucleophilic addition because of

   (a) More stable anion with negative charge on oxygen and less stable carbocation
   (b) Electromeric effect
   (c) Electronegativity difference of carbon and oxygen atoms
   (d) None of the above.

2. Wolff Kishner reduction is carried with

   (a) LiAlH4 in ether
   (b) Zn-Hg and HCl
   (c) H2 in the presence of Pd
   (d) NH2-NH2/ethylene glycol and KOH

3. The addition of HCN to carbonyl compounds is an example of

   (a) Electrophilic addition
   (b) Nucleophilic addition
   (c) Nucleophilic substitution
   (d) Electrophilic substitution

4. Oxidation of cyclohexene using acidified KMnO4 will give ……

   (a) adipic acid
   (b) hexane -1,6-dial
   (c) cyclohexane carboxylic acid
   (d) cyclopentane carboxylic acid

5. Which aldehyde will give Cannizzaro's reaction?

   (a) $CH_3 CH_2 CH_2 CHO$
   (b) $CH_3 CH_2 CHCHO$
   (c) $(CH_3)_3CCHO$
   (d) $(CH3)_2CH_2CH_2 CHO$

6. Carboxylic acids are more acidic than phenol and alcohol because of

   (a) Formation of dimers
   (b) Highly acidic hydrogen
   (c) Resonance stabilization of their conjugate base
   (d) Intermolecular hydrogen bonding

7. Which of the following orders of relative strengths of acids is correct?

(a) $ClCH_2COOH > FCH_2COOH > BrCH_2COOH$
(b) $ClCH_2COOH > BrCH_2COOH > FCH_2COOH$
(c) $BrCH_2COOH > ClCH_2COOH > FCH_2COOH$
(d) $FCH_2COOH > ClCH_2COOH > BrCH_2COOH$

8. When ethanal is heated with Fehling's solution it gives a precipitate of

(a) CuO
(b) Cu
(c) $Cu + Cu_2O + CuO$
(d) Cu_2O

9. Formic acid and acetic acid can be distinguished chemically by

(a) Reaction with HCl
(b) Iodoform test
(c) Reaction with NH_3
(d) Tollens' test

10. The major product in the given reaction is

$$CH_3\text{-}CH{=}CH\text{-}CH_2\text{-}CH_2\text{-}CN \xrightarrow[H2O]{DIBAL-H}$$

(a) $CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CN$
(b) $CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CHO$
(c) $CH_3\text{-}CH{=}CH\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}NH_2$
(d) $CH_3\text{-}CH{=}CH\text{-}CH_2\text{-}CH_2\text{-}CHO$

11. Which of the following conversions can be carried out by Clemmensen Reduction?

(a) Benzaldehyde into benzyl alcohol
(b) Cyclohexanone into cyclohexane
(c) Benzoyl chloride into benzaldehyde
(d) Benzophenone into diphenyl methane

12. In Clemmensen Reduction carbonyl compound is treated with……

(a) Zinc amalgam + HCl
(b) Sodium amalgam + HCl
(c) Zinc amalgam + nitric acid
(d) Sodium amalgam + HNO_3

13. Which is the most suitable reagent for the following conversion? CH_3-CH=C(CH_3)-CO-CH_3 → CH_3-CH=C(CH_3)-COO^-

(a) Tollen's reagent
(b) Benzoyl peroxide
(c) I_2 and NaOH solution
(d) Sn and NaOH solution

14. Cannizzaro's reaction is not given by…….

(a) C_6H_5CHO
(b) H CHO
(c) CCl_3-CHO
(d) CH_3-CHO

15. Which of the following compound is most reactive towards nucleophilic additionreactions?

(a) C_6H_5CHO
(b) H CHO
(c) CH_3-CO- CH_3
(d) CH_3-CHO

16. The correct order of increasing acidic strength is……

(a) Phenol < Ethanol < Chloroacetic acid < Acetic acid
(b) Ethanol < Phenol < Chloroacetic acid < Acetic acid
(c) Ethanol < Phenol < Acetic acid < Chloroacetic acid
(d) Chloroacetic acid < Acetic acid < Phenol < Ethanol

17. The correct order of decreasing acidic strength is…….

(a) Dichloro acetic acid< Trichloroacetic acid < Chloroacetic acid < Acetic acid
b) Trichloro acetic acid< Dichloroacetic acid < Chloroacetic acid < Acetic acid
c) Trichloro acetic acid > Dichloroacetic acid > Chloroacetic acid > Acetic acid
d) Dichloro acetic acid< Trichloroacetic acid < Chloroacetic acid < Acetic acid

18. Tollens reagent is

(a) Ammoniacal silver bromide
(b) Ammoniacal silver nitrate
(c) Ammoniacal silver iodide
(d) Ammoniacal cuprous oxide

19. Which of the following does not react with $NaHSO_3$

(a) Acetone
(b) Acetaldehyde
(c) Benzaldehyde
(d) benzophenone

20 . Aldol condensation will not occur in

a) HCHO
(b) CH_3 CHO
(c) CH_3 CO CH_3
(d) CH_3- CH_2- CHO

21. Arrange the following molecules in the increasing order of Pka values
a)Dichloro acetic acid< Trichloroacetic acid < Chloroacetic acid < Acetic acid
b)Trichloro acetic acid< Dichloroacetic acid < Chloroacetic acid < Acetic acid
c)Trichloro acetic acid > Dichloroacetic acid > Chloroacetic acid > Acetic acid
d)Dichloro acetic acid< Trichloroacetic acid < Chloroacetic acid < Acetic acid

22. Stephen reduction is used to prepare aldehydes from
(a) Acid chloride
(b) Alkane nitriles
(c) Acid amides
(d) Grignard reagent

23. Ozonolysis of 2,3-Dimethyl but-2-ene gives
(a) one molecule of acetone and one molecule of butanone
(b) two molecule of acetone
(c) two molecules of propanal
(d) one molecule of propanal and one molecule of propanone

24. Arrange the following molecules in the increasing order BP
(a) propane< popanal <propanone < propanol < propanoic acid
(b) propane> popanal >propanone > propanol > propanoic acid
(c) propane< popanone <propanal < propanol < propanoic acid
(d) propane< popanal <propanone < propanoic acid < propanol

25. Acetophenone and benzophenone can be distinguished by
(a) Iodoform test
(b) Tollens Test
(c) Fehling's test
(d) Benedicts test

26. Acetaldehyde and benzaldehyde can be distinguished by
(a) Iodoform test (b) Tollens Test
(c) Fehling's test (d) neutral $FeCl_3$

(a) a only
(b) both a and b
(c) both a and c
(d) d only

27. Arrange the following compounds in the decreasing order of their reactivity

innucleophilic addition reactions.

(I) Benzaldehyde, (II) p-Tolualdehyde, (III) p-Nitro benzaldehyde, (IV)Acetophenone.

(a) I >II >III > IV

(b) I >III >II > IV

(c) II >I >III > IV

(d) III >I >II > IV

28)

. $C_6H_6 \xrightarrow[\Delta]{CO + HCl} X + HCl$, X is

(a) C_6H_5CHO

(b) CH_3CHO

(c) CH_3COCH_3

(d) $C_6H_5COCH_3$

29) The IUPAC name of $CH_3COCH(CH_3)_2$ is

(e) 3- methylbutan-2-one

(f) 3,3-dimethyl propanone

(g) 1,1-dimethyl propanone

(h) isopropyl methyl ketone

30)The IUPAC name of $CH_3CH(OH)COOH$ is

(i) lactic acid

(j) 2-hydroxypropanoic acid

(k) 3- carboxypropanol

(l) 3-carboxy propan -2-ol

31)The purpose of S in Rosemonds reduction is

(m)to prevent the reduction of aldehyde to alcohol

(n) to prevent the oxidation of aldehyde to carboxylic acid.

(o) to increase the rate of reaction.(d)None of the above

32)$CH_3\text{-}CH{\equiv}CH \xrightarrow[H2O]{Hg+2}$ X, X is

(p) $CH_3\text{-}CO\text{-}CH_3$

(q) $CH_3\text{-}CH_2\text{-}CHO$

(r) CH_3-CH_2-CH_2-OH

(s) CH_3-CH(OH)-CH_3

33) R-CH_2-COOH $\xrightarrow[X2]{red\ P}$ R-C H_2(X) -COOH + HX, the reaction is

(a) Cannizaro reaction
(b)Clemmensons reduction
(c) HVZ reaction
(d) Kolbes reaction

34)The reagent that can be used to distinguish phenol and ethanoic acid is.

(t) Na metal
(u) Tollens reagent
(v) $NaHCO_3$
(w) Fehling solution

35)

$$C_6H_5\text{-}MgBr \xrightarrow[H3O+]{CO2} X + Mg(OH)Br$$

(a) $C_6H_5\text{-}CH_2\text{-}COOH$
(b) $C_6H_5\text{-}OH$
(c) $C_6H_5\text{-}COOH$
(d) $C_6H_5\text{-}O\text{-}C_6H_5$

36) substance X is heated with soda lime and gives ethane ,the substance X is

(a) ethanol
(b) ethanoic acid
(c) propanoic acid
(d) methanoic acid

37. The major product of nitration of benzoic acid is,

(a) 2-nitrobenzoic acid
(b) 4-nitrobenzoic acid
(c) 3-nitrobenzoic acid
(d) 2,4- dinitro benzoic acid

38)

$$X \xrightarrow[\Delta]{dil.\ NaOH} CH_3\text{-}CH = CH\text{-}CHO, \text{ X is}$$

(a) HCHO
(b) $CH_3\text{-}CHO$
(c) $CH_3\text{-}CH = CH\text{-}CH_2OH$
(d) $CH_3\text{-}CH(OH)\ CH\text{-}CHO$

39) Benzoyl chloride is prepared from benzoic acid by

(a) Cl_2/ $FeCl_3$
(b) Cl_2/ uv
(c) $SOCl_2$
(d) HCl

40. Which of the following can be reduced with Zn/Hg and HCl to give the corresponding hydrocarbon.

(a) Butanal
(b) Butan-2-one
(c) Butanoic acid
(d) Benzoyl chloride

(a) a only
(b) both band d
(c) both a and c
(d) both a and b

41) The product of the reaction

$CH_3–COOH \xrightarrow{P2O5}$ ..... is

(a) CO and H_2O
(b) $(CH_3–CO)_2O$
(c) $CH_3–COO-CH_3$
(d) None of the above

42) Electrolysis of an aqueous solution of *$CH_3–COONa$ gives*

(a) methane
(b) ethane
(c) ethene
(d) butane

43)Which of the following have the highest K_a value

a. formic acid
b. acetic acid
c. chloroacetic acid
d. fluroacetic acid

44)Toluene is oxidized to benzaldehyde by

a. alkaline $KMnO_4$
b. PCC
c. acidified $K_2Cr_2O_7$
d. CrO_2Cl_2

45)The oxidation of toluene to benzaldehyde using chromyl chloride is

(a) Stephan's reaction
(b) Étards reaction
(c) Gatterman Koch reaction
(d) ozonolysis

46)Benedict solution provides

(a) Cu^{+2}
(b) Cu^{+}
(c) Ca^{+2}
(d) Ba^{+2}

47)Fehlings solution B is

a) Copper sulphate solution
b) alkaline sodium potassium tartarate
c) Alkaline sodium citrate
d) ammoniacal silver nitrate

48) Carbonyl compounds can be converted to hydrocarbons by

(a) Clemensons reduction
(b) reduction using $NaBH_4$ or $LiAlH_4$
(c) Wolf Kishner reduction
(d) by both a and c

49) Oxidation of acetone using HNO_3 will give

(a) two molecules of acetic acid
(b) one molecule of propionic acid
(c) $CH_3COOH + H_2O + CO_2$
(d) two molecules of formic acid

50)

$C_6H_5\text{-}COCl + H_2 \xrightarrow{Pd/BaSO_4/S}$

(a) $C_6H_5\text{-}CH_2OH$

(b) $C_6H_5\text{-}CHO$

(c) C_6H_5COOH

(d) $C_6H_5COC_6H_5$

Answer key

1	A	11	B	21	B	31	A	41	B
2	D	12	A	22	B	32	A	42	B
3	B	13	C	23	B	33	C	43	D
4	A	14	D	24	A	34	C	44	D
5	C	15	B	25	A	35	C	45	B
6	C	16	C	26	C	36	C	46	A
7	D	17	C	27	D	37	C	47	B
8	D	18	B	28	A	38	B	48	D
9	D	19	D	29	A	39	C	49	C
10	D	20	A	30	B	40	D	50	B

ASSERTION - REASON TYPE QUESTIONS

Read the assertion and reason carefully to mark the correct option out of the options given below:

a. **If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.**
b. **If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.**
c. **If the Assertion is correct but Reason is incorrect**.
d. **If both the Assertion and Reason are incorrect.**

1. **Assertion:** The boiling points of aldehydes and ketones are higher than hydrocarbons and ethersof comparable molecular masses.
   Reason: There is a weak molecular association in aldehydes and ketones arising out of the dipole-dipole interactions.

2. **Assertion:** Compounds containing –CHO group are easily oxidised to corresponding carboxylicacids.
   Reason : Carboxylic acids can be reduced to alcohols by treatment with $LiAlH_4$

3. **Assertion:** Acetic acid does not undergo a haloform reaction.
   Reason: Acetic acid has no alpha hydrogens.

4. **Assertion:** Chloroacetic acid has a lower pKa value than Acetic acid.
   Reason: The – I effect of Cl further stabilizes the carboxylate anion formed by the loss of theproton.

5. **Assertion:** Lower aldehyde and ketones are soluble in water but the solubility decreases as molecular mass increases.
   Reason: Aldehydes and ketones can be distinguished by Tollen's reagent.

6. **Assertion:** Aldehydes undergo aldol condensation only if it has α-hydrogen.
   Reason: The a-hydrogen in aldehydes are acidic in nature because the anion formed by the lossof the a-hydrogen is resonance stabilized.

7. **Assertion:** Acetophenone and benzophenone can be distinguished by the iodoform test.
   Reason: Acetophenone and benzophenone both are carbonyl compounds.

8. **Assertion:** Benzaldehyde is more reactive than ethanal towards nucleophilic attack.
   Reason: The overall effect of –I and +R effect of phenyl group decrease the electron density onthe carbon atom of > C = O group in benzaldehyde.

9. **Assertion:** Ketones are less reactive than aldehydes.
   Reason: Ketones do not have alpha hydrogens

10. **Assertion:** Dry HCl is a must for the reaction of an aldehyde with alcohol to form hemiacetal.
    Reason: HCl protonates the carbonyl oxygen increasing the electrophilicity of the carbonyl carbon.

11. **Assertion:** Even though there are two NH_2 groups in semicarbazide, only one reacts with carbonyl compounds
Reason: Semicarbazide has two NH_2 groups out of which one is in resonance with the carbonylgroup.

12. **Assertion** : Lower aldehydes and ketones are soluble in water but the solubility decreases as the molecular masses increase
Reason: Distinction between aldehydes and ketones can be made by Tollens' test.

13. **Assertion**: Aldehydes react with Tollen's reagent to form silver mirror.
Reason: Both, aldehydes and ketones contain a carbonyl group.

14. **Assertion**: Aldol condensation can be catalysed both by acids and bases.
Reason: ββ Hydroxy aldehydes or ketones readily undergo acid catalysed dehydration.

15. **Assertion:** Ethanal and Propanone both gives iodoform test
Reason: both having –CO- CH_3 group

16. A**ssertion** : Benzaldehyde gives a positive test with Tollens reagent but not with Fehling's solution
Reason: Under normal circumstances, aldehydes that lack alpha hydrogens and so cannot forman enolate do not produce a positive test using Fehling's solution, which is a weaker oxidising agent than Tollen's reagent.

17. **Assertion**: Propanal is more reactive than propanone.
Reason- Due to the presence of alkyl groups on both sides of the carbonyl carbon, propanone is sterically more hindered than propanal, making it less reactive to nucleophilic attack.

18. **Assertion : Carboxylic acid is a stronger acid than phenol.**
Reason : Carboxylate ions are more polar and has less stearic hindrance

19. **Assertion:** CH_3CHO is more reactive than CH_3COCH_3 towards reaction with HCN.
Reason : CH_3CHO is more polar and has less stearic hindrance, therefore, more reactive withHCN than CH_3COCH_3.

20. **Assertion** : Carboxylic acids do not give reactions of carbonyl group.
Reason: Due to resonance

21. **Assertion** : There are two -NH_2 groups in semicarbazide ($H_2NNHCONH_2$).any one NH_2 group can involved in the formation of semicarbazone. **Reason** : Its due to steric hindrance and electronic effect

22. **Assertion** : Benzoic acid does not undergo Freifel Craft reaction
Reason : Carbonyl group in benzoic acid donate electron into thr ring through resonance

23. **Assertion** : Although phenoxide ion has more number of resonating structures than Carboxylate ion, Carboxylic acid is a stronger acid than phenol.
Reason : In carboxylate ions, negative charge is delocalised over two oxygen atoms which ismore stable. Phenoxide is less stable as negative charge is delocalised over one oxygen atomand carbon atoms of benzene ring.

24. **Assertion :** Carboxylic acids have greater boiling point than alcohols
Reason : Carboxilic acid have the greater ability to form dimers in solution

25. **Assertion** : Chloro acetic acid has lower pKa value than acetic acid
Reason : The –I effect of Cl further stabilises the carboxylate anion formed by the loss of the proton

26. **Assertion** : Benzaldehyde resists nucleophilic addition in comparison with ethanal
Reason: The phenyl group in benzaldehyde is too bulky and therefore prevents attack of Nucleophile

27. **Assertion** : Aldehydes undergo aldol condensation only if it has alpha hydrogen
Reason : The alpha hydrogen in aldehydes are acidic in nature because the anion formed by theloss of the alpha hydrogen is resonance stabilised .

28. **Assertion** : Reactivity of ketones is more than aldehyde..
Reason : The carbonyl carbon of ketones is less electrophilic as compared to aldehyde.

29. **Assertion** : Cannizzaro reaction is a self oxidation and reduction reaction of aldehyde donot having alphahydrogens
Reason : Benzaldehyde shows cannizzaro reaction and gives benzyl alcohol and sodium salt ofbenzoic acid

30. **Assertion:** 2, 2–Dimethyl propanal undergoes Cannizzaro reaction with concentrated NaOH.
: Cannizzaro is a disproportionation reaction.

31.Assertion: Acetaldehyde on treatment with dil NaOH it gives aldol.
Reason: Acetaldehyde molecules contain alpha hydrogen atom.

32.Assertion : The boiling points of aldehydes and ketones are higher than hydrocarbons and ethers of comparable molecular masses.
Reason : There is a weak molecular association in aldehydes and ketones arising out of the dipole-dipole interactions.

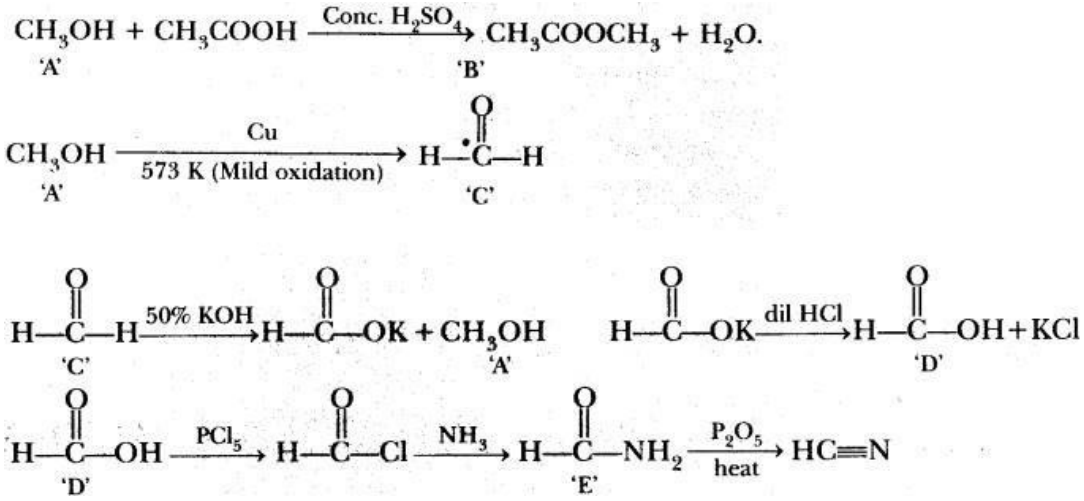
33.Assertion : Butan -2 – ol will give butanone on oxidation with alkaline $KMnO_4$ solution.
Reason : Aldehydes are easily oxidised to carboxylic acids on treatment with common oxidising agents like nitric acid, potassium permanganate, potassium dichromat, etc.

ANSWER KEY

1	**a**	**11**	**a**	**21**	**d**		
2	**b**	**12**	**b**	**22**	**c**		
3	**c**	**13**	**b**	**23**	**a**	**31**	**a**
4	**a**	**14**	**b**	**24**	**a**	**32**	**a**
5	**b**	**15**	**a**	**25**	**a**	**33**	**b**
6	**a**	**16**	**a**	**26**	**c**		
7	**b**	**17**	**a**	**27**	**a**		
8	**a**	**18**	**c**	**28**	**d**		
9	**c**	**19**	**a**	**29**	**b**		
10	**a**	**20**	**a**	**30**	**b**		

CASE BASED QUESTIONS

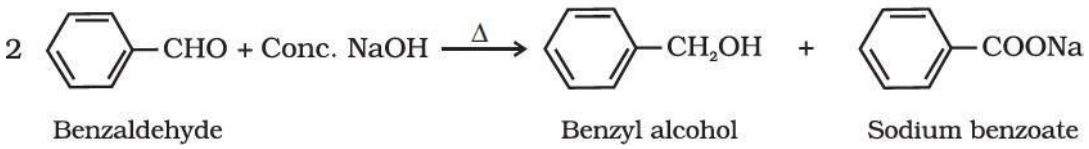
1. An organic compound (A) on treatment with acetic acid in the presence of sulphuric acid produces an ester (B). (A) on mild oxidation gives (C). (C) with 50% KOH followed by acidification with dilute HC1 generates (A) and (D). (D) with $PC1_5$ followed by reaction with ammonia gives (E). (E) on dehydration produces hydrocyanic acid. Identify the compounds A, B, C, D and E.



CASE – 2

Read the passage given below and answer the following questions :

When an aldehyde with no α-hydrogen reacts with concentrated aqueous NaOH, half the aldehyde is converted to carboxylic acid salt and other half is converted to an alcohol. In other words, half of the reactant is oxidized and other half is reduced. This reaction is known as Cannizzaro reaction



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

A mixture of benzaldehyde and formaldehyde on heating with aqueous NaOH solution gives

(a) benzyl alcohol and sodium formate
(b) sodium benzoate and methyl alcohol
(c) sodium benzoate and sodium formate
(d) benzyl alcohol and methyl alcohol

(ii) Which of the following compounds will undergo Cannizzaro reaction?

(a) CH_3CHO (b) CH_3COCH_3 (c) C_6H_5CHO (d) $C_6H_5CH_2CHO$

(iii) Trichloroacetaldehyde is subjected to Cannizzaro's reaction by using NaOH. The mixture of the products contains sodium trichloroacetate ion and another compound. The other compounds is

(a) 2, 2, 2-trichloroethanol

(b) trichloromethanol

(c) 2, 2, 2-trichloropropanol

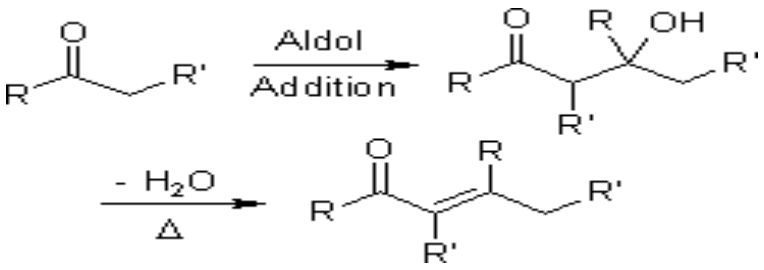
(d) chloroform.

Ans ; (i) a (ii) c (iii) a

Case – 3

Read the passage given below and answer the following questions :

`The addition reaction of enol or enolate to the carbonyl functional group of aldehyde or ketone is known as aldol addition. The β-hydroxyaldehyde or β-hydroxyketone so obtained undergo dehydration in second step to produce a conjugated enone. The first part of reaction is an addition reaction and the second part is an elimination reaction. Carbonyl compound having α-hydrogen undergoes aldol condensation reaction.



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

(i) Condensation reaction is the reverse of which of the following reaction?

(a) Lock and key hypothesis (b) Oxidation (c) Hydrolysis (d) Glycogen formation

(ii) Which of the following compounds would be the main product of an aldol condensation ofacetaldehyde and acetone?

(a) $CH_3CH=CHCHO$ (b) $CH_3CH=CHCOCH_3$

(c) $(CH_3)_2C=CHCHO$ (d) $(CH_3)_2C=CHCOCH_3$

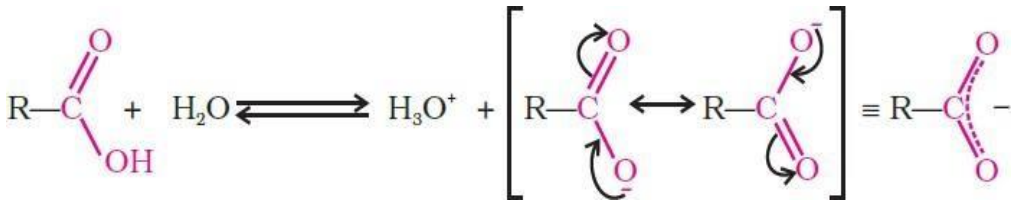
(iii) Which of the following will undergo aldol condensation?

(a) HCHO (b) CH_3CH_2OH (c) C_6H_5CHO (d) CH_3CH_2CHO

Ans (i) C (ii) b (iii) d

Case – 4

The carboxylic acids like alcohols evolve hydrogen with electropositive metals and form salts with alkalies similar to phenols. However, unlike phenols they react with weaker bases such as carbonates and hydrogen carbonates to evolve carbon dioxide. This reaction is used to detect the presence of carboxyl group in an organic compoundCarboxylic acids dissociate in water to give resonance stabilised carboxylate anions and Hydronium ion. Smaller the p*Ka*, the stronger the acid (the better it is as a proton donor). Strong acidshave p*Ka* values < 1, the acids with p*Ka* values between 1 and 5 are considered to be moderately strong acids, weak
Acids have pKa values between 5 and 15, and extremely weak acids have p*Ka* values >15.



(i) Which acid of each pair shown here would you expect to be stronger?

(a) CH_2FCO_2H or (b) CH_2ClCO_2H

(ii) Which one of the following is the correct order of acidic strength?

(a) $CF_3COOH > CHCl_2COOH > HCOOH > C_6H_5CH_2COOH > CH_3COOH$

(b) $CH_3COOH > HCOOH > CF_3COOH > CHCl_2COOH > C_6H_5CH_2COOH$

(c) $HCOOH > C_6H_5CH_2COOH > CF_3COOH > CHCl_2COOH > CH_3COOH$

(d) $CF_3COOH > CH_3COOH > HCOOH > CHCl_2COOH > C_6H_5CH_2COOH$

(iii) Which of the following acids has the smallest dissociation constant?

(a) $CH_3CHFCOOH$ **(b) FCH_2CH_2COOH**

(c) $BrCH_2CH_2COOH$ **(d) $CH_3CHBrCOOH$**

Ans (i) a (ii) a (iii) c

QUESTION BANK 1 MARK :

1)Write a test to differentiate between pentan-2-one and

pentan-3-one.

2) Arrange the following compounds in increasing order of their reactivity ,In nucleophilic addition reactions:

ethanal, propanal, propanone, butanone.

3) Rearrange the following compounds in the increasing order of their boiling points

CH_3CHO, CH_3CH_2OH, $CH_3CH_2CH_3$

4)Which of the following compounds would undergo the Cannizzaro reaction?

Benzaldehyde, Cyclohexanone, 2- Methylpentanal.

5) Write the structure of 3-oxopentanal.

6) Write the product when cyclohexanecarbaldehyde reacts with Tollen's reagent.

7) Which of the following compounds will give butanone on oxidation with alkaline KMnO4 solution?

a) Butan-1-ol

b) Butan -2-ol

c) both of these

d) none of these

8) What kind of compounds undergo Cannizaro reactions ?

(a) Ketones with no α - hydrogen

(b) Aldehydes with α - hydrogen

(c) Carboxylic acids with α - hydrogen

(d) Aldehydes with no α – hydrogen

2 MARK…

1) Account for the following:-

(i) Chloroacetic acid $Cl\text{-}CH_2COOH$ is a stronger acid than acetic acid CH_3COOH.

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

2) Give a simple chemical test to distinguish between:

(i) Acetophenone and Benzophenone

(ii) Benzaldehyde and Ethanal

3) : Illustrate the following reactions giving a chemical equation for each:

a) Rosenmund reduction

b) Wolff kishner reduction.

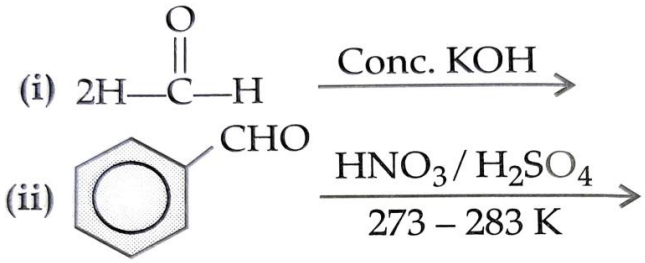
4) Arrange the following compounds in increasing order of their property as indicated :

(i) CH3COCH3, C6H5COCH3, CH3CHO

(reactivity towards nucleophilic addition reaction)

(ii) Cl-CH_2-COOH, F-CH_2-COOH, CH_3-COOH (acidic character)

5) Complete the following reactions



6) Arrange the following compounds in increasing order of their reactivity in nucleophilic addition reactions.
(i)Ethanal,Propanal,Propanone,Butanone.
(ii)Benzaldehyde, *p*-Tolualdehyde, *p*-Nitrobenzaldehyde, Acetophenone

3 MARKS

1) How would you convert the following:

(I)Phenol to benzoquinone

(ii) Propanone to 2-methylpropan-2-ol

(iii) Propene to propan-2-ol

2) (a) Describe the following reactions giving a chemical equation in each case:

(i) Cannizzaro's reaction (ii) Decarboxylation reaction iii) Stephen reaction.

3) How would you obtain

(i) Benzoquinone from phenol?

(ii) Propan-2-ol from propene?

(iii) 2- Methylpropan-2-ol from methyl magnesium bromide?

4) Give chemical tests to distinguish between

(i) Phenol and Benzoic acid

(ii) Benzophenone and Acetophenone

iii) Acetaldehyde and Benzaldehyde

5) Do the following conversions in not more than two steps:

(i) Benzoic acid to benzaldehyde

(ii) Ethyl benzene to Benzoic acid

(iii) Propanone to Propene

6) Draw the structures of the following compounds:
(i) 4-methyl pent-3-en-2-one

(ii) 4-Chlocopentan-2-one

4(iii) 4-Methylpent-3-en-2-one

7) Give reasons:

a)Electrophilic substitution in benzoic acid takes place at meta position.

b)Carboxyilic acids are higher boiling liquids than aldehydes,ketones and alcohols of comparable molecular mass.

c)4-nitrobenzoic acid is more acidic than benzoic acid.

8)

(i) What type of aldehydes undergo Cannizaro reaction?

ii)Write the equations involved in the following reactions:

(a) Wolff-Kishner reduction

(b) Etard reaction

9) Give reasons for the following:

(i) Ethanal is more reactive than acetone towards nucleophilic addition reaction.

(ii) $(CH_3)_3C$-CHO does not undergo aldol condensation.

(iii) Carboxylic acids are higher boiling liquids than alcohol.

10)

(i) Account for the following:

(a) CI-CH2COOH is a stronger acid than CH3COOH.

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

(ii) Write the chemical equation to illustrate the following name reaction Rosenmund reduction.

5 MARKS

1) (a) How would you account for the following:

(i)Aldehydes are more reactive than ketones towards nucleophiles.

(ii)The boiling points of aldehydes and ketones are lower than of the corresponding acids.

(iii)The aldehydes and ketones undergo a number of addition reactions.

(b)Give chemical tests to distinguish between:

(i) Acetaldehyde and Benzaldehyde

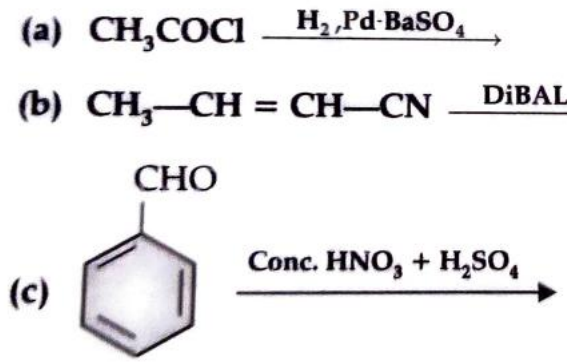
(ii)Propanone and propanol

2) (i) What is meant by the following terms ? Give an example of the reaction in each case.

(a) Aldol

(b) Semicarbazone

(i) Complete the following:



3) .(a) Account for the following :

(i) CH3CHO is more reactive than CH3COCH3 towards reaction with HCN.

(ii) Carboxylic acid is a stronger acid than phenol.

(b) Write the chemical equations to illustrate the following name reactions :

(i) Wolff-Kishner reduction

(ii) Aldol condensation

(iii) Cannizzaro reaction

4) A compound 'A' with formula $C_5H_{10}O$ gives a positive 2, 4 –DNP test but a negative Tollen's test It can be oxidizing to carboxylic acid 'B' of molecular formula $C_3H_6O_2$, when treated with alk. $KMnO_4$ under vigorous conditions. The salt of 'B' gives a hydrocarbon 'C' on Kolbes' electrolytic decarboxylation. Identify A, B.C & write chemical equations.

5) a) Illustrate the following name reactions by giving example:
(i) Cannizzaro's reaction (ii) Clemmensen reduction
b) An organic compound A contain 69.77% carbon, 11.63% hydrogen and rest oxygen. The molecular mass of the compound is 86. It does not reduce Tollen's reagent but forms an addition compound with sodium hydrogen sulphite and gives positive iodoform test. On vigorous oxidation it gives ethanoic and propanoic acids. Derive the possible structure of compound 'A'.

6) a) How will you bring about the following conversions:
(i) Ethanol to 3-hydroxybutanal (ii) Benzaldehyde to Benzophenone.
(b) An organic compound A has the molecular formula C8H16O2. It gets hydrolysed with dilute sulphuric acid and gives a carboxylic acid B and an alcohol C. Oxidation of C with chromic acid also produced B. C on dehydration reaction gives but-1-ene. Write equations for the reactions involved

7) a)Arrange the following compounds in an increasing order of their indicated property
(i) Benzoic acid, 4-Nitrobenzoic acid, 3,4-Dinitrobenzoic acid, 4-Methoxybenzoic acid (acid strength)
(ii) CH3CH2CH(Br)COOH, CH3CH(Br) CH2COOH, (CH3)2CHCOOH, CH3CH2CH2COOH (acid strength)
(b) How would you bring about the following conversions:
(i) Propanone to Propene
(ii) Benzoic acid to Benzaldehyde
(iii) Bromobenzene to 1-phenylethanol

8) (a) Give chemical tests to distinguish between (i) Propanol and propanone (ii) Benzaldehyde and acetophenone
(b) Arrange the following compounds in increasing order of their property as indicated:
(i) Acetaldehyde, Acetone, Methyl tert-butyl ketone (reactivity towards HCN)
(ii) Benzoic acid, 3,4-Dinitrobenzoic acid, 4-Methoxybenzoic acid (acid strength)
(iii) CH3CH2CH(Br)COOH, CH3CH(Br)CH2COOH, (CH3)2CHCOOH (acid strength)

9) (a) Give reasons for the following:
(i) Ethanal is more reactive than acetone towards nucleophilic addition reaction.
(ii) (CH3)3C—CHO does not undergo aldol condensation.
(iii) Carboxylic acids are higher boiling liquids than alcohols.

(a) Give a simple chemical test to distinguish between
i)Acetophenone and Benzophenone
(ii) Benzaldehyde and Ethanal

10) (a) How will you convert the following:
(i) Propanone to Propan-2-ol (ii) Ethanal to 2-hydroxy propanoic acid (iii) Toluene to benzoic acid
(b) Give simple chemical test to distinguish between:
(i) Pentan-2-one and Pentan-3-one (ii) Ethanal and Propanal

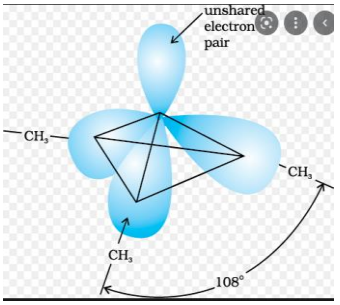
CHAPTER-12

AMINES

GIST OF THE LESSON

Amines can be considered as derivatives of ammonia, obtained by replacement of one, two or all the three hydrogen atoms by alkyl or aryl groups.

For example:CH_3NH_2, $C_6H_5NH_2$, $(CH_3)_2NH$, $(CH_3)_3NH$.



STRUCTURE OF AMINES:

In Amines N atom is sp^3 hybridized and have triagonal pyramidal structure.

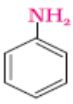
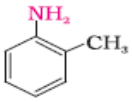
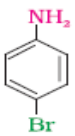
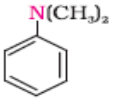
CLASSIFICATION:

Amines are classified as 1^0,2^0,3^0depending on the number of hydrogen atoms replaced by alkyl or aryl group in ammonia molecule.

NH_3 → RNH_2 → RR'NH→ RR'R''NH

NOMENCLATURE:

In IUPAC system alkyl amines are named as alkanamines.

Amine	Common name	IUPAC name
CH_3–CH_2–NH_2	Ethylamine	Ethanamine
CH_3–CH_2–CH_2–NH_2	*n*-Propylamine	Propan-1-amine
$CH_3-\underset{\displaystyle NH_2}{\underset{\vert}{CH}}-CH_3$	Isopropylamine	Propan-2-amine
$CH_3-\underset{\displaystyle H}{\underset{\vert}{N}}-CH_2-CH_3$	Ethylmethylamine	N-Methylethanamine
$CH_3-\underset{\displaystyle CH_3}{\underset{\vert}{N}}-CH_3$	Trimethylamine	N,N-Dimethylmethanamine
$C_2H_5-\underset{\displaystyle C_2H_5}{\underset{\vert}{N}}-\overset{1}{CH_2}-\overset{2}{CH_2}-\overset{3}{CH_2}-\overset{4}{CH_3}$	*N,N*-Diethylbutylamine	N,N-Diethylbutan-1-amine
$NH_2-\overset{1}{CH_2}-\overset{2}{CH}=\overset{3}{CH_2}$	Allylamine	Prop-2-en-1-amine
$NH_2-(CH_2)_6-NH_2$	Hexamethylenediamine	Hexane-1,6-diamine
	Aniline	Aniline or Benzenamine
	*o*-Toluidine	2-Methylaniline
	*p*-Bromoaniline	4-Bromobenzenamine or 4-Bromoaniline
	*N,N*-Dimethylaniline	N,N-Dimethylbenzenamine

PREPARATION OF AMINES:

(1) REDUCTION OF NITRO COMPOUNDS:

Nitro compounds are reduced to amines by passing hydrogen gas in the presence of finely divided nickel, palladium or platinum and also by reduction with metals in acidic medium.

$$RNO_2 \xrightarrow{H_2/Pd/Ethanol} RNH_2$$

$$RNO_2 \xrightarrow{Sn/HCl \text{ Or } Fe/HCl} RNH_2$$

(2) AMMONOLYSIS OF ALKYL HALIDES:

The process of cleavage of the C-X bond by ammonia molecule is known as ammonolysis. The reaction is carried out in a sealed tube at 373K.

$$NH_3 + RX \rightarrow RNH_3^+X^-$$

$$RNH_2 \xrightarrow{RX} R_2NH \xrightarrow{RX} R_3N \xrightarrow{RX} R_4N^+X^-$$

The free amine can be obtained from ammonium salt by treatment with a strong base.

$$RNH_3^+X^- + NaOH \rightarrow RNH_2 + H_2O + NaX$$

(3) REDUCTION OF NITRILES:

Nitriles on reduction with $LiAlH_4$ or catalytic hydrogenation produce primary amines.

$$RCN \xrightarrow[Na(Hg)/C_2H_5OH]{H_2/Ni} RCH_2NH_2$$

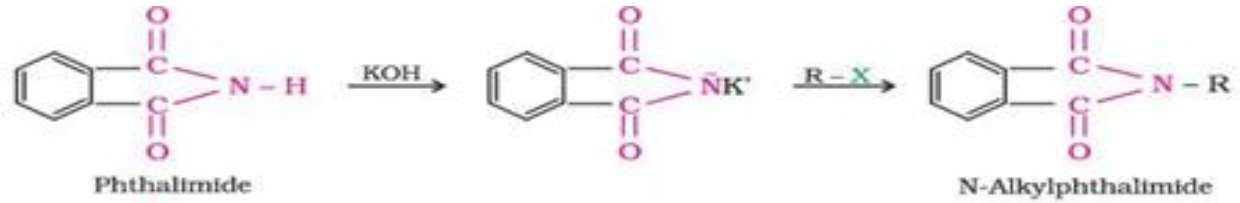
(4) REDUCTION OF AMIDES:

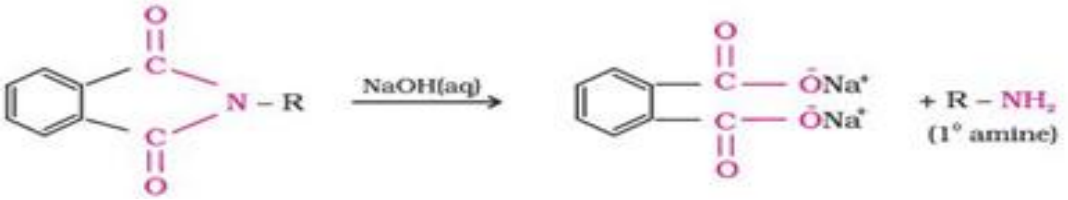
The amides on reduction with $LiAlH_4$ yield amines.

$$RCONH2 \xrightarrow{LiAlH_4/H_2O} RCH_2NH_2$$

(5) GABRIEL PHTHALIMIDE SYNTHESIS:

It is used for the preparation of primary amines. Phthalimide on treatment with ethanolic KOH forms potassium salt of phthalimide which on heating with alkyl halide followed by alkaline hydrolysis produces the corresponding alkyl amine. Aromatic primary amines cannot be prepared by this method because aryl halides do not undergo nucleophilic substitution with the anion formed by the phthalimide.





(6) HOFFMANN BROMAMIDE DEGRADATION REACTION:

Hoffmann developed a method for preparation of primary amines by treating with bromine in an aqueous or ethanolic solution of NaOH. In this degradation reaction, migration of an alkyl or aryl group takes place from carbonyl carbon of the amide to the nitrogen atom. The amide so forced contains one carbon less than that present in the amide.

$$RCONH_2 + Br_2 + 4NaOH \rightarrow RNH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

1. PHYSICAL PROPERTIES:

The lower aliphatic amines are gases with fishy odour. Primary amines wit 3 or more carbon atoms are liquid and still higher ones are solid. Aniline and other aryl amines are usually colorless but get colored on storage due to atmospheric oxidation.

Lower aliphatic amines are soluble in water because they can form hydrogen bonds with water molecules. Solubility decreases with increase in molar mass of amines due to increases in size of the hydrophobic alkyl part. Higher amines are insoluble in water.

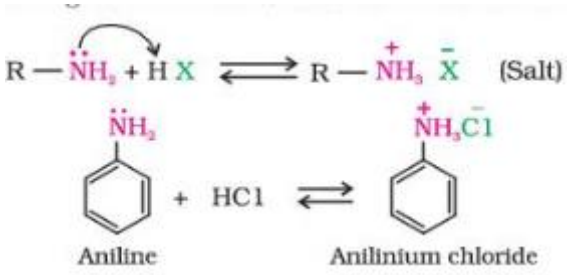
Primary and secondary amines are engaged in intermolecular hydrogen bonding and undergoes association. Tertiary amines do not have intermolecular hydrogen bonding hence no association of molecules. The order of boiling points are as follows.

Primary › Secondary› Tertiary

2. CHEMICAL PROPERTIES:

(1) BASIC NATURE OF MINES:

Amines reacts with acids to form salts.



Amine salts on treatment with a base like NaOH regenerate the parent amine.

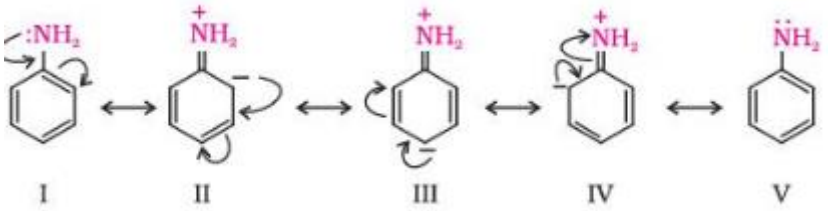
$$RNH_3^+X^- + NaOH \rightarrow RNH_2 + H_2O + NaX$$

The order of basicity of amines in the gaseous phase :$3^0 \rangle \ 2^0 \rangle 1^0 \rangle NH_3$

The order of basic strength in case of methyl and ethyl substituted amines in aqueous solution is as follows:

$$(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$$
$$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$$

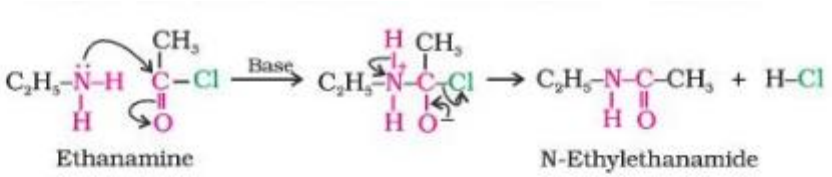
Aryl amines are less strong than amines and ammonia since lone pair on nitrogen is not available for donation.

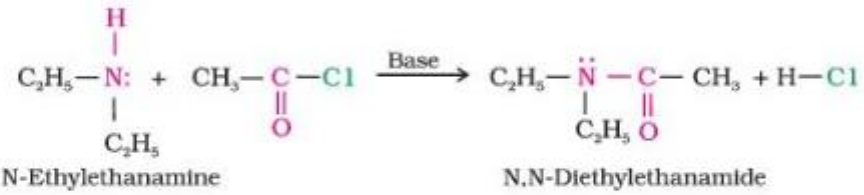


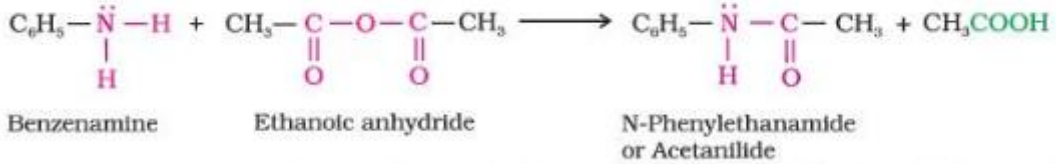
In case of substituted amines electron releasing groups like $-OCH_3$,$-CH_3$ increase the basic strength whereas electron withdrawing groups like $-No_2$,$-SO_3H$,-COOH,-X decrease it

(2) ACYLATION:

Aliphatic and aromatic primary and secondary amines reacts with acid chlorides ,anhydrides and esters by nucleophilic substitution reaction.







Amines also react with benzoyl chloride (C_6H_5COCl). This reaction is known as benzoylation.

CH_3NH_2 + C_6H_5COCl → $CH_3NHCOC_6H_5 + HCl$

Methanamine — Benzoyl chloride — N – Methylbenzamide

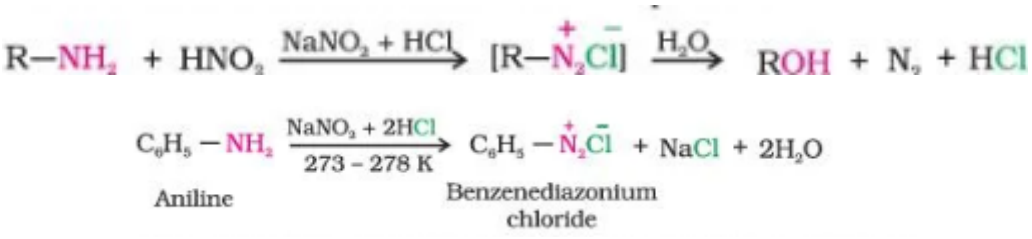
(3) CARBYLAMINE REACTION:

Aliphatic and aromatic primary amines on heating with chloroform and ethanolic KOH form isocynides or carbylamines which are foul smelling substances. It is used as test for primary amines.

$$R-NH_2 + CHCl_3 + 3KOH \xrightarrow{Heat} R-NC + 3KCl + 3H_2O$$

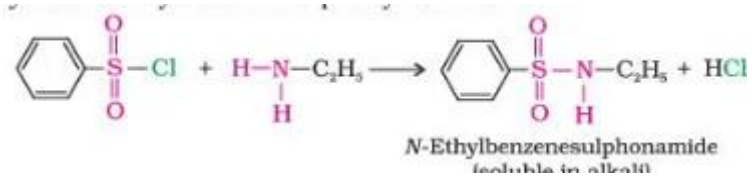
(4) REACTION WITH HNO_2, NITRIC ACID:

Primary aliphatic amines react with nitric acid to form alcohols while primary aromatic amines form diazonium chloride.

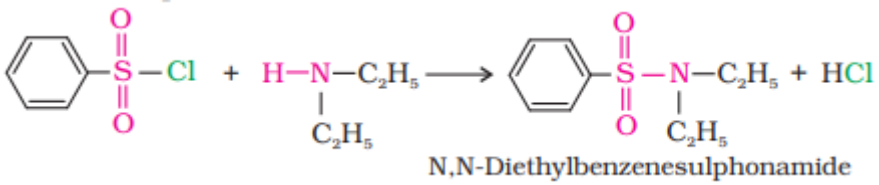


(5) REACTIOIN WITH ARYL SULPHONYL CHLORIDE: HINSBERG TEST

The reaction of benzene sulphonyl chloride with primary amine yields N-ethylbenzenesulphonyl amide which is soluble in alkali.



In reaction with secondary amine ,N,N-diethyl benzenesulphonamide is formed which is insoluble in alkali.

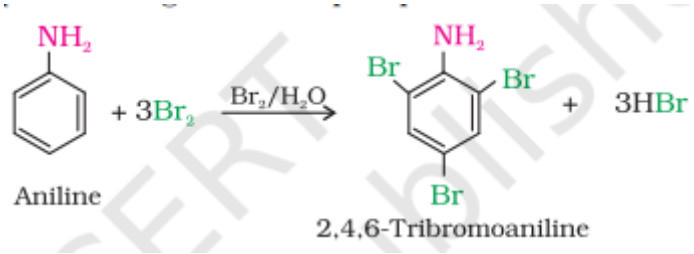


Tertiary amines do not react with benzene sulphonyl chloride due to lack of hydrogen atom.

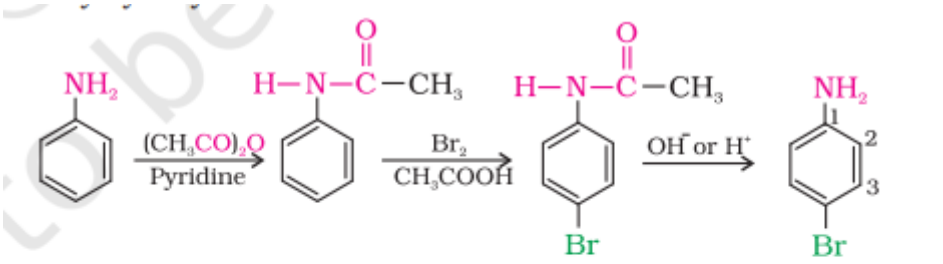
(6) ELECTROPHILIC SUBSTITUTION:

(1) BROMINATION:

Aniline reacts with bromine water at room temperature to give a white precipitate of 2,4,6-tribromoaniline.



For getting mono substituted product –NH2 group is to be deactivated with acetic anhydride.

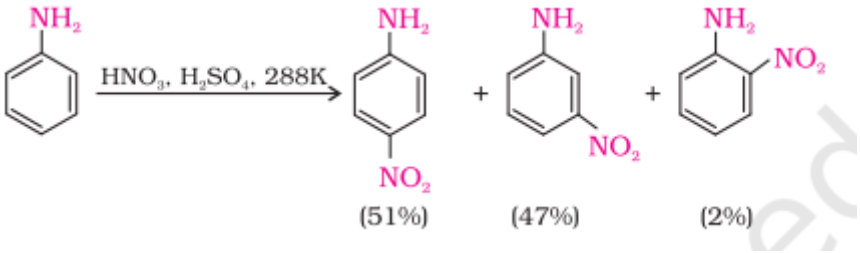


The lone pair of electrons on nitrogen of acetanilide interacts with oxygen atom due to resonance as shown below:

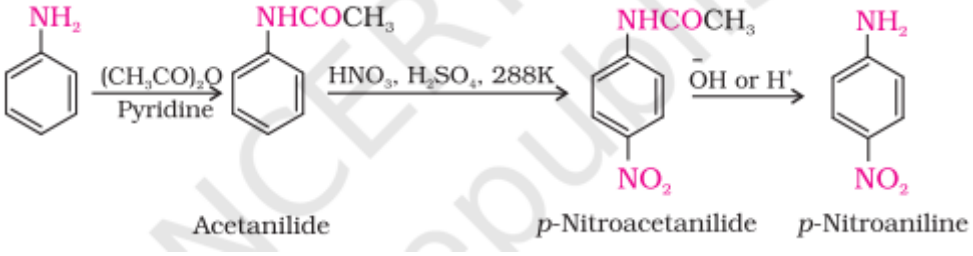
(2) NITRATION:

Nitration gives mixture of ortho, meta and para products.

In acidic medium aniline is protonated to anilinium ion which is meta directing. That is why besides ortho par products considerable amount of meta product is also formed.

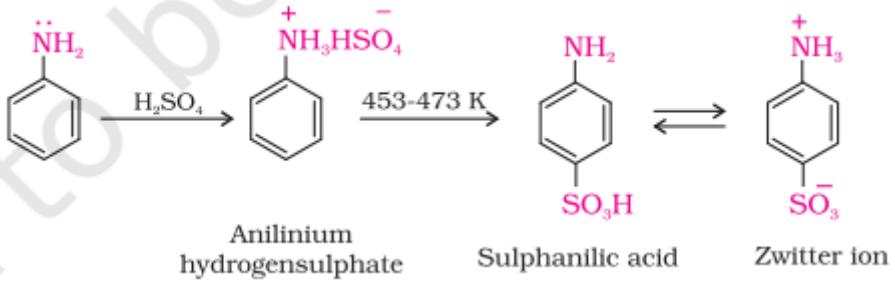


Mono substituted product is formed by protecting amino group.



(3) SULPHONATION:

Aniline reacts with conc. sulphuric acid to form anilinium hydrogensulphate which on heating with sulphuric acid at 453-473k produces suphanilic acid.



Aniline does not undergo Friedel-Crafts reaction due to salt formation with aluminum chloride, the Lewis acid, which is used as a catalyst.

3. DIAZONIUM SALTS:

(1) PREPARATION:

Benzenediazonium chloride is prepared by the reaction of aniline with nitrous acid at 273-278K.

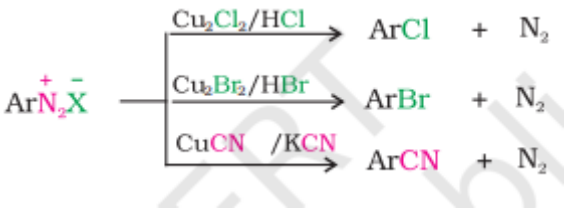
$$C_6H_5NH_2 + NaNO_2 + 2HCl \xrightarrow{273-278K} C_6H_5N_2^+Cl^- + NaCl + 2H_2O$$

(2) CHEMICAL PROPERTIES:

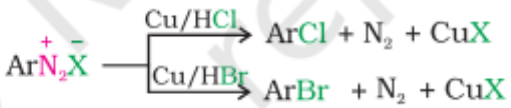
A. REACTION INVOLVING DISPLACEMENT OF NITROGEN:

1. REPLACEMENT BY HALIDE OR CYNIDE ION:

SANDMEYER'S REACTION:



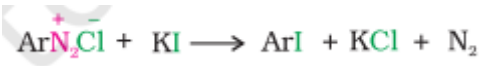
GATTERMAN REACTION:-



The yield in Sandmeyer reaction is found to be better than Gattermann reaction.

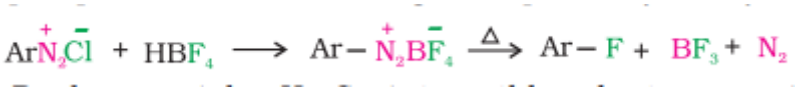
2. REPLACEMENT BY IODIDE ION:-

Iodine can be introduced on treatment with KI



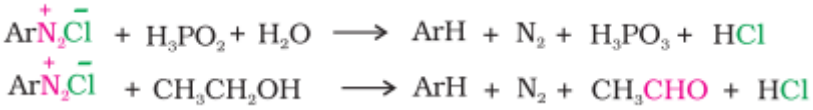
3. REPLACEMENT WITH FLUORIDE ION:-

When arenediazonium chloride is treated with fluoro boric acid,arene diazonium fluoroborate is precipitated which on heating decomposes to yield aryl fluoride.



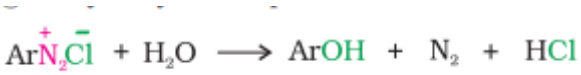
4. REPLACEMENT BY HYDROGEN:-

Benzene diazonium chloride can be converted to benzene on treatment with H_3PO_2 or ethanol.



5. REPLACEMENT BY HYDROXYL GROUP:-

If the temperature of the diazonium salt solution is allowed to rise upto 283K,the salt gets hydrolysed to phenol.



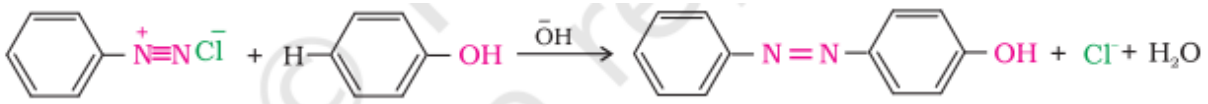
6. REPLACEMENT BY $–NO_2$ GROUP:

When diazonium fluoroborate is heated with aqueous sodium nitrite solution in the presence of copper,the diazonium group is replaced with $–NO_2$ group.

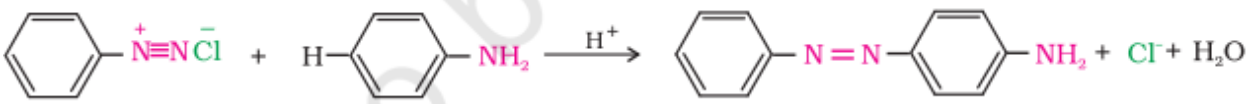
B. REACTION INVOLVING RETENTION OF DIAZO GROUP:-

COUPLING REACTION:

The diazo compounds on reaction with ethanol or amine in presence of alkali give azo products.



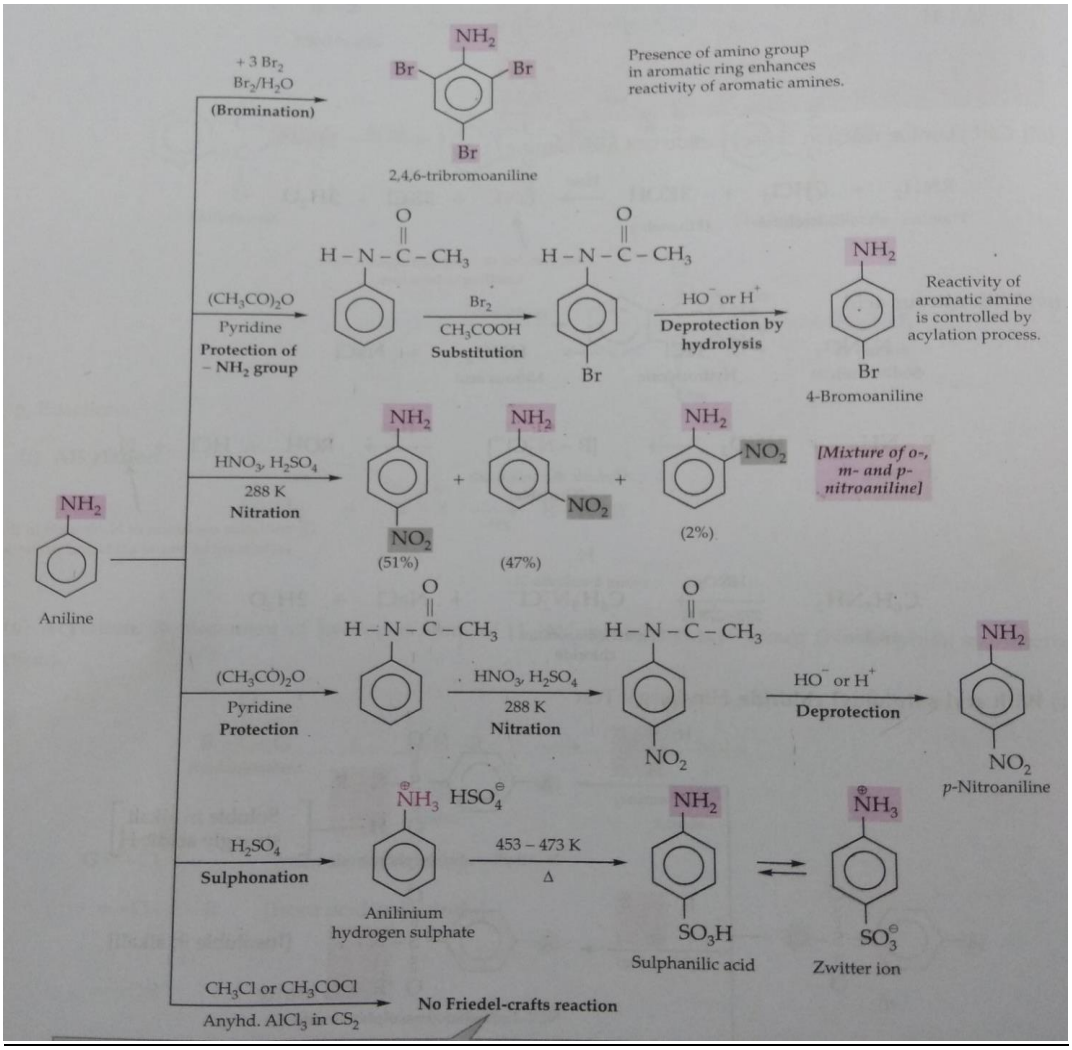
p-Hydroxyazobenzene (orange dye)



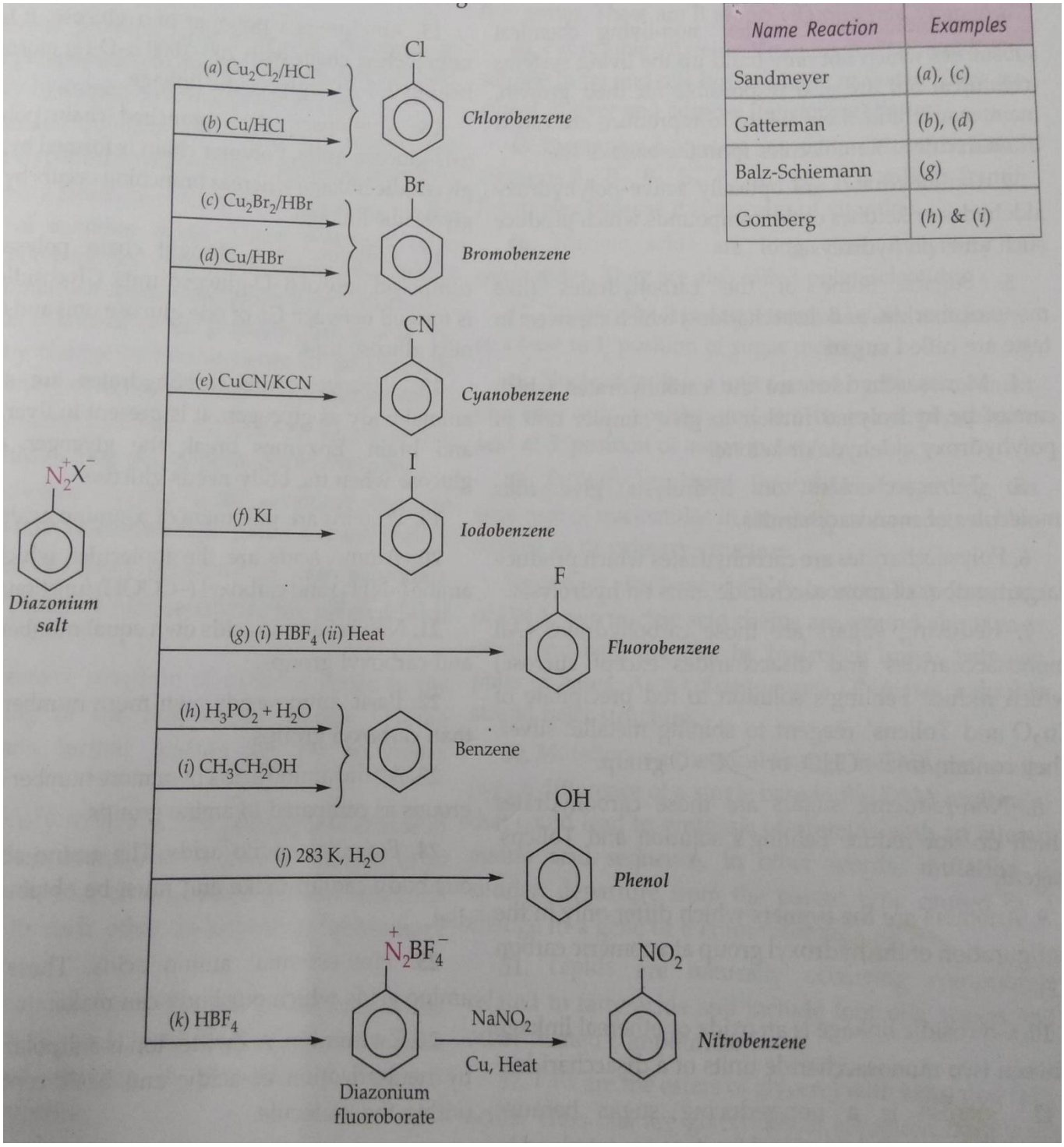
p-Aminoazobenzene (yellow dye)

CONCEPT MAP

1. ELECTROPHILIC REACTIONS OF ANILINE:



2. REACTIONS OF BENZENE DIAZONIUM CHLORIDE:-



Name Reaction	Examples
Sandmeyer	(*a*), (*c*)
Gatterman	(*b*), (*d*)
Balz-Schiemann	(*g*)
Gomberg	(*h*) & (*i*)

SHORT ANSWER TYPE QUESTIONS:

1. Write the chemical equations involved when $C_2H_5NH_2$ is treated with
   (1) CH_3COCl/Pyridine (2) $CHCl_3$+KOH.
   A. (1) $C_2H_5NH_2$+ CH_3COCl/Pyridine $\rightarrow CH_3CONHC_2H_5$

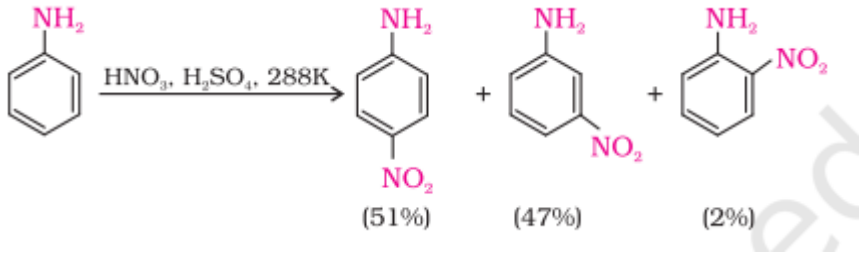
   (2) $C_2H_5NH_2$+ $CHCl_3$+3KOH(Alcoholic) $\rightarrow C_2H_5NC$+3KCl+$3H_2O$

2. How will you convert (1)Aniline to Bromobenzene(2)Aniline to Benzene?
   $NaNO_2$/HCl/5^0C CuBr/HBr
   A. (1) $C_6H_5NH_2 \rightarrow C_6H_5N_2Cl \rightarrow C_6H_5Br$
   (2) $NaNO_2$/HCl/5^0C H_3PO_2/H2O
   A. (1)$C_6H_5NH_2 \rightarrow C_6H_5N_2Cl \rightarrow C_6H_6$

3. Why aniline does not undergo Friedel -Crafts reaction?
   A. Aniline does not undergo Friedel-Crafts reaction due to salt formation with aluminum chloride, the Lewis acid, which is used as a catalyst.

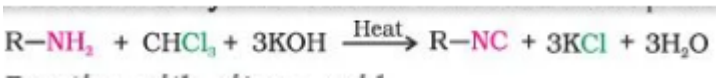
4. Nitration of aniline yields considerable amounts of meta products. Why?

A. Nitration gives mixture of ortho, meta and para products.
In acidic medium aniline is protonated to anilinium ion which is meta directing. That is why besides ortho par products considerable amount of meta product is also formed.



5. Why cannot aromatic primary amines be prepared by Gabriel phthalimide synthesis?
   A. Aromatic primary amines cannot be prepared by this method because aryl halides do not undergo nucleophilic substitution with the anion formed by the phthalimide.

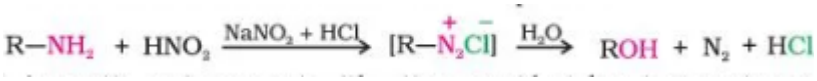
6. Write equations of the following name reactions?
   (1) Carbylamine reaction
   (2) Hofmann's bromamide degradation reaction.
   A. (1) Carbylamine reaction
   Aliphatic and aromatic primary amines on heating with chloroform and ethanolic KOH form isocynides or carbylamines which are foul smelling substances. It is used as test for primary amines.

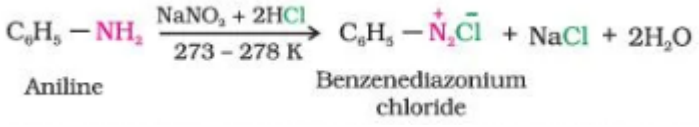


   (2) Hofmann's bromamide degradation reaction
   Hoffmann developed a method for preparation of primary amines by treating with bromine in an aqueous or ethanolic solution of NaOH. In this degradation reaction, migration of an alkyl or aryl group takes place from carbonyl carbon of the amide to the nitrogen atom. The amide so fored contains one carbon less than that present in the amide.

$RCONH_2 + Br_2 + 4NaOH \rightarrow RNH_2 + Na_2CO_3 + 2NaBr + 2H_2O$

7. Write the reactions of aromatic and aliphatic primary amines with nitrous acid?
   A. Primary aliphatic amines reacts with nitric acid to form alcohols while primary aromatic amines form diazonium chloride.





8. Why do primary amines have higher boiling point than tertiary amines?
   A. Primary amines are associated with inter molecular hydrogen bonding while tertiary amines does not.

9. Why are aliphatic amines stronger bases than aromatic amines?
   A. In aliphatic amines alkyl group increases the electron density on N of $–NH_2$ group while in aromatic amines lone pair on N is not available for donation since it is involved in conjugation with pi electrons of benzene ring.

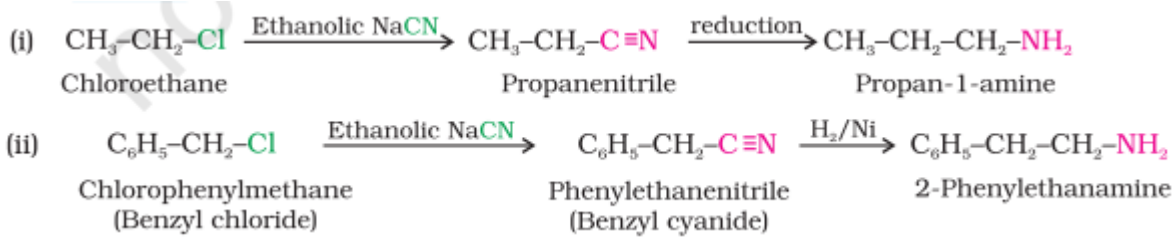
10. Why are amines less acidic than alcohols of comparable molecular masses?
    A. Amines are having $–NH_2$ group which donates lone pair of electron hence basic. Alcohols can provide hydronium ions hence highly acidic in nature.

11. pK_b of aniline is more than that of methylamine. Why?
    A. Aniline is a weaker base than methylamine since lone pair on N is not available for donation since it is involved in conjugation with pi electrons of benzene ring.

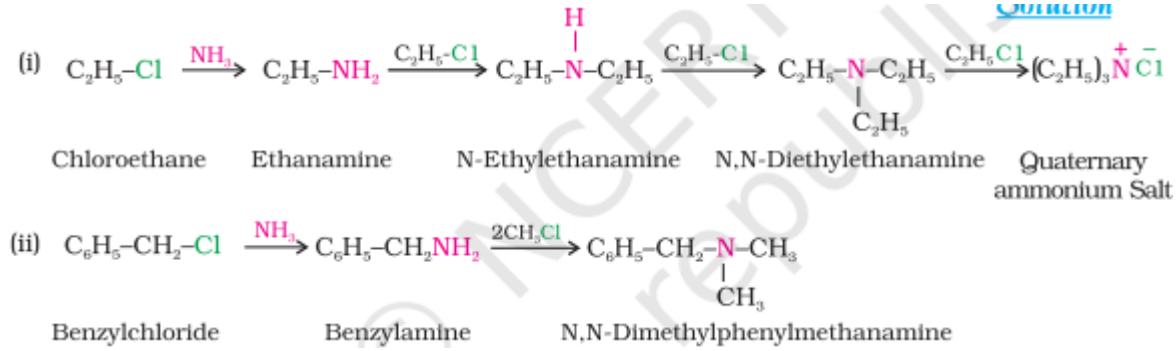
12. Ethylamine is soluble in water whereas aniline is not. Why?
    A. Ethylamine can form hydrogen bonding with water while aniline can not due bulky phenyl group.

13. Give one chemical test to distinguish between the following pairs of compounds
    (1) Methylamine and Dimethylamine
    (2)Aniline and benzylamine
    A. (1) Methylamine on reaction with chloroform and alcoholic KOH gives foul smelling methyl isocynide while dimethylamine does not.
    (2) Aniline on treatment with nitrous acid forms Benzene diazonium chloride which on coupling with phenol forms orange dye while benzylamine does not.

14. Write the chemical equatios for the following conversions(1)Chloro ethane to Propanamine(2)Benzyl chloride to 2-Phenylethanamine.



15. Write the chemical equations for the following reactions:
    (1) Reaction of ethanolic NH_3 with C_2H_5Cl
    (2) Ammonolysis of benzyl chloride and reaction of amine so formed with 2 moles of CH_3Cl

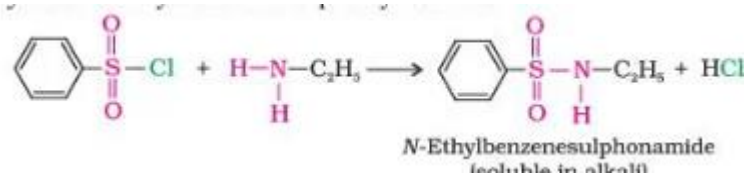


LONG ANSWER TYPE QUESTIONS:-

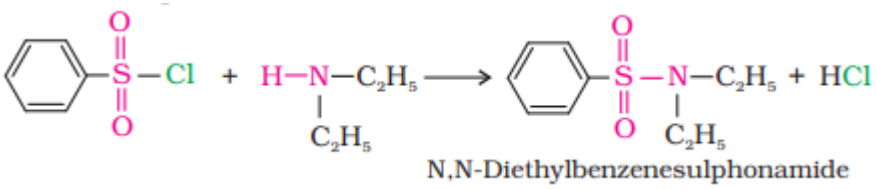
1. How will you distinguish between primary ,secondary and tertiary amines? Write the chemical equations involved?

A. Primary, secondary and tertiary amines can be distinguished by Hinsberg test.

The reaction of benzene sulphonyl chloride with primary amine yields N-ethylbenzenesulphonyl amide which is soluble in alkali.



In reaction with secondary amine, N,N-diethyl benzenesulphonamide is formed which is insoluble in alkali.



Tertiary amines do not react with benzene sulphonyl chloride due to lack of hydrogen atom.

2. Complete the following reactions:

(1) $C_6H_5NH_2+CHCl_3+alc.KOH \rightarrow$

(2) $C_6H_5N_2Cl+H_3PO_2+H_2O\rightarrow$

(3) $C_6H_5NH_2+H_2SO_4\rightarrow$

(4) $C_6H_5N_2Cl+C2H5OH\rightarrow$

(5) $C_6H_5NH_2+(CH_3CO)_2O\rightarrow$

A. (1) $C_6H_5NH_2+CHCl_3+alc.3KOH \rightarrow C_6H_5NC+3KCl+3H_2O$

(2) $C_6H_5N_2Cl+H_3PO_2+H_2O\rightarrow C6H6+ H_3PO_3+N_2+HCl$

(3) $C_6H_5NH_2+H_2SO_4\rightarrow C_6H_5NH_3^+SO_4^-$

(4) $C_6H_5N_2Cl+C_2H_5OH\rightarrow C_6H_6+CH_3CHO+ N_2+HCl$

(5) $C_6H_5NH_2+(CH_3CO)_2O\rightarrow C_6H_5NHCOCH_3$

3. An aromatic compound A on treatment with aqueous ammonia and heating forms a compound B which on heating with Br_2 and KOH forms a compound C of molecular formula C_6H_7N.Write the structures and IUPAC names of A, B, C.

A. C: C_6H_7N ie $C_6H_5NH_2$

C is obtained from B on treating with Br_2 and KOH

$$B \xrightarrow{Br_2 \text{ and KOH}} C_6H_5NH_2$$

Hence B is $C_6H_5CONH_2$

$$C_6H_5CONH_2 \xrightarrow{Br_2 \text{ and KOH}} C_6H_5NH_2$$

B is obtained from A on treatment with aqueous ammonia and heating

$$A + NH_3 \rightarrow C_6H_5CONH_2$$

Hence A is C_6H_5COOH

$C_6H_5COOH+NH_3 \rightarrow C_6H_5CONH_2$

A: C_6H_5COOH:Benzoic acid

B: $C_6H_5CONH_2$:Benzamide

C: $C_6H_5NH_2$:Aniline

4. Accomplish the following conversions:

(1) Nitrobenzene to benzoic acid

(2) Benzoic acid to aniline

(3) Benzamide to toluene

(4) Aniline to benzyl alcohol

(5) Ethanoic acid to methanamine

A (1) $C_6H_5NO_2 \xrightarrow{Sn/HCl} C_6H_5NH_2 \xrightarrow{HNO_2/5^0C} C_6H_5N_2Cl \xrightarrow{H_3PO_2+H_2O} C_6H_6 \xrightarrow{CH_3Cl/AlCl_3} C_6H_5CH_3 \xrightarrow{KMnO_4/H^+} C_6H_5COOH$

(2) $C_6H_5COOH \xrightarrow{NH3/heat} C_6H_5CONH_2 \xrightarrow{Br_2 \text{ and KOH}} C_6H_5NH_2$

(3) $C_6H_5CONH_2 \xrightarrow{Br_2 \text{ and KOH}} C_6H_5NH_2 \xrightarrow{HNO_2/5^0C} C_6H_5N_2Cl \xrightarrow{H_3PO_2+H_2O} C_6H_6 \xrightarrow{CH_3Cl/AlCl_3} C_6H_5CH_3$

(4) $C_6H_5NH_2 \xrightarrow{HNO_2/5^0C} C_6H_5N_2Cl \xrightarrow{H_3PO_2+H_2O} C_6H_6 \xrightarrow{CH_3Cl/AlCl_3} C_6H_5CH_3 \xrightarrow{KMnO_4/H^+} C_6H_5COOH$

$LiAlH_4$
→ $C_6H_5CH_2OH$

NH3/heat Br_2 and KOH
(5) $CH_3COOH \rightarrow CH_3CONH_2 \rightarrow C_6H_5NH_2$

5. Write the chemical equations of the following name reactions;
(1) Diazotization
(2) Sandmeyers reaction
(3) Gattermann reaction
(4) Gabriel pthalimide synthesis
(5) Ammonolysis

A.

(1) $C_6H_5NH_2 + NaNO_2 + 2HCl \xrightarrow{273\text{-}278K} C_6H_5\overset{+}{N_2}\overset{-}{Cl} + NaCl + 2H_2O$

(2)

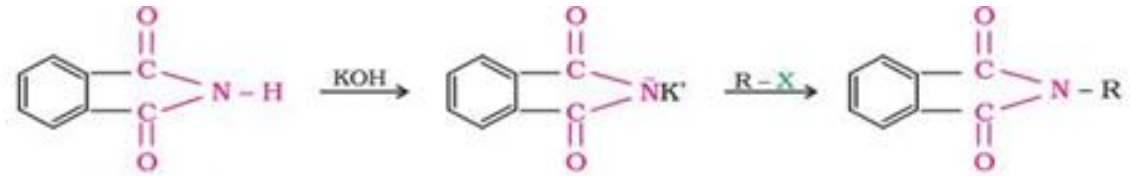
$$ArN_2X \xrightarrow{Cu_2Cl_2/HCl} ArCl + N_2$$
$$ArN_2X \xrightarrow{Cu_2Br_2/HBr} ArBr + N_2$$
$$ArN_2X \xrightarrow{CuCN/KCN} ArCN + N_2$$

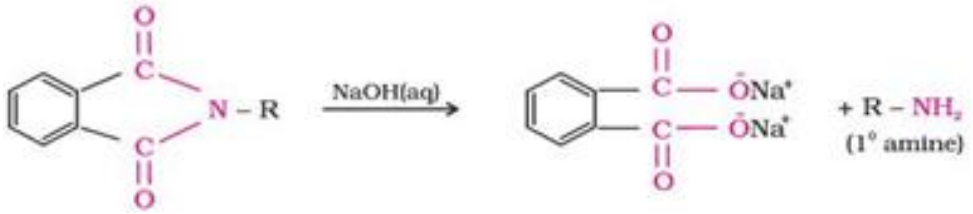
(3)

$$ArN_2X \xrightarrow{Cu/HCl} ArCl + N_2 + CuX$$
$$ArN_2X \xrightarrow{Cu/HBr} ArBr + N_2 + CuX$$

The yield in Sandmeyer reaction is found to be better than Gattermann reaction.

(4)





(5) $RNH_2 \xrightarrow{RX} R_2NH \xrightarrow{RX} R_3N \xrightarrow{RX} R_4N^+X^-$

MULTIPLE CHOICE QUESTIONS

1. What is the correct IUPAC name of H2N-(CH2)5-NH2?
    a. Pentan-1,5-diamine
    b. 1,5-Diaminopentane
    c. Pentamethylenediamine
    d. Pentane-1,5-diamine
2. Which of the following does not react with Hinsberg reagent?
    a. C2H5NH2
    b. (CH3)2NH
    c. (CH3)3N
    d. CH3 CH(NH2)CH3
3. Which of the following amines are insoluble in water?
    a. Methanamine
    b. Ethanamine
    c. Propanamine
    d. Benzenamine
4. Which of the following is formed when an alkyl primary amine reacts with nitrous acid?
    a. Alkyl nitrite
    b. Secondary amine
    c. Nitroalkane
    d. Alcohol
5. Arrange the following compounds in increasing order of basicity: CH3NH2, (CH3)2 NH, NH3, C6H5NH2 in aqueousmedium
    a. C6H5NH2 < NH3 < (CH3)2NH < CH3NH2
    b. CH3NH2 < (CH3)2NH < NH3 < C6H5NH2
    c. C6H5NH2 <NH3 < CH3NH2<(CH3)2NH

d. (CH3)2NH < NH3 < C6H5NH2 < CH3NH2

6. The correct IUPAC name for CH2 = CHCH2NHCH3 is
    a. Allylmethylamine
    b. 2-amino-4-pentene
    c. 4-aminopent-1-ene
    d. N-methylprop-2-en-1-amine
7. C3H8N cannot represent
    a. 1° ammine
    b. 2° ammine
    c. 3° ammine
    d. Quartemary ammonium salt
8. In this reaction acetamide is converted to methanamine
    a. Gabriel phthalimide synthesis
    b. Carbylamine reaction
    c. Stephen's reaction
    d. Hoffmann bromamide reaction
9. Which of the following is not a final product of the reaction between propylamine and nitrous acid?
    a. CH3CH2CH2N2Cl
    b. CH3CH2CH2OH
    c. N2 gas
    d. HCI
10. Hinsberg's reagent is
    a. Benzenesulphonic acid
    b. Benzenesulphonyl chloride
    c. p-toluenesulphonyl chloride
    d. Chlorosulphuric acid
11. Starting from propanoic acid, the following reactions were carried out, what is the compound Z?
    a. CH3-CH2−Br
    b. CH3-CH2−NH2
    c. CH3-CH2-COBr
    d. CH3−CH2−CH2−NH2
12. Aniline in a set of reactions yielded a product D. The structure of D would be
    a. C6H5CH2OH
    b. C6H5CH2NH2
    c. C6H5NHOH
    d. C6H5NHCH2CH3.
13. The hybridisation state of N of R2NH
    a. sp3
    b. sp2
    c. sp
    d. dsp2
14. Reduction of CH3CH2NC with hydrogen in presence of Ni or Pt as catalvst gives
    a. CH3CH2NH2
    b. CH3CH2NHCH3
    c. CH3CH2NHCH2CH3

d. (CH3)3N

15. When hypophosphorous acid is treated with diazonium salts, it is reduced to which of the following compound?
    a. Arene
    b. Methane
    c. Ethyl alcohol
    d. Amines

ANSWERS

1. D
2. C
3. D
4. D
5. C
6. D
7. D
8. A
9. A
10. B
11. A
12. A
13. A
14. B
15. A

ASSERTION -REASON TYPE QUESTIONS

Choose the correct answer from 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: Alkylation of amines gives polysubstituted product where as acylation of amines gives a monosubstituted product Reason: Steric hindrance of an acyl group prevents the approach of further acyl groups.
2	Assertion: Anilinium chloride is more acidic than ammonium chloride Reason: Anilinium ion is resonance stabilized.
3	Assertion: Gabriel phthalimide reaction can be used to prepare aryl and alkyl amines Reason: Aryl halides have same reactivity as alkyl halides towards nucleophilic substitution reactions.
4	Assertion: Aniline does not undergo Friedel -Crafts reaction Reason: Friedel-Crafts reaction is electrophilic substitution reaction
5	Assertion: CuCl2 gives a deep blue colored solution with ethyl amine Reason: Ethylamine molecules coordinate with cupric ions forming a blue coloured complex.

6	Assertion: Aniline reacts with bromine water to form 2,4,6-tribromoaniline Reason: Aniline is resonance stabilized
7	Assertion: Acetanilide is less basic than aniline Reason: Acetylation of aniline results in decrease of electron density on nitrogen
8	Assertion: N,N diethyl benzene sulphonamide is insoluble in alkali. Reason: Sulponyl group attached to nitrogen is strong electron withdrawing group
9	Assertion: Amides on oxidation yields amines Reason: Amides on treating with lithiumaluminiumhydride gives amines
10	Assertion: The order of boiling points of isomeric amines is Primary>Secondary>Tertiary Reason: Intermolecular association is more in primary ,then in secondary and least in tertiary amines.
11	Assertion: Aliphatic amines are weaker base than ammonia Reason:+I effect of alkyl group results in high electron density on nitrogen atom.
12	Assertion: Pkb value of aniline is low, Reason: The unshared pair on nitrogen atom to be in conjugation with the benzene ring making it less available
13	Assertion: The order of basicity of amines in gaseous state is different than those in aqueous solution Reason: In aqueous solution solvation is also to be takes in to account.
14	Assertion: Only a small amount of HCl is required to initiate the reduction of Nitro compounds with iron scrap and HCl Reason: FeCl2 formed gets hydrolysed to release HCl during the reaction.
15	Assertion: Hinsberg's reagent does not react with tertiary amines Reason: No hydrogen atom is attached to nitrogen of amino group.

ANSWERS

1.	C Due to delocalization of the lone pair of electrons of the nitrogen atom over the carbonyl group in the acyl derivative, the electron density on the N atom decreases to such an extent that it does not act as a nucleophile at all.
2.	C Ammonia is a stronger base than aniline and the conjugate acid of aniline is more acidic than conjugate acid of ammonia
3.	D Gabriel phthalimide reaction is used to prepare only primary alkyl amines. Aryl halides do not undergo nucleophilic substitution reactions.
4.	B AlCl3 forms a salt with aniline which deactivates the benzene ring
5.	A
6.	B -NH2 group is ortho para directive
7.	A In amides the -CO group is stronger dipole than N-C dipole, hence the ability of NC group to act as a base is restricted in presence of C=O dipole,
8.	A N,N-diethyl benzene does not have acidic hydrogen, hence insoluble.
9.	D Amides on reduction gives amines
10.	A Tertiary amines do not have intermolecular association due to the absence of hydrogen atom available for hydrogen bond formation.
11.	D Aliphatic amines are stronger bases than ammonia
12.	D pKb value of aniline is high
13.	A
14.	A
15	A

CASE BASED QUESTIONS

1	The basicity of amines of different classes do not follow a simple pattern because the number of groups bonded to nitrogen affects the electron density at the nitrogen atom. And, the stability of the conjugate acid in the solvent has a major effect on basicity. Thus, the basicity of amines can be explained only for amines with similar structures at the nitrogen atoms. The basicity of an amine is increased by electron-donating groups and decreased by electron-withdrawing groups. Aryl amines are less basic than alkyl-substituted amines because some electron density provided by the nitrogen atom is distributed throughout the aromatic ring. Basicity is expressed using *K*b values measured from the reaction of the amine with water. An alternate indicator of basicity is p*K*b, which is −log *K*b. A strong base has a large *K*b and a small p*K*b. The basicity of amines is also expressed by the acidity of their conjugate acids. A strong base has a weak conjugate acid, as given by a small value of *K*a and a large p*K*a. [Robert J. Ouellette, J. David Rawn, in Organic Chemistry Study Guide, 2015] a) pKb values for NH_3 , CH_3NH_2,$(CH_3)_2NH$ and $(CH_3)_3N$ has 4.75,3.38,3.27 and 4.22 respectively. Write them in the decreasing order of basic strength. Usually the order of basicity of amines will be different from the expected order. b) Which are the three main factors affecting basicity of amines? c) Write the decreasing order of basicity for CH3CH2NH2,(CH3CH2)2NH and (CH3CH2)3N d) Compare the basicity of m-toluidine and Aniline. Answer a) (CH3)2NH> CH3NH2>(CH3)3N>NH3 b) +I effect ,extent of hydrogen bonding with water molecules and steric effects of the alkyl group c) (CH3CH2)2NH>(CH3CH2)3N> CH3CH2NH2>NH3 d) m-Toluidine is more basic than aniline due to +I effect from meta position

2.	Amines have higher boiling points than hydrocarbons of comparable molecular weight because the C—N bond is more polar than a C—C bond. Also, primary and secondary amines can form intermolecular hydrogen bonds because they can act as both hydrogen bond donors and acceptors. Tertiary amines have no hydrogen atoms bonded to the nitrogen atom and therefore are not hydrogen bond donors. Thus, tertiary amines cannot form intermolecular hydrogen bonds. As a result, they have lower boiling points than primary and secondary amines of comparable molecular weight. Amines have lower boiling points than alcohols because nitrogen is less electronegative than oxygen. As a result the N—H bond is less polar than the O—H bond, and the hydrogen bond in amines is weaker than the hydrogen bond in alcohols.[Robert J. Ouellette, J. David Rawn, in Organic Chemistry (Second Edition), 2018] a) The boiling point of Ethyl alcohol is more than that of ethyl amine. Give reason b) The order of boiling points for the following amines is $CH_3CH_2CH_2NH_2$> $(CH_3CH_2CH_2)$ NH>(CH_3CH_2) N(CH_3),Explain c) Arrange the following in the increasing order of molecular mass. $CH_2CH_2NH_2$,HCOOH,CH_3CH_2OH,$CH_3CH_2CH_3$ ANSWERS a) N is less electronegative than oxygen and the hydrogen bond in amines are weaker than that in alcohols. b) The boiling points of amines follows the order primary>secondary>tertiary Primary amines have 2 ,secondary amines have 1 while tertiary amines have no hydrogen linked to nitrogen. Among these compounds of comparable molecular masses ,order of extend of hydrogen bond is hydrocarbons <amines<alcohols<carboxylic acids c) Hence the order of given compounds of comparable molecular masses is $CH_3CH_2CH_3$< $CH_2CH_2NH_2$< CH_3CH_2OH< HCOOH

3.	Basicity of aliphatic amines in aqueous solution depends on +I effect, extent of hydrogen bonding with water molecules, steric effects of the alkyl group. In aromatic amines it depends on effect of substituents on the ring. Basicity of aralkyl amines, as the electrons are not conjugated with benzene ring and not de- localized. Hence electron pair is available for protonation. In aromatic amines ortho effect refers mainly to the set of steric effects and some bonding interactions along with polar effects caused by the various substituents which are in a given molecule altering its chemical properties and physical properties. In a general sense the ortho effect is associated with substituted benzene compounds. Anything ortho to the amine, no matter whether it is electron donating or withdrawing, will decrease the basicity of the aromatic amine. This is because of the ortho effect, which is basically steric effect. The protonated amine will have a greater steric interaction with the ortho group, so it will be less stable. a) Compare the basicity of aniline, m-nitroaniline, p- nitroaniline and ortho nitroaniline b) Compare the basicity of benzylamine, aniline, methyl amine and ammonia c) Aniline has pKb =9.38,p-aminophenol has pKb =8.50 and o-aminophenol has pKb=9.28, but m-aminophenol has pKb=9.80. Explain. ANSWER a) o-nitroaniline<p-nitroaniline<m-nitroaniline<Aniline(ewg decreases the basicity due to ortho effect o-nitro aniline is the weak one among substituted anilines) b) aniline<ammonia<benzylamine<methyl amine (methyl group is more electron donating than benzyl group, hence methyl amine is stronger base, in benzyl amine electrons are not delocalised. Hence better base than aniline but ammonia with pKb value4.75 is more basic than benzylamine(pKb=4.70) c) Here though -OH group is in ortho position o-aminophenol is stronger base than aniline (pkb=9.38) and m-aminophenol(pKb=9.80) due to stabilisation of anilinium ion by hydrogen bonding.

QUESTION BANK

VSA: 1 Mark

SA: 2 Marks

LA: 3 Marks

VLA: 5 Marks

VSA

1. Give reasons for the following:
Primary amines have higher boiling point than tertiary amines. *(1/3, AI 2016, Delhi 2008C)*

2. Arrange the following in the increasing order of their boiling point:
$_2H_5NH_2$, C_2H_5OH, $(CH_3)_3N$ *(1/5, Delhi 2015)*

3. Give a simple chemical test to distinguish between the following pair of compounds:
$(CH_3)_2NH$ and $(CH_3)_3N$ *(1/5, Delhi 2015)*

4. Arrange the following in increasing order of basic strength:
Aniline, *p*-nitroaniline, and *p*-toluidine *(AI 2015C)*

5. Why do amines act as nucleophiles? *(AI 2007)*

6. Complete the following reaction equation: $C_6H_5N_2Cl + H_3PO_2 + H_2O$ ----- >
(Delhi 2015C, AI 2013, 2012)

SA

7. Give reasons for the following:

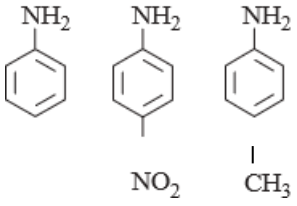
(i) Aniline does not undergo Friedel-Crafts reaction.

(ii) $(CH_3)_2NH$ is more basic than $(CH_3)_3N$ in an aqueous solution. *(2/3, AI 2016, 2014)*

8. Arrange the following in increasing order of their basic strength:

(i) $C_6H_5NH_2$, $C_6H_5NHCH_3$, $C_6H_5CH_2NH_2$

(ii)



(AI 2015)

9. How do you convert the following:

a. $C_6H_5CONH_2$ to $C_6H_5NH_2$

b. Aniline to phenol *(2/3, AI 2015)*

10. Illustrate the following reactions giving suitable example in each case:

a. Ammonolysis

b. Acetylation of amines *(2/5, Foreign 2017)*

11. Give one chemical test each to distinguish between the following pairs of compounds:

(i) Ethylamine and aniline

(ii) Aniline and *N*-methylaniline *(AI 2008C)*

12. Write chemical equations for the following conversions:

(i) Nitrobenzene to benzoic acid

(ii) Aniline to benzyl alcohol. *(2/3, Delhi 2012)*

LA

13. Write the structures of main products when aniline reacts with the following reagents:

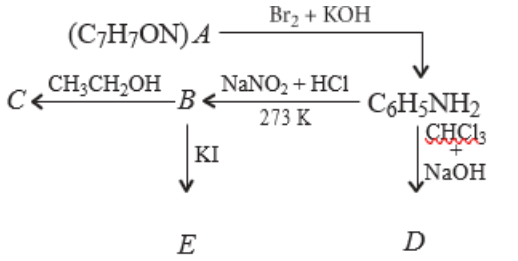
a. Br_2 water

b. HCl

c. $(CH_3CO)_2O$/pyridine *(3/5, Delhi 2015)*

VLA

14. An aromatic compound '*A*' of molecular formula C_7H_7ON undergoes a series of reactions as shown below. Write the structures of *A*, *B*, *C*, *D* and *E* in the following reactions:

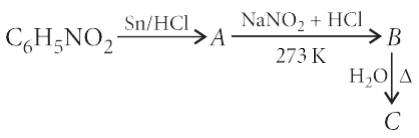


(Delhi 2015)

15. (i) Write the structures of main products when benzenediazonium chloride ($C_6H_5N_2^+Cl^-$) reacts with the following reagents:

(a) HBF_4 (b) Cu/HBr

(ii) Write the structures of *A*, *B* and *C* in the following reactions:

(a) 

(b) $CH_3Cl \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow[273\ K]{HNO_2} C$

ANSWERS

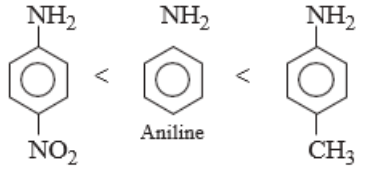
1. Primary amines (R – NH2) have two hydrogen atoms on nitrogen which can undergo intermolecular hydrogen bonding whereas no such hydrogen bonding is present in tertiary amines (R3N). So, primary amines boil at a higher temperature than tertiary amines.

2. Increasing order of boiling points : $(CH_3)_3N < C_2H_5NH_2 < C_2H_5OH$

Tertiary amine does not have hydrogen to form hydrogen bonding and hydrogen bonding in alcohol is stronger than that of amines because oxygen is more electronegative than nitrogen.

3. When treated with benzenesulphonyl chloride (Hinsberg's reagent), $(CH_3)_2NH$ forms insoluble *N*, *N*-dialkylbenzene sulphonamide which is insoluble in KOH whereas tertiary amine does not react at all.

4.



p-nitroaniline *p*-toluidine

5. Because the electron pair of nitrogen can coordinate with the electron deficient electrophiles

6.

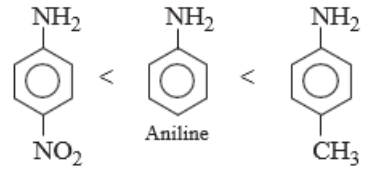
$$C_6H_5N_2Cl + H_3PO_2 + H_2O \longrightarrow C_6H_6 + N_2 + H_3PO_3 + HCl$$

7. (i) In Friedel - Crafts reaction, $AlCl_3$ is added as a catalyst which is a Lewis acid. It forms a salt with aniline due to which the nitrogen of aniline acquires positive charge. This positively charged nitrogen acts as a strong deactivating group, hence aniline does not undergo Friedel - Crafts reaction.

(ii) In aqueous solution 2° amine is more basic than 3° amine due to the combination of inductive effect, solvation effect and steric reasons.

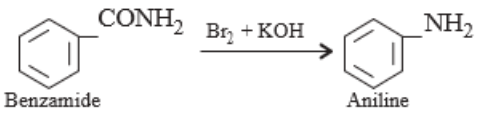
8. (i) $C_6H_5NH_2 < C_6H_5NHCH_3 < C_6H_5CH_2NH_2$ $C_6H_5NH_2$ and $C_6H_5NHCH_3$ are less basic than aliphatic amine $C_6H_5CH_2NH_2$ due to lone pair of nitrogen is in conjugation with benzene ring. But due to +*I* effect of —CH_3 group in $C_6H_5NHCH_3$, it is more basic than $C_6H_5NH_2$..

(ii)

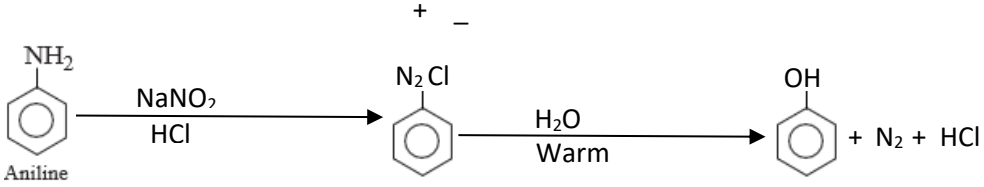


p-nitroaniline *p*-toluidine

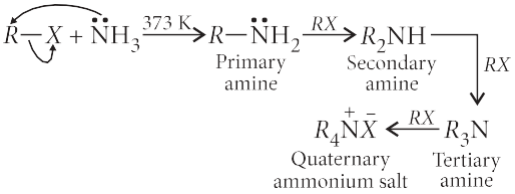
9. (i)



(ii)

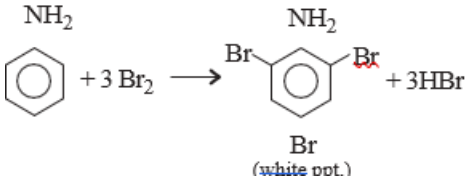


10. (i) Alkyl halides when treated with ethanolic solution of ammonia give a mixture of primary, secondary, tertiary amines and quaternaryammonium salt.



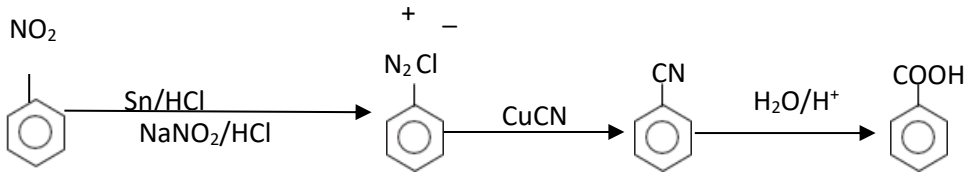
(ii) Acylation of amines. The process of introducing an acetyl group in a molecule is called acetylation.

11. Aniline gives white or brown precipitate with bromine water.



(ii) Aniline gives carbylamine test, *i.e.*, on treatmentwith alc. KOH and chloroform followed by heatingit gives offensive odour of phenylisocyanide but *N*-methylaniline being secondary amine, does not show this test

12.



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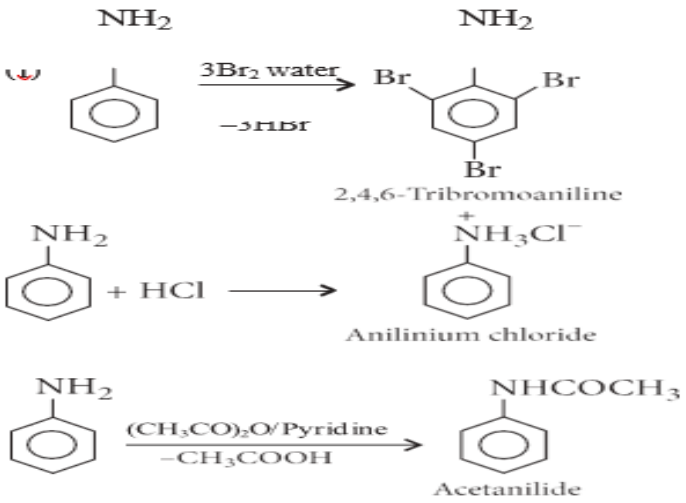

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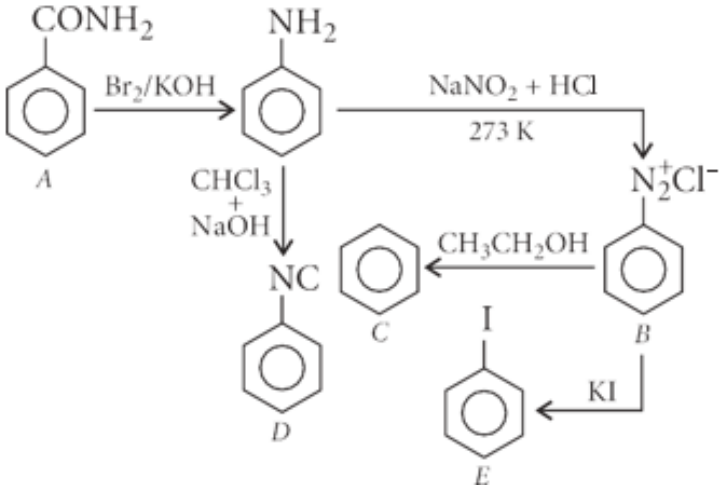
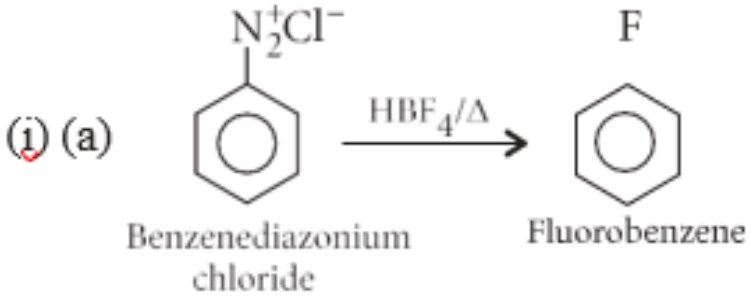
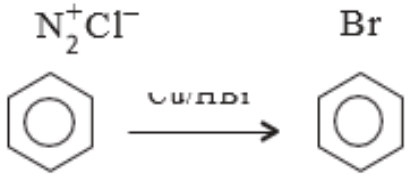


14.





(b) Benzenediazonium Bromobenzene

(i) $C_6H_5NO_2 \xrightarrow{Sn + HCl} C_6H_5NH_2$ (A)

$C_6H_5NH_2$ (A) $\xrightarrow[273\ K]{NaNO_2 + HCl}$ $C_6H_5N_2^+Cl^-$ (B) $\xrightarrow{H_2O}$ C_6H_5OH (C)

x`

(ii) $CH_3Cl \xrightarrow{KCN} CH_3CN$ (A) $\xrightarrow{LiAlH_4} CH_3CH_2NH_2$ (B)

$CH_3CH_2NH_2$ (B) $\xrightarrow[273\ K]{HNO_2}$ CH_3CH_2OH (C)

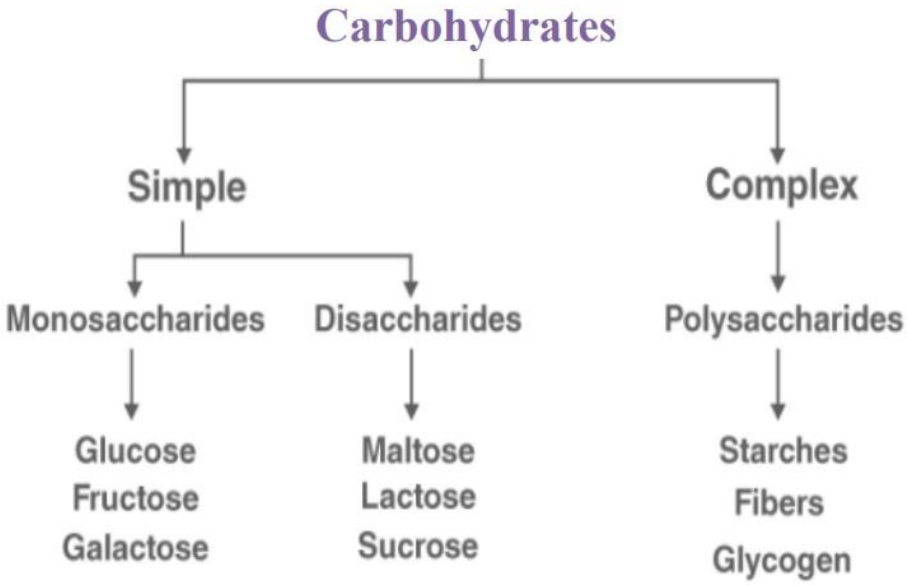
CHAPTER-14

BIOMOLECULES

Introduction: The complex organic substances like carbohydrates, proteins, nucleic acids and amino acids etc. which combine in a specific manner to produce living systems and maintain it are called biomolecules. The branch of chemistry that deals with the study of chemical reactions that occur in living organisms is called biomolecules.

Carbohydrates: They are polyhydroxy-aldehydes or ketones or substances which give these substances on hydrolysis and contain at least one chiral atom. They have general formula of C x (H 2 O) y Rhamnose ($C_6H_{12}O_5$), deoxyribose ($C_5H_{10}O_4$) are known which are carbohydrates by their chemical behaviour does not obey this formula.

Classification of Carbohydrates: Carbohydrates



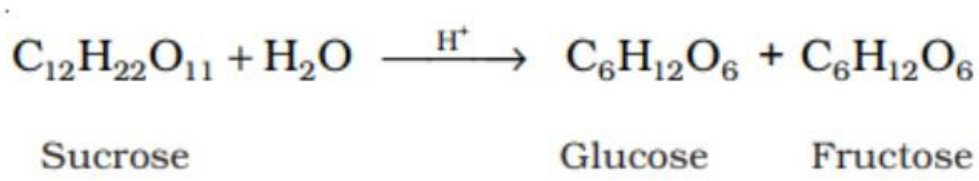
Monosaccharide:

These are simplest carbohydrate which can't be hydrolysed further into smaller compounds. They are called as aldose or ketose depending upon whether they have aldehyde or ketone group. Depending upon the number of carbon atoms present they are called as triose, tetrose, pentoses, hexoses etc. Most of the monosaccharides are sweet smelling crystalline solids, water soluble and are also capable of diffusing through cell membranes.

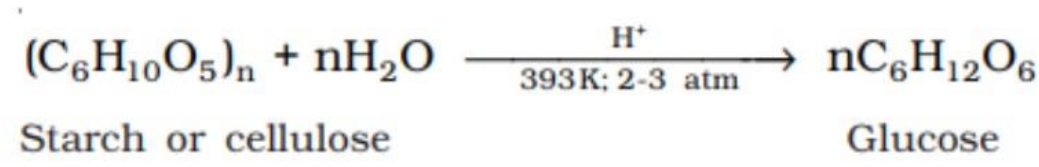
For example: Glucose is aldohexose while fructose is a ketohexose. Both of them have 6 carbon atoms. The simplest monosaccharide is a triose (glyceraldehyde) $C_3H_6O_3$

Preparation of glucose:

1. From sucrose (Cane sugar): If sucrose is boiled with dilute HCl or H2SO4 in alcoholic solution, glucose and fructose are obtained in equal amounts.



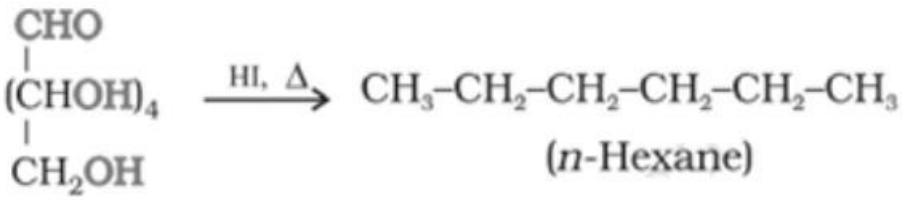
2. From starch: Commercially glucose is obtained by hydrolysis of starch by boiling it with dilute H2SO4 at 393 K under pressure.



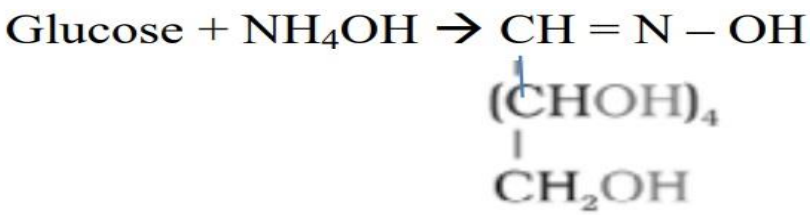
Structure of glucose: Glucose is an aldohexose and is also known as dextrose. It is the monomer of many of the larger carbohydrates, namely starch, cellulose.

1. Its molecular formula was found to be C6H12O6.

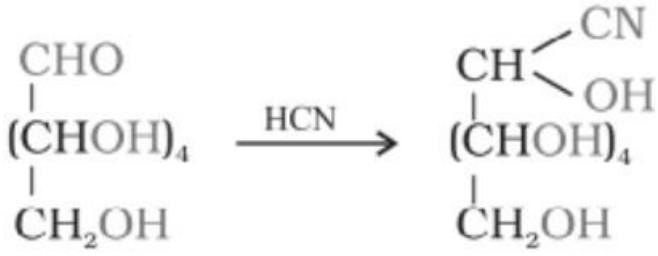
2. On prolonged heating with HI, it forms n-hexane, suggesting that all the six carbon atoms are linked in a straight chain.



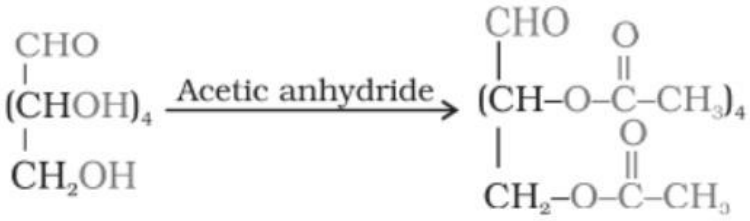
3. Glucose reacts with hydroxylamine to form a Glucose oxime.



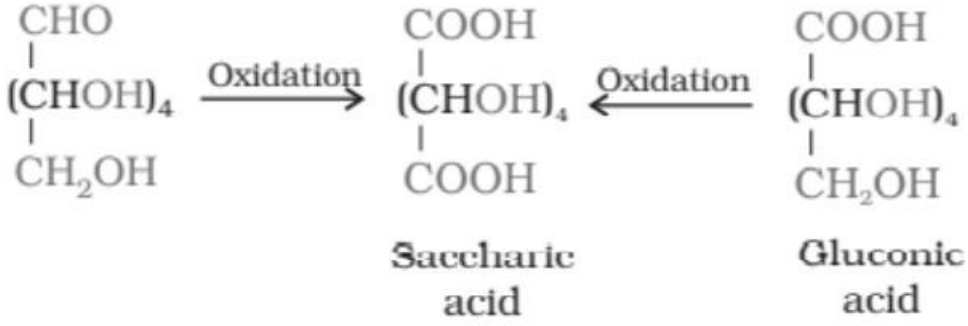
4. Glucose reacts with a molecule of hydrogen cyanide to give cyanohydrin.



5. Acetylation of glucose with acetic anhydride gives glucose pentaacetate which confirms the presence of five –OH groups.

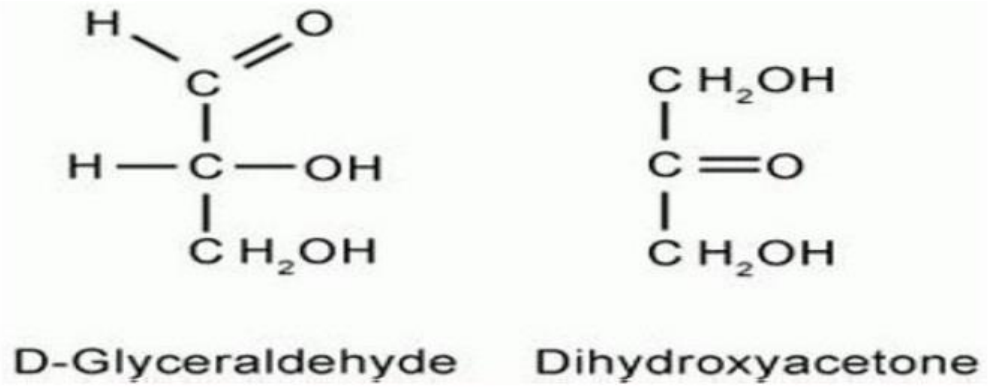


6. On oxidation with nitric acid, glucose as well as gluconic acid both yield a dicarboxylic acid, saccharic acid. This indicates the presence of a primary alcoholic (–OH) group in glucose.



Glyceraldehyde and Dihydroxyacetone: They have one or more asymmetric carbon and are optically active.

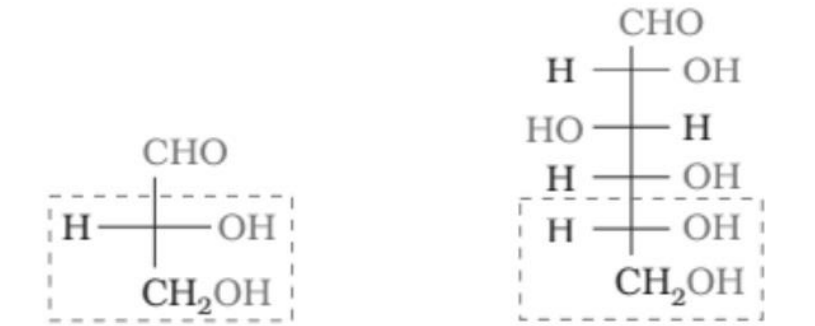
Their structures are:



Configuration: All naturally occurring monosaccharides belong to D—series that is OH group at their penultimate C-atom.

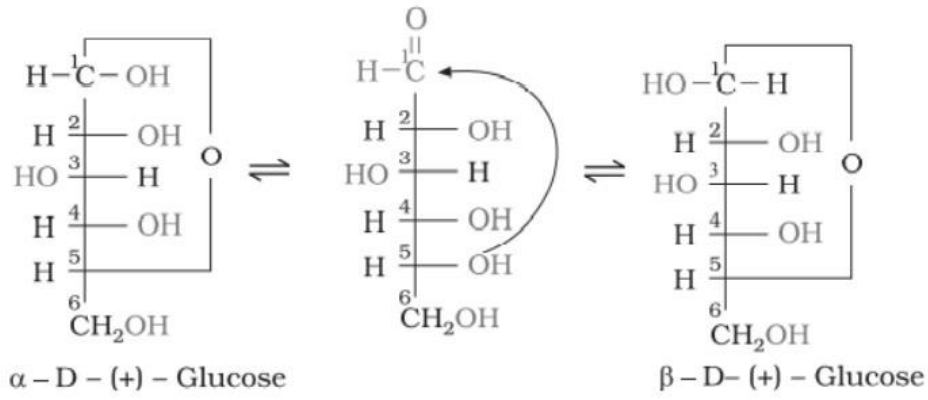
Structures of (+) – Glyceraldehyde and (-) – Glyceraldehyde

Structures of D-(+) – Glyceraldehyde and D-(+) - Glucose

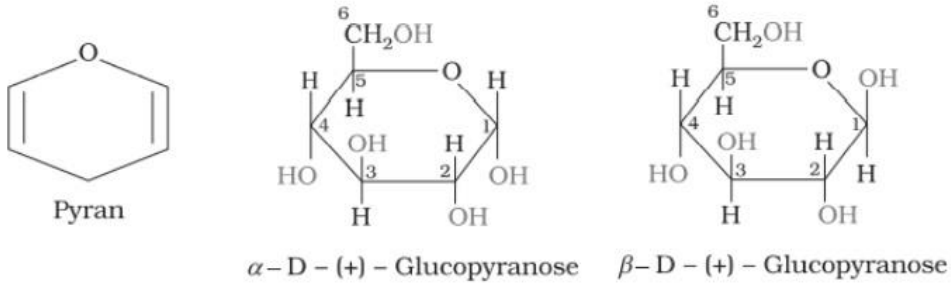


D– (+) – Glyceraldehyde D–(+) – Glucose

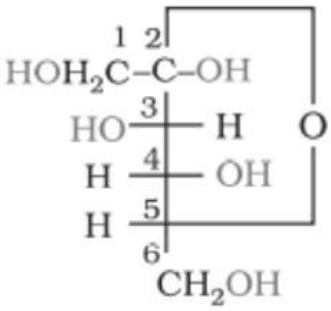
Cyclic structure of glucose:



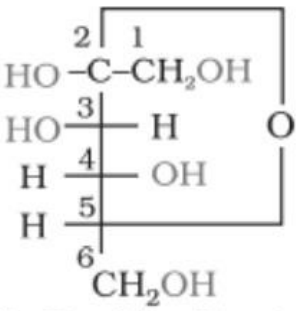
The two cyclic hemiacetal forms of glucose differ only in the configuration of the hydroxyl group at C1, called anomeric carbon. Such isomers, i.e., α-form and β-form, are called anomers. The six membered cyclic structure of glucose is called pyranose structure (α– or β–), in analogy with pyran. Pyran is a cyclic organic compound with one oxygen atom and five carbon atoms in the ring. The cyclic structure of glucose:



Fructose is a ketohexose and has the molecular formula C6H12O6. The ring, thus formed is a five membered ring and is named as furanose with analogy to the compound furan. Furan is a five membered cyclic compound with one oxygen and four carbon atoms.

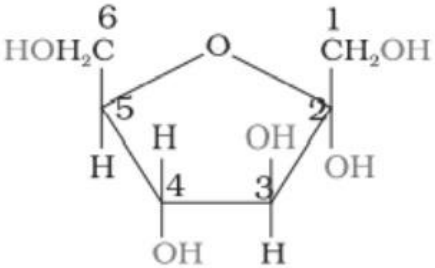


α – D – (–) – Fructofuranose

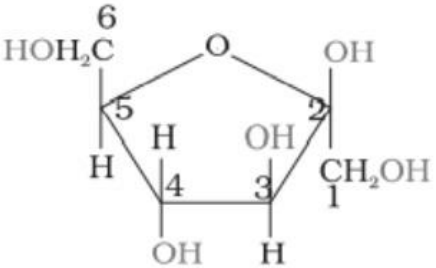


β – D – (–) – Fructofuranose

The cyclic structures of two anomers of fructose are represented by Haworth structures as given.

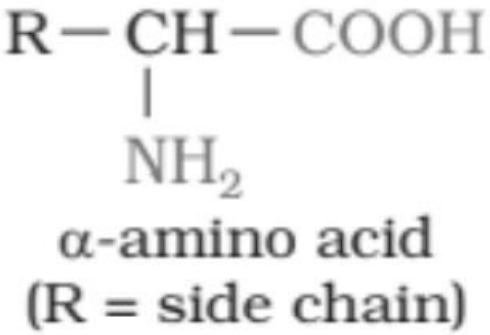


α – D – (–) – Fructofuranose



β – D – (–) – Fructofuranose

Amino acids: Amino acids contain amino (–NH2) and carboxyl (–COOH) functional groups. A simple amino acid can be represented:



α-amino acid

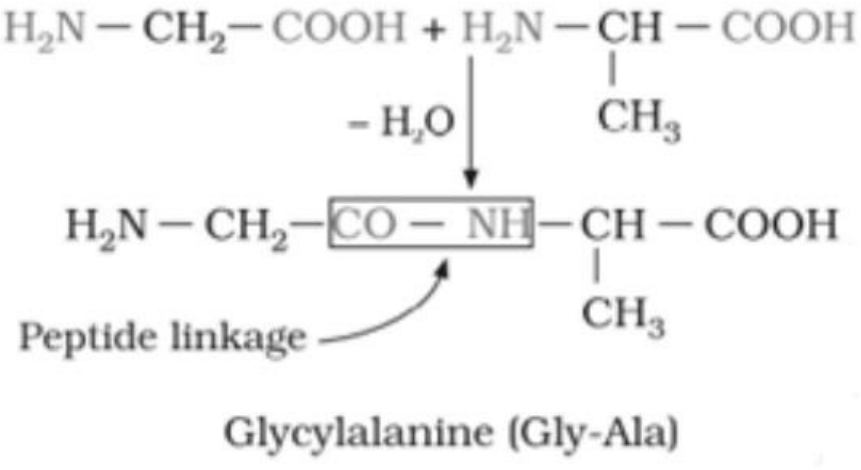
(R = side chain)

Due to transfer of proton from carboxy to amino group, alpha amino acid exists as dipolar ion or called as Zwitter ion.

Difference between Essential and Nonessential Amino Acids

	Essential Amino Acids	Nonessential Amino Acids
Definition	These cannot be made by the body therefore; these are required through our diet or food supplements.	These can be made by our body or are always available.
Number	9 essential amino acids are known out of 20 amino acids.	11 out of the 20 amino acids are known to be non-essential amino acids.
Food sources	Various sources of food that provide essential amino acids include quinoa, egg and meat, chicken and vegetables protein.	These can be produced within our body from other amino acids and their components as well.
Functions	These function in building and repairing muscle tissues and they form precursor molecules for neurotransmitters formation in the brain.	These are very helpful for the removal of toxins, promoting brain functioning and synthesizing RBC and WBC in our bodies.
Deficiency Known	Deficiency of these amino acids is highly probable as these are provided with the help of food and proper diet.	Deficiency of these amino acids is rare as can be produced by the body; however, in case of starvation and illness, deficiency may be seen.
Names	Leucine, isoleucine, histidine, lysine, methionine, threonine, phenylalanine, tryptophan and valine	Arginine, alanine, aspartic acid, asparagine, cysteine, glutamine, glutamic acid, proline, glycine, serine and tyrosine.

Proteins: Proteins are the polymers of α-amino acids and they are connected to each other by peptide bond or peptide linkage. Peptide linkage is an amide formed between –COOH group and –NH2 group. The reaction between two molecules of similar or different amino acids, proceeds through the combination of the amino group of one molecule with the carboxyl group of the other. This results in the elimination of a water molecule and formation of a peptide bond –CO–NH–. The product of the reaction is called a dipeptide because it is made up of two amino acids. For example, when carboxyl group of glycine combines with the amino group of alanine we get a dipeptide, glycylalanine.



Glycylalanine (Gly-Ala)

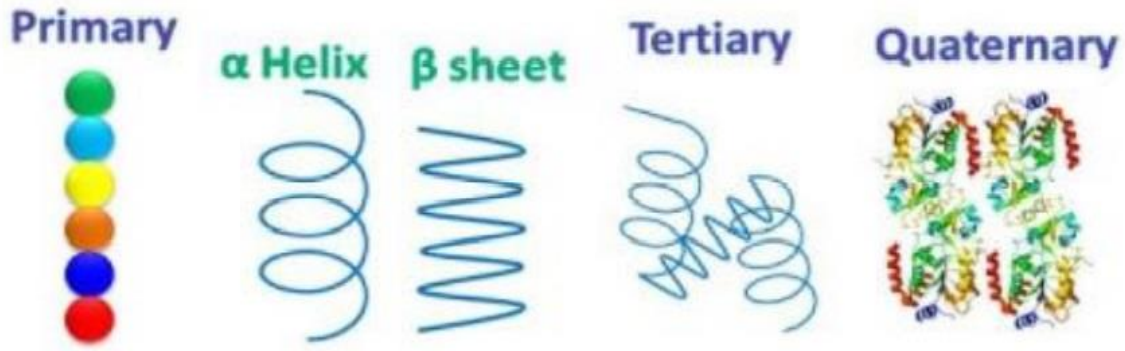
Proteins are complex nitrogenous molecules which are essential for the growth and maintenance of life. Structurally, proteins are long polymers of amino acids linked by peptide (-CO—NH-) bond.

Structure of proteins: Proteins have three structures:

• Primary structure

• Secondary structure (Alpha helix and Beta pleated sheet)

• Tertiary structure (Fibrous proteins and Globular proteins)



Forces that stabilize protein structures: The forces that are present are as follows:

• Hydrogen bonding: These forces operate between a partially positive hydrogen and partially negative atom like O or N on the same or on another molecule.

• Anionic bonding: A bonding between cation and anion of side chains resulting in side linkage.

• Hydrophobic bonding: Some side chains in same amino acid are hydrophobic. In aqueous solutions proteins fold in such a way that these chains get clustered inside the folds. The polar side chains which are hydrophilic lie on the outside or surface of proteins.

• Covalent bonding: The bond occurs between S atoms of two residues between two adjacent chains.

Denaturation of proteins

• The globular proteins, which are soluble in water on heating or on treatment of mineral acids or bases, undergo coagulation or precipitation to give fibrous proteins which are insoluble in water.

• After coagulation, proteins lose their biological activity this is called denaturation.

• It can be reversible or irreversible.

• Coagulation of lactalbumin to form cheese and coagulation of albumins are examples of denaturation.

Classification of proteins on the basis of composition:

• Simple proteins: On hydrolysis they give only amino acids. Example: Globulins and albumin

• Conjugated proteins: They contain non protein group attached to the protein part. These non-protein groups are called prosthetic groups. Example: Nucleoprotein contains nucleic acid, phosphor-protein contains phosphoric acid, glycolproteins contains carbohydrates etc.

• Derived proteins: These are the degradation products obtained by the hydrolysis of simple and conjugated proteins. Example: Peptides, peptones etc

• Fibrous proteins: They are long and thread like and tend to lie side by side to form fibers. In some cases, they are held together by hydrogen bonds at many points. These proteins serve as a chief structural material of animal tissues.

• Globular proteins: The molecules of these proteins are folded into compact units and form spheroid shapes. Intermolecular forces are weak. These proteins are soluble in water or aqueous solution of acids, bases or salts. Globular proteins make up all enzymes, hormones, fibrinogen etc.

FIBROUS AND GLOBULAR PROTEINS:

PROPERTIES	FIBROUS PROTEINS	GLOBULAR PROTEINS
SHAPE	LONG & NARROW	ROUNDED/SPHERICAL
ROLE	STRUCTURAL (STRENGTH & SUPPORT)	FUNCTIONAL (CATALYSTS & TRANSPORT)
SOLUBILITY	INSOLUBLE IN WATER	SOLUBLE IN WATER
SEQUENCE	REPETITIVE AMINO ACIDS	IRREGULAR AMINO ACIDS
STABILITY	LESS SENSITIVE TO CHANGES IN HEAT & pH	LESS SENSITIVE TO CHANGES IN HEAT & pH

Role of proteins

• They act as enzymes and transport agents.

• They are structural materials for nails, hair etc.

• Antibodies formed in body are globular proteins.

• They are metabolic regulators like insulin etc.

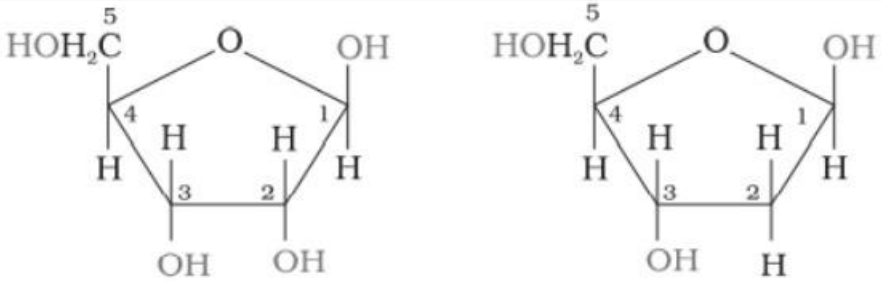
Hydrolysis of proteins

Proteins are hydrolyzing when boiled with acids or alkalis or when treated with enzymes. Every protein has an isoelectric point at which their ionization is minimum. Proteins have charged

groups i.e., NH 3 + and COO - at the ends of peptide chain. They are amphoteric in nature. Protein accepts a proton in strong basic solution. The pH at which the protein molecule has no net charge is known as isoelectric point.

Nucleic acids: The particles in nucleus of the cell, responsible for heredity, are called chromosomes which are made up of proteins and another type of biomolecules called nucleic acids. These are mainly of two types, the deoxyribonucleic acid (DNA) and ribonucleic acid (RNA).

Structure of nucleic acids: In DNA molecules, the sugar moiety is β-D-2-deoxyribose whereas in RNA molecule, it is β-D-ribose.



β–D–ribose β–D–2–deoxyribose

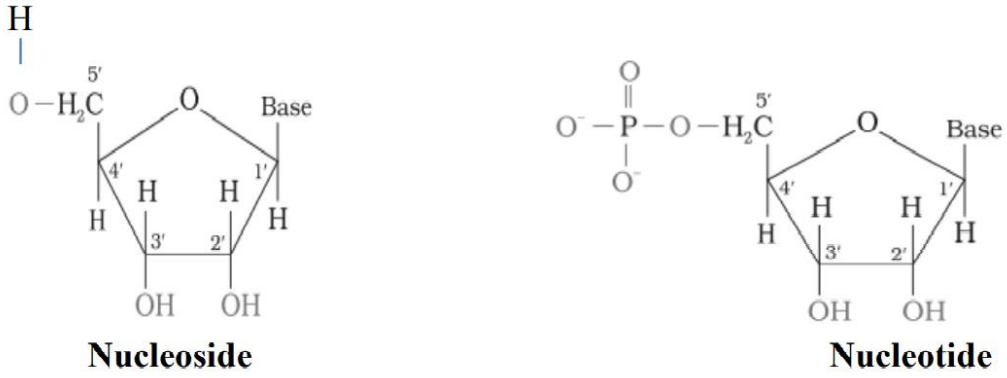
The nitrogenous base and a pentose sugar are called as nucleosides. The nitrogenous base, a pentose sugar and a phosphate group are called as nucleotides.

Each nucleotide consists of 3 parts:

• A pentose sugars

• A nitrogenous base

• A phosphate groups



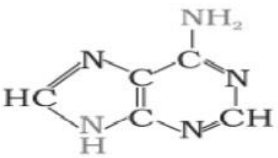
Nucleoside **Nucleotide**

Nitrogenous bases are of two types: Purines and Pyrimidines

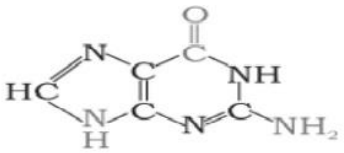
Purines: adenine and guanine

Pyrimidines: cytosine, thiamine and uracil

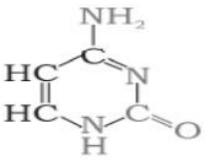
DNA contains four bases viz. adenine (A), guanine (G), cytosine (C) and thymine (T). RNA also contains four bases; the first three bases are same as in DNA but the fourth one is uracil (U).



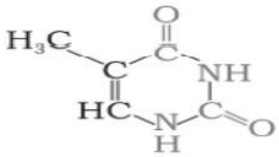
Adenine (A)



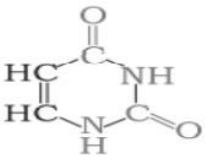
Guanine (G)



Cytosine (C)



Thymine (T)



Uracil (U)

Types of nucleic acids: Deoxyribonucleic acid (DNA) & Ribonucleic acid (RNA)

Main point of differences between DNA and RNA:

DNA (Deoxyribonucleic acid)	RNA (Ribonucleic acid)
1.It occurs mainly in the nucleus of the cell.	1.It occurs in the cytoplasm of the cell.
2.It has double stranded α-helix structure in which two strands are coiled spirally in opposite directions.	2.It has single stranded α-helix structure
3.The sugar molecule is 2-deoxyribose.	3.The sugar molecule is ribose.
4.Nitrogenous base uracil is not present.	4.Nitrogenous base thymine is not present.
5.DNA has unique property of replication.	5.RNA usually does not replicate.
6.It is responsible for the transmission for heredity character.	6.Helps in protein biosynthesis
7.DNA molecules are very large; their molecular masses may vary from $6 \times 10^6 - 16 \times 10^6$ u.	7.RNA molecules are much smaller with molecular mass ranging from $2 \times 10^4 - 4 \times 10^4$ u.

MULTIPLE CHOICE QUESTIONS

1. Glucose reacts with hydroxylamine to form an oxime. This confirms the presence of
a) straight chain of six carbon atoms
b) carbonyl group
c) primary alcoholic group
d) secondary alcoholic group

2. The symbols D and L in the name of Carbohydrate represents
a) Dextro rotatory nature
b) Laevo rotatory nature
c) The relative configuration of a particular isomer
d) The optical activity of compounds

3. Which of the following is incorrect for glucose?
a) It contains four >CHOH groups.
b) It contains one $–CH_2OH$ group.
c) It contains one –CHO group.
d) It contains one >C=O group.

4. To which position of sugar moiety, nucleoside is linked to phosphoric acid in a nucleotide?
a) 2’
b) 3’
c) 4’
d) 5’

5. Vitamin A is
a) Retinol
b) Ascorbic acid
c) Thiamine
d) Calciferol

6. Which sugar is present in RNA?
a) Glucose
b) Fructose
c) D-Ribose
d) D-2-Deoxyribose

7. Which of the following amino acid is neutral?
a) Aspartic acid
b) Glycine
c) Lysine
d) Arginine

8. A secondary structure of protein is stabilized by
a) H-bond
b) peptide bond
c) ionic bond
d) disulphide bond

9. How many amino acids are present in insulin?
a) 25
b) 20
c) 51
d) 52

10. Which of the following reagents does not react with glucose?
a) NH2OH
b) HCN

c) 2, 4 –DNP reagent
d) Br2 water

11. What are the hydrolysis products of lactose?
a) ***β***–D-galactose and ***β*** –D-Glucose
b) α –D-Glucose and α –D-Glucose
c) α –D-Glucose and ***β*** –D-Fructose
d) None of these

12. Which of the following is/are example(s) of denaturation of protein?
a) Coagulation of egg white
b) Curding of milk
c) Clotting of blood
d) Both (a) and (b)

13. Which of the following vitamins given below is water-soluble?
a) Vitamin C
b) Vitamin D
c) Vitamin A
d) Vitamin E

14. Scurvy is caused due to deficiency of
a) Vitamin B_1
b) Vitamin B_2
c) Ascorbic acid
d) Glutamic acid

15. Nucleotides are joined together by
a) Glycosidic linkage
b) Peptide linkage
c) Hydrogen bonding
d) Phosphodiester linkage

ANSWER KEY

1	b	6	d	11	a
2	c	7	b	12	d
3	d	8	a	13	a
4	d	9	c	14	c
5	a	10	c	15	d

ASSERTION REASON TYPE QUESTIONS

Answer the following questions selecting the appropriate option given below:

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, but reason is incorrect statement

d) Assertion is incorrect, but reason is correct statement

1. **Assertion:** Sucrose is a non-reducing sugar.

Reason: Sucrose has glycosidic linkage.

2. **Assertion:** Glucose reacts with hydroxylamine to form an oxime and also adds a molecule of hydrogen cyanide to give cyanohydrin.

Reason: The carbonyl group is present in the open chain structure of glucose.

3. **Assertion:** Deoxyribose, $C_5H_{10}O_4$ is a carbohydrate.

Reason: Carbohydrates are hydrates of carbon so compounds which follow $C_x(H_2O)_y$ formula are carbohydrates.

4. **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.

5. **Assertion:** All naturally occurring α-aminoacids except glycine are optically active.

Reason: Most naturally occurring amino acids have D-configuration.

6. **Assertion:** Glucose gives a reddish brown precipitate with Fehling's solution.

Reason: Reaction of glucose with Fehling's solution gives CuO and gluconic acid.

7. **Assertion:** Fructose reduces Fehling's solution and Tollens' reagent.

Reason: Fructose does not contain any aldehyde group.

8. **Assertion:** The K_a values of alpha amino acids are very low.

Reason: alpha Amino acids have zwitterionic structures.

9. **Assertion:** Keratin is a globular protein.

Reason: Enzymes are globular proteins.

10. **Assertion:** The two strands of DNA are complementary.

Reason: Cytosine always pairs with guanine and thymine pairs with adenine.

ANSWER KEY

1	b
2	a
3	c
4	a
5	c
6	c
7	b
8	b
9	d
10	a

SHORT ANSWER TYPE QUESTIONS

1.Name the sugar present in milk. How many monosaccharide units are present in it? What are such oligosaccharides called?
ANS: Lactose is present in milk. It has 2 monosaccharide units. They are glucose and galactose. These are called disaccharides.

2.What is the effect of denaturation on the structure of proteins?
ANS: During denaturation, the protein molecules uncoil from an ordered and specific conformation into a more random confirmation. Denaturation does not change the primary structure of protein but results from arrangement of secondary and tertiary structures.

3.Why vitamin C cannot be stored in our body?
ANS: Vitamin C cannot be stored in our body because it is soluble in water and is readly excreted in urine and cannot be stored in our body.

4.Name the 3 nitrogenous bases having pyrimidine ring present in nucleic acids.
ANS: Cytosine Thymine and uracil

5.Distinguish between globular protein and fibrous protein.
ANS; In globular proteins,the molecules are folded together into compact units forming spheroidal shapes. The peptide chains are held by hydrogen bonds, but these forces are comparatively weak. These are soluble in water. eg. albumin, insulin.

Fibrous proteins consist of linear thread like molecules which tend to lie side by side to form fibres. The molecules are held together at many points by hydrogen bonds or disulphide bonds.eg. keratin. Myosin

6.What is meant by (a) a peptide linkage (b) a glycosidic linkage
ANS: (a) Peptide bond is formed by the condensation of two or more same or different alpha amino acids. The condensation occurs between amino acids with the elimination of water. In this case, the carboxyl group of one amino acid and amino group of another amino acid get condensed with the elimination of water molecule. The resulting- CONH – linkage is called peptide linkage.
(b)Two monosaccharide units are linked to each other by a bond called glycosidic linkage.

7.Define the following terms
(a) nucleotide (b) anomers (c)essential amino acids
Ans: (a) A unit formed by the combination of a nitrogen containing heterocyclic base, a pentose sugar and a phosphoric acid group.
(b)The anomers are the isomers formed due to the change in configuration of – OH group at C1 of glucose. eg. alpha and beta forms of glucose.
(c)The amino acids which cannot be made by our bodies and must be supplied in our diet for the growth of the body are called essential amino acids.

8. (a) Write one reaction of D-glucose which cannot be explained by its open chain structure.
(b) What type of linkage is present in nucleic acids
ANS: (a)Despite having aldehydic (-CHO) group, glucose does not react with NaHSO3 to form addition product.
(b)phosphodiester linkage.

9. Write two differences between DNA and RNA

ANS: The bases present in RNA are guanine, adenine, cytosine and uracil.
Uracil is not present in DNA. Instead, it contains thymine.
DNA has double stranded alpha helix structure in which two strands are coiled spirally in opposite directions. The sugar molecule present in DNA is 2-deoxyribose.
RNA has single stranded alpha helix structure. The sugar molecule present in RNA is ribose.

10. Where does the water present in the egg go after boiling the egg?
Ans. When an egg is boiled in water, the water present in egg is used in denaturation of protein probably through H-bonding.

11.Which one of the following is a disaccharide: Starch, Maltose, fructose, glucose?
ANS: Maltose

12.Name two water soluble vitamins, their sources and diseases caused due to their deficiency.
ANS: Vitamin C, Vitamin B
Sources: milk, pulses. wheat bran, sea food, yeast etc
deficiency diseases: Beri-Beri

13.What are enzymes?
Ans: The enzymes are biological catalysts produced by living cells which catalyse the biochemical reactions. Without enzymes,the living process would be very slow to sustain life. All enzymes are proteins.

14.Write a reaction which shows that all the carbon atoms in glucose are linked in a straight chain.
ANS: When glucose is heated with HI and red P, at 100^0C for a long period, it gives n-hexane.
$CH_2OH(CHOH)_4CHO$ ---------- $CH_3(CH2)_4CH_3$

15.What are the products of hydrolysis of maltose.?
ANS: GLUCOSE, it gives two molecules of glucose.

$$C12H22O11 + H2O \rightarrow 2\ C6H12O6$$

LONG ANSWER TYPE QUESTIONS:

1. Which sugar is called invert sugar? Why is it called so?
   ANS: Sucrose is called invert sugar. The sugar obtained from sugar beet is a colourless, crystalline and sweet substance. It is very soluble in water and its aqueous solution is dextrorotatory. On hydrolysis with dilute acids or enzyme invertase, cane sugar gives equimolar mixture of D-(+)-GLUCOSE and D-(-)- FRUCTOSE. So, sucrose is dextrorotatory but after hydrolysis gives dextrorotatory glucose and laevorotatory fructose. Since there is change in the sign of rotation from dextro before hydrolysis to laevo after hydrolysis , the reaction is called inversion reaction and the mixture is called invert sugar.

2. Enumerate the reactions of D-glucose which cannot be explained by its open chain structure.
   Ans. (i) Despite having aldehyde group, glucose does not give Schiff test and 2,4-DNP test.
   (ii)Glucose does not react with sodium hydrogen bisulphite to form addition product.
   (iii)The pentaacetate of glucose does not react with hydroxyl amine showing the absence of free -CHO group.

3. What happens when D-glucose is treated with the following reagents? (i) HI (ii) Bromine water (iii) HNO3
   Ans. (i) when glucose is treated with HI, it forms n-hexane.
   (ii) when glucose is treated with Bromine water, gluconic acid is formed.
   (iii) when glucose is treated with nitric acid, Saccharic acid is formed.

4. Define the following as related to proteins (i)Peptide linkage (ii) Primary structure (iii) Denaturation.
   Ans. (i)Peptide linkage- Peptide bond is formed by the condensation of two or more, same or different α-amino acids. -CO -NH- linkage is called peptide linkage.
   (ii) Primary structure- Primary structure of proteins give the sequence in which amino acids are linked in one or more polypeptide chains of proteins.
   (iii) Denaturation- A process that changes the physical and biological properties without affecting the chemical composition of a protein is called denaturation. The denaturation is caused by certain physical or chemical treatments such as in pH, temperature, presence of some salts or certain chemical agents.

5. Differentiate the following :
   (i) Globular and fibrous proteins. (ii) Nucleoside and a nucleotide.
   Ans. (i) Fibrous proteins: They are long and thread like and tend to lie side by side to form fibers. In some cases, they are held together by hydrogen bonds at many points. These proteins serve as a chief structural material of animal tissues. Examples, keratin, collagen
   Globular proteins: The molecules of these proteins are folded into compact units and form spheroid shapes. Intermolecular forces are weak. These proteins are soluble in water or aqueous solution of acids, bases or salts. Globular proteins make up all enzymes, hormones, fibrinogen etc. Examples, hemoglobin, insulin
   (ii) The nitrogenous base and a pentose sugar are called as nucleosides. The nitrogenous base, a pentose sugar and a phosphate group are called as nucleotides.

CASE BASED QUESTIONS

Case I

Amino acids are building blocks of proteins. More than 300 amino acids have been described, but only 20 amino acids take part in protein synthesis. Amino acids are necessary for protein synthesis and have various functions in the body. It is necessary to take them in the diet because their deficiency results in decrease formation of protein or protein is not formed as a result protein deficiency may occur. It is concluded that amino acids play important role in our body. All α-amino acids exist as zwitter ions each of which has a specific isoelectric point. Above isoelectric point, a α-amino acid exists as an anion. Two or three or many α-amino acids join together to form di- or tri- or polypeptides or proteins respectively.

1. In proteins, α-amino acids are joined together by
a) phosphodiester linkage
b) glycosidic linkage
c) peptide linkage
d) hydrogen bonding

2. Which of the following α-amino acids is not optically active?
a) Leucine
b) Valine

c) Alanine
d) Glycine

3. The correct structure of the dipeptide gly-ala is
a) H_2N-CH_2-CO-NH-CH_2-COOH
b) H_2N-$CH(CH_3)$-CO-NH-CH2-COOH
c) H_2N-CH_2-CO-NH-$CH(CH_3)$-COOH
d) H_2N-CH_2-CO-NH-$CH(CH_2SH)$-COOH

4. Which of the following amino acids is an essential amino acid?
a) Glycine
b) Valine
c) Alanine
d) Glutamic acid

5. α-amino acid at its isoelectric point exists as
a) $H_3N^+ – CHR – COO^-$
b) $H_2N – CHR – COOH$
c) $H_2N – CHR – COO^-$
d) $H_3N^+ – CHR – COOH$

CASE II

Carbohydrates are polyhydroxy aldehydes or ketones and are also called saccharides. Monosaccharides containing aldehyde group are called aldoses while those containing a keto group are called ketoses. Glucose is an example of monosaccharides. Glucose ($C_6H_{12}O_6$) is an aldohexose and its open chain structure was assigned on the basis of many reactions as evidences like presence of carbonyl group, presence of straight chain, presence of five-OH groups, etc. Glucose is correctly named as D(+)Glucose. Glucose is found to exist in two different crystalline forms which are named as α and ***β***.

1. Glucose on oxidation with nitric acid gives a dicarboxylic acid called saccharic acid. This result validates the fact that glucose possesses

a) –CHO group
b)-OH group
c) straight chain
d) both –CHO and $–CH_2OH$ groups at the terminals of the chain

2. The pentaacetate of glucose does not react with hydroxyl amine indicating the absence of
a)-OH group
b) -CHO group
c)-COOH group
d) $–CH_2OH$ group

3. α-D(+)-glucose and ***β***- D(+)-glucose are

a) enantiomers
b) conformers
c) epimers
d) Anomers

4. Which of the following pairs give positive Tollen's test?
a) Glucose, Fructose
b) Glucose, Sucrose
c) Fructose, Sucrose
d) Sucrose, Maltose

5. Which of the following is a keto hexose?
a) Glucose
b) Galactose
c) Fructose
d) Mannose

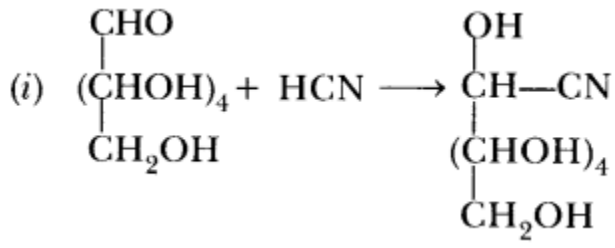
ANSWER KEY

I		II	
1	c	1	d
2	d	2	b
3	c	3	d
4	b	4	a
5	a	5	c

QUESTION BANK

1:(i)Which one of the following is a disaccharide: starch, maltose, fructose, glucose?
(ii) What is the difference between acidic amino acid and basic amino acid?
(iii) Write the name of the linkage joining two nucleotides.
Answer:
(i) Maltose
(ii) Acidic amino acid contains 2 carboxylic acids groups and 1 amino group. Basic amino acids contain 2 amino and one —COOH group.
(iii) Phospho diester linkage.

2:(i) Write the product obtained when D-glucose reacts with HCN.
(ii) What type of bonding stabilizes the α-helix structure of proteins?
(iii) Write the name of the disease caused by the deficiency of vitamin B12
Answer:



(ii) H-Bonding

(iii) Pernicious anaemia.

3. Classify the following as monosaccharides disaccharides and polysaccharides- Glucose, Sucrose, maltose, ribose, glycogen, lactose, fructose.
Ans.

Monosaccharide	Disaccharides	Polysaccharides
Glucose	Sucrose	Glycogen
Fructose	Maltose	
Ribose	Lactose	

4. Write the sequence of bases in the complementary strand of the given strand –
A G G C T T A A C C T
Ans. The sequence of bases in the complementary sequence is –
T C C G A A T T G G A

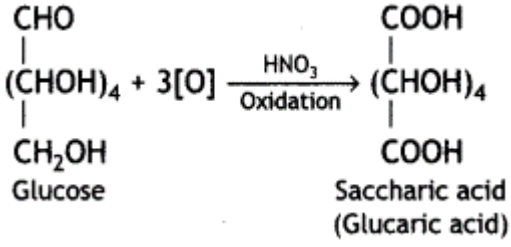
5. Name the forces responsible for secondary and tertiary structure.
Ans. The forces which are responsible for tertiary structure of proteins are hydrogen bonds, disulphide linkage, vanderwalls and electrostatic forces of attraction.

6. Why cannot vitamin C be stored in our body?
Ans.Vitamin C cannot be stored in our body because it is water soluble. As a result, it is readily excreted in the urine.

7. What are reducing sugars?
Ans. Reducing sugars are carbohydrates that reduce Fehling's solution and Tollen's reagent. All monosaccharides and disaccharides, excluding sucrose, are reducing sugars.

8. Write two main functions of carbohydrates in plants.
Ans.Two main functions of carbohydrates in plants are:
(i) Polysaccharides such as starch serve as storage molecules.
(ii) Cellulose, a polysaccharide, is used to build the cell wall.

9. Write the structure of th e product obtained when glucose is oxidised with nitric acid.



10. Write a reaction that shows that all the carbon atoms in glucose are linked in a straight chain.
Answer: When glucose is heated with HI and red P at 100°C for a long period, it gives n-hexane.

$$\underset{\text{Glucose}}{CH_2OH(CHOH)_4CHO} \xrightarrow[\text{red P, 100°C}]{HI} \underset{n\text{-Hexane}}{CH_3(CH_2)_4CH_3}$$

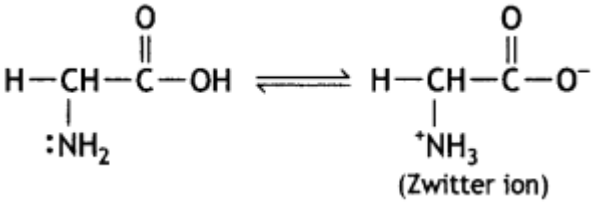
The formation of n-hexane suggests that all six carbon atoms in glucose are arranged in a straight chain.

11. What is the difference between a glycosidic linkage and a peptide linkage?
Answer: Glycosidic linkage is the linkage that joins two monosaccharides through an oxygen atom (-O-). Peptide linkage is the linkage that joins two amino acids through -CONH- bond.

12. What is the difference between Nucleotide and Nucleoside?
Answer: The molecules in which one of the nitrogen bases (purines or pyrimidine) is bonded with a sugar molecule (ribose or deoxyribose) is a nucleoside. The nucleoside linked with the phosphate group is called a nucleotide.

13. Glucose does not give 2, 4-DNP test and Schiff's test. Why?
Answer: Glucose has a cyclic structure in which the -CHO group is not free because it forms a hemiacetal linkage with the -OH group at C-5. Therefore, it does not give 2, 4-DNP test although it has -CHO group.

14. Write the Zwitter ion structure of glycine.
Answer:



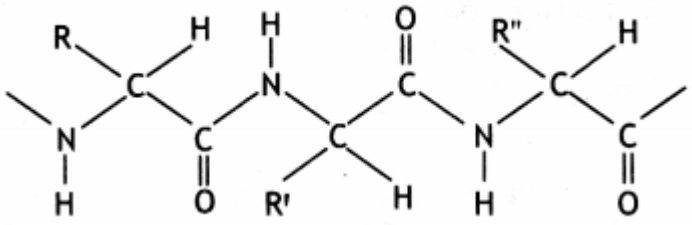
(Zwitter ion)

15. Define the following terms with a suitable example of each:
(a) Anomers
Answer:
Anomers: Carbohydrates that differ in configuration at the glycosidic carbon (i.e. C1 in aldoses and C2 in ketoses) are called anomers. For example, α-D-glucose and β-D- glucose.

(b) Essential amino acids
Answer:
Essential amino acids: The amino acids which cannot be made by our bodies and must be supplied in our diet are called essential amino acids. For example, valine, leucine, etc.

(c) Denaturation of protein
Answer:
A process that changes the native conformation of a protein is called denaturation. The denaturation can be caused by changes in pH, temperature, presence of salts of certain chemical agents. The denatured protein will lose its biological activity. During denaturation, the protein molecule uncoils from an ordered and specific conformation into a more random conformation and protein precipitates from the solution. For example, when an egg is boiled in water, the globular proteins present in it change to a rubber-like insoluble mass.

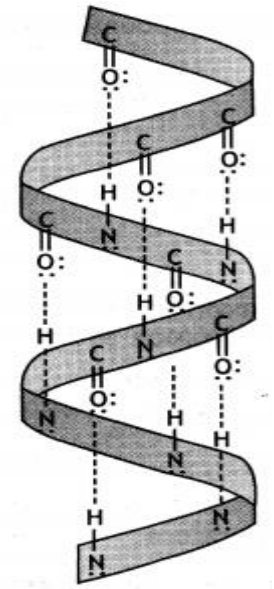
16. Describe what do you understand by primary structure and secondary structure of proteins.
Answer:
Primary structure:
The sequence in which the amino acids are linked in one or more polypeptide chains of a protein is called the primary structure.



The primary structure is usually determined by its successive hydrolysis with enzymes or mineral acids.

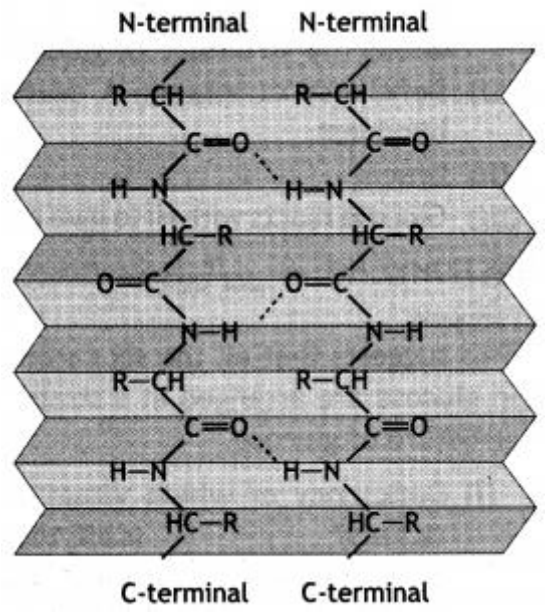
Secondary structure: The secondary structure gives the manner in which the polypeptide chains are folded or arranged. Therefore, it gives the shape or conformation of the protein molecule. This arises from the plane geometry of the peptide bond and hydrogen bond between the —C=O and N—H groups of different peptide bonds. Pauling and Corey studied that there are two common types of structures:

(i) α – Helix structure: In this structure, the formation of hydrogen bonding between amide groups within the same chain causes the peptide chains to coil up into a spiral structure (Fig. 1). This is called the a-helix.



(ii) β-pleated sheet structure: In this structure, all polypeptide chains are stretched out to nearly maximum extension and then laid side by side in a zigzag manner to form a flat sheet. Each

chain is held to the two neighbouring chains by a hydrogen bond. These sheets are stacked one upon another to form a three-dimensional structure called β-pleated sheet structure (Fig. 2).



17. How are vitamins classified? Name the vitamin responsible for the coagulation of blood.
Answer: Vitamins are classified into:
Water-insoluble vitamins: These are fat-soluble substances E.g. Vitamin A, D, E and K.
Water-soluble vitamins: These include Vitamin B-Complex and Vitamin C (except B12).
Vitamin K or phylloquinone is responsible for the coagulation of blood.

18. Glucose is an aldose sugar but it does not react with sodium hydrogen sulphite. Give a reason.
Ans: An aldehyde group is present in glucose. It, on the other hand, does not react with sodium hydrogen sulphite to generate bisulphite addition products. This is because this reaction takes place in the presence of a free aldehyde group, but there is no free - CHO group in glucose's structure.

19. How would you explain the amphoteric behaviour of amino acids?
Ans: In a single molecule, amino acids have both an acidic (carboxyl group) and a basic (amino group). They neutralise each other in aqueous solutions. A proton is released by the carboxyl group, whereas it is accepted by the amino group. Amino acids react with both acids and bases in their zwitterionic form, displaying amphoteric behaviour.

20. The two strands in DNA are not identical but complementary. Explain.
Ans: Despite the fact that the two strands of DNA are not similar, they are joined together through hydrogen bonds. Adenine and cytosine create hydrogen bonds with thymine and guanine, respectively. As a consequence, the two strands function as a complement to one another.


Best Wishes!